DESIGN OF CATALYSTS FOR THE ABATEMENT OR DECOMPOSITION OF ANTHROPOGENIC CARBON DIOXIDE, METHANE AND NITROUS OXIDE.

This thesis is submitted to the University of Surrey in consideration for the award of the higher degree of Doctor of Philosophy (Ph.D.) in Chemistry.


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MATERIAL REDACTED AT REQUEST OF UNIVERSITY
“Loss of coastal habitats and other basic resources could see the migration of an estimated 100 million people by 2100 – the world’s biggest refugee crisis.”

Robert Watson,
Chairman of the International Panel for Climate Change (IPCC), 2000 [1]

Abstract

Carbon dioxide (CO$_2$), methane (CH$_4$) and nitrous oxide (N$_2$O) are major greenhouse gases (GHG). The aim of this research was to develop improved catalysts for CO$_2$-CH$_4$ reactions and N$_2$O decomposition via sol gel (SG) routes.

0.5 wt % Rh/TiO$_2$ (SG) was prepared and found to be effective for the decomposition of N$_2$O. This served the purpose of removing atmospheric N$_2$O and decomposing this green mono-propellant for satellite microthrusters; where it could also be a competitor of commercial Shell 405 (36 wt. % Ir/Al$_2$O$_3$) catalysts.

The CO$_2$-CH$_4$ reaction was studied in a temperature-programmed (TP) mode. In the $\alpha$ region there appeared to be no reaction occurring but during the $\beta$ region the full catalytic reaction was observed. Interestingly, pulses of CO$_2$ produced little O. However, CH$_4$ pulses produced both H and CH$_x$. In steady state catalysis the ratio of reactant consumption (CO$_2$/CH$_4$) was generally 1 : 1. Almost all catalysts considered here produced CO and H$_2$ only during the CH$_4$ pulse.

Heterogeneous photocatalysis of dry reforming of CH$_4$ and decomposition of N$_2$O on present catalyst surfaces was shown to be possible.

Materials were characterised before and after use with a range of analytical techniques including Fourier transform infrared (FT-IR) spectroscopy with CO, Raman spectroscopy, X-ray diffraction (XRD), Brunauer Emmett & Teller (BET) physisorption, scanning electron microscopy (SEM), energy dispersive analysis of X-rays (EDAX) and X-ray photoelectron spectroscopy (XPS). These techniques showed that the unused pre-calcined (773 K) catalyst surface was clean from organic species, but that in dry reforming there was an accumulation of carbonaceous species (as seen above) on the used surface. Furthermore turnover frequency (TOF) for ceramic foam (CF) catalyst was found to be as good as Shell 405 (see Chapter 7). The keynote finding was that catalyts can be designed and used to reduce the environmental impact of GHG emissions and provide routes to other commercial processes.

Acknowledgements

Upon completion of this thesis, the author would like to acknowledge and show gratitude first and foremost to the Almighty Creator.

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This thesis is dedicated in its entirety in eternal loving memory to the author’s dearest late father: the late Mr. A. Ahmed (14th June. 1938 – 13th March. 1999). It is also dedicated in loving memory to the author’s late Uncle: Mr. O.U.A. Choudhury (15th July. 1934 – 3rd February. 1997). Thank You dearest mother, Shageda Begum Choudhury, such wonderful brothers: Khaled and little brother Sayed, little sister Zaheda (Pema) and sister Rehana; Uncle Khalil, Auntie Zaheda, Maryam, Batool, Mujib and little Humayra. Thanks for putting up with ALL the difficult years and thanks for all the fantastic, unforgettable memories. A final dedication is also due to the author’s wife, Feroza Hoque Choudhury (Popy).
Statement of Declaration and copyright notice

No other award has been conferred at this or any other educational institution for the work presented herein. All work is the author's own unless otherwise stated. No work may be reproduced without prior permission. © F. Ahmed. 2004.


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<td>$E_a$</td>
<td>activation energy (kJmol$^{-1}$)</td>
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<tr>
<td>atmos.</td>
<td>atmospheres</td>
</tr>
<tr>
<td>L</td>
<td>Avogadro constant ($6.023 \times 10^{23}$ molecules)</td>
</tr>
<tr>
<td>$S_{n2}$</td>
<td>bimolecular nucleophilic substitution</td>
</tr>
<tr>
<td>$2\theta$</td>
<td>Bragg angle in XRD</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmett and Teller</td>
</tr>
<tr>
<td>$t$</td>
<td>crystallite size (Å)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density (g/cm$^3$)</td>
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<tr>
<td>EDAX</td>
<td>energy dispersive analysis of X-ray</td>
</tr>
<tr>
<td>H</td>
<td>enthalpy</td>
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<tr>
<td>S</td>
<td>entropy</td>
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<tr>
<td>K</td>
<td>equilibrium constant or the unit of absolute temperature</td>
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<tr>
<td>FID-GC</td>
<td>flame ionising detector – Gas chromatography</td>
</tr>
<tr>
<td>FR</td>
<td>flow rate (cm$^3$ min$^{-1}$)</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infra red</td>
</tr>
<tr>
<td>v</td>
<td>frequency</td>
</tr>
<tr>
<td>$t_g$</td>
<td>gelation time</td>
</tr>
<tr>
<td>$G$</td>
<td>Gibbs free energy</td>
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<tr>
<td>g</td>
<td>grams</td>
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<tr>
<td>GHG</td>
<td>greenhouse gas</td>
</tr>
<tr>
<td>HAP/VOC</td>
<td>hazardous air pollutants / volatile organic compounds</td>
</tr>
<tr>
<td>R</td>
<td>gas constant (8.314 JK$^{-1}$mol$^{-1}$)</td>
</tr>
<tr>
<td>J</td>
<td>joules</td>
</tr>
<tr>
<td>m</td>
<td>metres or milli</td>
</tr>
<tr>
<td>$\mu$</td>
<td>micro</td>
</tr>
<tr>
<td>mmHg</td>
<td>millimetre mercury</td>
</tr>
<tr>
<td>$V_m$</td>
<td>monolayer volume</td>
</tr>
<tr>
<td>NDIR</td>
<td>non-dispersive infra red</td>
</tr>
<tr>
<td>n</td>
<td>number of moles / nano / arbitrary number taken to be in uniformity with 1</td>
</tr>
<tr>
<td>$p/p_0$</td>
<td>partial pressure or relative pressure</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>ppb</td>
<td>parts per billion</td>
</tr>
<tr>
<td>Pa</td>
<td>Pascal</td>
</tr>
<tr>
<td>h</td>
<td>Planck’s constant ($6.626 \times 10^{-34}$ JHz$^{-1}$)</td>
</tr>
<tr>
<td>PSD</td>
<td>pore size distribution</td>
</tr>
<tr>
<td>P</td>
<td>pressure (Pa, atmos. or mmHg)</td>
</tr>
<tr>
<td>$k$</td>
<td>rate constant of the forward reaction or kilo</td>
</tr>
<tr>
<td>$k_{-1}$</td>
<td>rate constant of the reverse reaction</td>
</tr>
<tr>
<td>$t_{res}$</td>
<td>residence time</td>
</tr>
<tr>
<td>RGA</td>
<td>residual gas analyser</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>s</td>
<td>seconds</td>
</tr>
<tr>
<td>$S_{BET}$</td>
<td>surface area as assessed by the BET method (m$^2$/g)</td>
</tr>
<tr>
<td>T</td>
<td>Temperature (K)</td>
</tr>
<tr>
<td>TP</td>
<td>temperature programmed</td>
</tr>
<tr>
<td>TPR</td>
<td>temperature programmed reduction</td>
</tr>
<tr>
<td>$t$</td>
<td>time (s) or (min)/crystallite size</td>
</tr>
<tr>
<td>$t_{max}$</td>
<td>time at which the profile reaches maximum peak-height from $t_{eq}$</td>
</tr>
<tr>
<td>$t_{ini}$</td>
<td>time of injection</td>
</tr>
<tr>
<td>UV</td>
<td>ultra violet</td>
</tr>
<tr>
<td>$S_{n1}$</td>
<td>unimolecular nucleophilic substitution</td>
</tr>
<tr>
<td>$v$</td>
<td>volume (cm$^3$)</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>wavelength</td>
</tr>
<tr>
<td>wrt</td>
<td>with respect to</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XRDLB</td>
<td>X-ray diffraction line broadening</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>STP</td>
<td>Standard temperature and pressure (i.e. 298 K and 101.325 kPa)</td>
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CHAPTER I:  
Introduction  

1.1. Introduction 

Earth is a complex system comprising of many components. It consists of a perfect and natural balance of weather systems, seasons, clouds, water vapour, nutrients, minerals, land masses, oceans etc. However some imbalance to this system is caused by man. Waste from the manufacturing and chemical industries is a major cause of air pollution [1] and stratospheric ozone (O_3) depletion [2-3]. Hence poor air quality and poor quality of life (in terms of health problems) can ensue.

*Global warming* (also known as the *greenhouse effect*) is a growing problem since the world is faced with a catastrophe within the next century or so (see section 1.6). The seriousness of this problem has even been addressed by leading scientists like Professor Sir David King, the government’s Chief Scientific Advisor. Greenhouse gas (GHG) emissions will need to be controlled under ever more stringent government legislation and European directives (see section 1.8). Controlling their emissions is vital if a rise in sea levels, for instance, is to be avoided. This requires new environmental technology.

1.2. Environmental Protection and Environmental Conservation 

Environmental protection implies direct action(s) imposed or measures taken in order to prevent damage to the environment and its eco-system. The measures adopted may be political, economic, industrial and/or environmental.

Environmental conservation concerns maintaining and preserving the environment within its natural framework. As an example, the environment would be conserved if fish in rivers were safe from chemical contamination. However, certain measures may need to be taken by various groups in order to ensure less river pollution.

Within the present context, environmental conservation is when no GHGs are emitted from anthropological sources, and hence the natural ecosystem is preserved (e.g.  

carbon cycle), whereas environmental protection includes government initiatives to impose measures that aim to control the emissions of GHGs.

1.3. Environmental impact

Environmental pollution can relate to air, water and soil. Air pollution can be caused by CO, platinum metals (PMs), NOx, SOx and hazardous air pollutants (HAP) or volatile organic compounds (VOC). These can result from fossil fuel combustion. Europe alone emits 15 million tonnes of VOCs every year [4] from the sources shown in Figure 1.1.

![Pie chart showing sources of European VOC emissions (2000)](image)

**Fig. 1.1.** - Sources of European VOC emissions (2000)

The extent to which the environment is affected as a result of these pollutants is called the *environmental impact*. 

---

1. Introduction.

1.4. Global Warming

The background to the present research is the environmental impact of global warming. This results from the excess heat being trapped in the upper stratosphere. Linked with this problem is the destruction of the ozone (O₃) layer. This layer protects the earth from the damaging UV rays (that can cause serious illnesses like skin cancer) from the sun. The concept of global warming is illustrated in *Figure 1.2*:

![Figure 1.2 - A representation of 'global warming' (greenhouse effect)](image)

The term 'greenhouse effect' was first used and predicted by Svante August Arrhenius (Swedish physical chemist, 1859-1927) as early as 1896 [5-6]. However, at that time, the problem was not taken very seriously. It is only recently that interest has been raised to counter this serious problem. With time, the occurrence of environmental and global damage seems virtually inevitable.

Global warming is a natural and essential feature of the atmosphere without which the planet would be uninhabitable. This process works by the principle that certain atmospheric gases (or greenhouse gases) allow short wave radiation from the sun to pass through them unabsorbed, while at the same time absorbing some of the long wave radiation reflected back into space. This means that more heat is received from
the sun than is lost back to space, keeping the Earth's surface some 30 to 35 K warmer than it would otherwise be.

It is generally agreed that there is global warming, but there is a huge debate regarding the causes of it [7] i.e. whether it is due to natural causes or from anthropological sources.

The Intergovernmental Panel on Climate Change (IPCC) believe that man is adding to (and changing) the levels of the gases responsible for the greenhouse effect and is therefore making this warming significantly more pronounced. Figure 1.3 shows how the global temperature will increase over the next century or so; perhaps as much as 6 K without the Kyoto Protocol policy (i.e. the global climate treaty (Japan. 1997)) [8]. However, with the Kyoto Protocol guidelines and further restrictions, this may only be up to 2 K. It also shows the countries that are most responsible for greenhouse gas (GHG) emissions:

![Global Temperature Change Forecast](image1)
![Greenhouse gas emissions](image2)

**Fig. 1.3. – Global temperatures and contribution to this from countries [9].**

Globally 1998 was the warmest year ever recorded and eight of the ten warmest years fell within the last decade. Global ice sheets have decreased in size and thickness and so has global snow cover. During the Earth's history there have been warmer periods, but this is the most rapid temperature rise since the end of the last ice age. Hence evidence is mounting that emissions from anthropogenic sources are affecting the global climate, and the current warming has exceeded the expected natural fluctuations [10].
1.5. Greenhouse gases (CO₂, N₂O, CH₄, SOₓ, and NOₓ)

The three main greenhouse gases that cause global warming are CO₂ (critical temperature, $T_c = 304.1$ K), CH₄ [11] and N₂O with global warming potentials (GWP) of 1, 21 and 290 respectively [12-13]. Table 1.1 below shows various GHGs in the atmosphere with their respective GWP (i.e. CO₂ equivalence) over a 20 year and 100 year period [14]:

Table 1.1 – Various GHGs with their respective GWP over a 20 year and 100 year period.

<table>
<thead>
<tr>
<th>GHG</th>
<th>GWP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 yr</td>
</tr>
<tr>
<td>CO₂</td>
<td>1</td>
</tr>
<tr>
<td>CH₄</td>
<td>56</td>
</tr>
<tr>
<td>N₂O</td>
<td>280</td>
</tr>
<tr>
<td>HFC-32</td>
<td>2,100</td>
</tr>
<tr>
<td>HFC-23</td>
<td>9,100</td>
</tr>
<tr>
<td>SF₆</td>
<td>16,300</td>
</tr>
<tr>
<td>CFC’s</td>
<td>10,000</td>
</tr>
</tbody>
</table>

A GWP of 21 therefore means that it would require an equivalence of 21 molecules of CH₄ to have the same effect in the atmosphere as one of CO₂. Hence CO₂ is the largest contributor to the problem with man-made sources producing as much as 30 Gtonnes of it per year, mostly from the combustion of fossil fuel [15-16] followed closely by CH₄ and N₂O. Sulphur oxides and nitrogen oxides have a considerably lesser impact. However they are still environmentally damaging since they cause acid rain. These cause damage to the eco-system such as fishes in rivers and building and architectural corrosion. Effort in this area has meant that since 1990 sulphur dioxide emissions have fallen by 75 % and nitrogen oxides by 52 % [17]. The thesis will however concentrate on the abatement and decomposition of the three main gases (CO₂, CH₄ and N₂O) that cause global warming, even though the others are environmentally damaging within a wider context.
CO₂ is a colourless gas at room temperature and occurs naturally in the atmosphere. It plays an important part in photosynthesis (see section 1.9.2) and in animal and plant respiration (as shown by the CO₂ cycle in Figure 1.4). It sublimes at 194.5 K and is produced by the complete combustion of carbon or by heating metal carbonates. It is soluble in water and detected by the formation of a white precipitate with a solution of Ca(OH)₂. It is used in mineral waters under pressure and as a refrigerant. It also has uses as a chemical reagent (RMgX gives RCO₂MgX [18]) and as a fire extinguisher.

CO₂ is a symmetrical, linear molecule with a simple O=C=O structure and a bond angle of 180° (as predicted by valence shell electron pair repulsion (VSEPR) theory [19]). Hence, both C=O bonds are the same length. Molecular orbital (MO) theory [20] indicates that in addition to the two σ bonds between C and O, there are also two π bonds across the whole molecule. Since π bonds do not affect the shape of the molecule (they merely shorten the bond length), the remaining s and p orbitals from the C atom overlap with the p orbitals from the two O atoms to form a linear molecule. The MO notation for the molecule is l a 2 , 2 a 2 , l 7 4 , 3 a 2 , 2 k 4 * , 4 a 2 * where * indicates anti-bonding orbitals. Thermodynamically, it is very stable with C=O bond energies of 803 kJmol⁻¹ [21]. The amount of CO₂ in existence is a balance of the CO₂ cycle:
This CO₂ cycle is disturbed by the action of human beings (i.e. anthropogenic sources). A considerable amount of CO₂ is produced and emitted into the atmosphere by the chemical and manufacturing industry (e.g. cement production, burning of fossil fuel). In addition, transport and deforestation [23] contribute to the increased CO₂ emissions of GHGs. Table 1.2 summarises the main sources of CO₂ emission and how they have contributed to the problem of global warming over the last 30 years or so [24].

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Industry</td>
<td>78.3</td>
<td>56.1</td>
<td>48.0</td>
<td>40.7</td>
</tr>
<tr>
<td>Transport</td>
<td>20.7</td>
<td>27.8</td>
<td>36.9</td>
<td>38.6</td>
</tr>
<tr>
<td>Domestic</td>
<td>53.4</td>
<td>47.7</td>
<td>42.5</td>
<td>41.4</td>
</tr>
<tr>
<td>Services</td>
<td>32.8</td>
<td>32.6</td>
<td>31.8</td>
<td>26.8</td>
</tr>
</tbody>
</table>

CO₂ emissions from automobiles such as diesel engines [25] are increasing, especially with the increased volume of traffic over the years. Government initiatives and environmental concerns seem to have curbed some industrial emissions.

Plant respiration and decomposition of organic material release more than 10 times the amount of CO₂ than that released by human activity, but these have generally been in balance (i.e. CO₂ cycle) [22] during the centuries leading up to the industrial revolution. Since then these amounts have increased by as much as 30%. CO₂ emissions in the atmosphere however may not be the only factor that contributes to global warming. It is worth noting that during the Solar Eclipse on 11th August 1999, several astronomers carried out a series of experiments (BBC TV) in order to determine the temperature of the Sun. They came to the conclusion that in fact the Sun was becoming brighter, implying that it was getting hotter, and therefore can be considered as a cause factor for global warming.

Other greenhouse gases include methane (CH₄), nitrous oxide (N₂O), chlorofluorocarbons (CFC) (manmade) and ozone (O₃), and in addition aerosols (from man-made sulphur emissions) are important. Since the early 1990’s CFC’s have been
1. Introduction.

banned due to the damage they have caused to the ozone layer, which protects the earth from the damaging UV rays. Sulphate aerosols however last only a few days in the atmosphere and can easily be removed by acid rain, but CO$_2$, CH$_4$ and N$_2$O are of real concern since they can remain in the atmosphere for many decades. GHG emissions therefore need to be cut down (abatement), or in the case of CO$_2$, recycled into more useful organic precursors (adaptation) like hydrocarbons and high value oxygenates (see section 1.14 and Chapter 7). Hence, the urgent need for the abatement and adaptation of GHGs is therefore justified.

1.6. The consequences

The effects of global warming and a changing climate will not be felt equally across the globe. Ice caps are melting causing the sea levels to rise [26] and the land to disappear over the next century or so. Particularly vulnerable will be low-lying coastal areas and small island states e.g. the Ganges, the Nile, China’s Pearl River, the Marshall Islands [27] and Bangladesh, of which 37% of the land already lies below three metres, and this will be even more severe with the effects of climate change [28]. These changes would cause problems to the eco-system in terms of endangering certain species, possibly to extinction. The ice caps around Chile are already melting and ecological damage may therefore be expected [29] in the near future. The rise in temperature will cause a warmer climate and inevitably a shift of tropical infections and diseases (Malaria and tetse fly bringing related diseases in the future) that are normally associated with tropical countries as the norm. This will shift to what are presently the cooler parts of the world. Associated with this has also been the floods and drought in (eastern) Europe during 2002.

The reduction of GHGs may provide long-term health benefits in terms of reducing the impact on human health (e.g. “lessened spread of malarial mosquitoes, fewer extreme climate events, and lower impacts on food production” [30]).
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a) Change in average annual rainfall

Fig. 1.5(a) and Fig. 1.5(b) above indicate severe climatic changes in terms of annual temperature and rainfall. This problem is obviously not just restricted to the UK alone since the entire planet is said to be affected.

b) Change in average annual temperature

1.7. Renewable Energy Resources

Fossil fuels (i.e. coal, oil and natural gas) are an example of limited energy resources. This means that these resources cannot be renewed and are in very limited supply. The sea takes up approximately 70% of the world’s surface. 12% or so is either ice or deserts, and only about 18% of what is left can support human life. In this regard, man is using enormous amounts of fuel for energy. For example, in the UK, electricity generation is based on nearly 80% fossil fuels and 60% on coal [31]. In turn, a large amount of waste is produced which if not effectively managed and treated, could cause long-term environmental damage. Furthermore, since coal, oil and natural gas are in limited supply, alternative forms of energy resources need to be found and used.

The alternative energy resources are those that are in essence, not limited, and hence can be renewed [32]. They may produce less CO₂. Renewable and alternative energy resources (such as solar [33-34], hydro (H₂O), hydrogen, nuclear [35-36], wind power etc) are already making a tremendous impact, in terms of generating electricity. Another useful source of energy is that of geothermal, by extracting energy from old meteorite craters [37]. Electric cars operating via solar energy and fuel cells are said to be the norms of futuristic travel [38]. In this regard, cars that are powered by H₂ fuel cells achieved 1,200 mpg [39]. Solar power is also being used in housing projects [40]. As one of the products of dry reforming, hydrogen can be used within the context of Hydrogen power. As mentioned, this concept has been developed within
recent times [41-44]. Nuclear and hydro power are already making a dramatic impact with regards to the generation of electricity to countless homes and businesses across the globe. There have even been government initiatives to encourage the use of renewable energy resources [45-46]. Under such schemes, a percentage of electricity sold by utility companies is generated from renewable resources. This is currently at 4.3 % and is set to rise to 10.4 % by 2010. Previously, this figure was 20 % by 2020, but now the aim is to reach 15.4 % by 2015. This illustrates that the limited supply of fossil fuel is a real problem in terms of meeting energy demands of the future. Cleaner sources of fuel can produce less CO\textsubscript{2} (see Figure 1.6):

![Figure 1.6 - Sources of CO\textsubscript{2} emissions [47]](image)

where on the y-axis, 1 = present Internal Combustion Engine (ICE) using “clean” fuel, 2 = hybrid-electric ICE using clean fuel, 3 = fuel cells using clean fuel, 4 = fuel cells using CH\textsubscript{3}OH from natural gas, 5 = fuel cells using H\textsubscript{2} from natural gas, 6 = fuel cells using hydrogen from biomass and 7 = fuel cells using H\textsubscript{2} from solar, wind or nuclear power.

1.8. Control of greenhouse gases (GHG) for Sustainable Development

Environmental concerns have naturally led to methods for GHG control. This, in essence, is the concept of sustainable development [48-49]. In 1987, the UN World Commission on Environment and Development defined Sustainable Development as “meeting the needs of the present without compromising the ability of future
generations to meet their needs" [50-51]. This is also linked to the concept of Green Chemistry, which aims to design chemical processes that deliberately reduce or eliminate HAPs and VOCs.

The government (e.g. Department of Trade and Industry [DTI]) has legislated on environmental issues so as to provide guidelines for minimising waste and harmful emissions into the atmosphere. Such government policies include: carbon taxation, energy saving (e.g. Combined heat and power, CHP), recycling and sequestration – utilisation (e.g. CO$_2$ + CH$_4$ → 2CO + 2H$_2$ or EOR, enhanced oil recovery, etc). Recent studies show that CO$_2$ emissions do not necessarily fall when energy saving measures are introduced [52] and that one therefore needs to improve and increase CO$_2$ utilisation.

Carbon taxation (i.e. the introduction of the European carbon tax [53]) has certain advantages in terms of raising responsibility and awareness for this important issue. It can help to reduce the overall environmental impact in terms of reducing CO$_2$ emissions by encouraging industry and consumers to reduce their carbon-based energy. The tax is levied on the basis of fossil fuel use in proportion to their carbon content. The main disadvantage with this scheme is that large companies with considerable market share and profit margin may still continue to emit these gases despite the tax, simply because they can afford to do so, especially since increasing profit margin is more beneficial in the longer term.

International meetings have also addressed Global Warming and various agreements were reached ([54-57], The Hague Summit (2000) [58-59] and the Earth Summit in Johannesburg, South Africa (2002)). These meetings highlighted the need for sustainable development and "more attention and international co-operation" [60]. Present EU legislation aims to reduce man-made emissions to about 7 million tonnes by 2010 [4]. Despite political problems of reaching consensus, such as the isolation of the US whilst 186 countries ratified the Kyoto Protocol in July 2001 [61], there has on the whole been effort concentrated on achieving control of GHGs.
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Pressure groups (e.g. Greenpeace, Friends of the Earth, Confederation of British Industry (CBI) and Trade Union Congress (TUC)) have also expressed their concerns. Non-governmental organisations such as the Environment Agency and the IPCC [62] have advised governments and industry to pursue the challenge of reducing GHG emissions. It is not surprising therefore that companies such as BP are taking the stance to introduce green diesel in order to substantially reduce emissions into the atmosphere.

In 1972, Sawyer [63] discussed the issue of Global Warming and the first conference on World Climate was convened in 1979, followed by the 1985 international conference in Australia. To help reduce the threat of global warming, the UK government made an important commitment along with other nations at the 1992 Earth Summit in Rio, to return CO$_2$ emissions to 1990 levels by the year 2000. The UK met this obligation and following the 1997 Kyoto Earth Summit, the UK set an even more demanding goal to cut CO$_2$ emissions by 20% below 1990 levels by the year 2010. In an historic deal, 178 countries have agreed how to tackle climate change. The compromise reached after a day and a night of intensive talks culminating in the Bonn Agreement meant that the Kyoto Protocol came into force [64]. This agreement aimed to control the emissions of 6 GHGs: CO$_2$, CH$_4$, N$_2$O, HFC's, PFC's and SF$_6$ [65]. Most of the emission reduction were however targeted in the first three [66]. As ministers, environmentalists and lobbyists from 180 countries gathered in the Hague for the UN Climate Change in November 2000, problems already started to emerge, especially when the USA saw it as against its national interests to comply to the previously agreed limits [67-68]. The Rio Declaration stated that "where there are threats of serious or irreversible damage, scientific uncertainty shall not be used to postpone cost-effective measures to prevent environmental degradation" [69]. The UN World Summit in Johannesburg in 2002 has further developed the agenda for sustainability over the next decade. As part of its strategy the government introduced a levy on energy at the point of use. The impact the Climate Change Levy has had on the public is an increase in energy costs of £150,000 pounds per year. Nevertheless, this will mean a vital start of a marginal 1 - 3% cut in greenhouse gases, although scientists are demanding 60 - 80% cuts to see a real difference.

12

To reduce the volume of energy purchased and the consequent environmental impact, schemes have been designed to specifically save energy by literally cutting out wasteful use of energy, or saving unused and unwanted energy – “good housekeeping”. It is said that a modest 5 % saving in this way could reduce consumption by 4 million kWh, reduce CO\textsubscript{2} emissions by 1,200 tonnes and save £85,000 every year [70].

Finding effective technologies to limit the emissions of these gases into the atmosphere has become increasingly stringent within recent times. However technology alone is not enough; in fact both effective cleaner technologies and policy changes are required [71]. Hence, political intervention and government policy allows the administering and monitoring of the control of emissions from large multinational and corporate chemical, pharmaceutical and manufacturing industries. CO\textsubscript{2} is emitted as by-products and waste from these industries, and also from catalytic convertors in automobiles. CH\textsubscript{4} is also emitted from these industries often as by-products of cracking processes and as waste from other chemical processes. Hence, more efficient fossil fuel combustion is required. N\textsubscript{2}O is to a lesser extent emitted from these industries, and a significant proportion is also emitted from automobiles.

It is clear therefore that a combination of abatement, adaptation and geo-engineering strategies will be required to reduce the threat of global climate change, and the technologies chosen will need to be ever more sophisticated and stringent in order to meet the expectations and demands of an ever increasing environmentally conscience world.

1.9. Chemical and physical utilisation of CO\textsubscript{2} to lower emission rates

CO\textsubscript{2} is naturally utilised in :

(i) absorption in oceans (in the sense of forming carbonates), and
(ii) photosynthesis [72].
Despite these being natural processes, it may be possible to utilise CO$_2$ using these (i.e. geo-engineering). In order to reduce the effects of global warming, it is argued that carbon will need to be disposed of safely, just like nuclear waste is [73]. This process requires the extraction of CO$_2$ (i.e. capture) followed by storing it somewhere safe (i.e. sequestration) [74]. Out of the two, the capturing aspect is more complicated and expensive. Using existing technology, mono-ethanolamine absorber can be used to capture concentrated carbon on a large scale from say a coal-fired power station. The technique is impractical however, for small emitters like cars and houses. An alternative and cleaner method is to use the 'integrated gasifier combined cycle' approach, which is based on steam reformation (see section 1.13). The main disadvantage is that either technique is very expensive. *Tables 1.3 and 1.4* below summarise the techniques for CO$_2$ capture and sequestration [73, 75-76]:

**Table 1.3. - Reducing atmospheric CO$_2$ concentration (Capture)**

<table>
<thead>
<tr>
<th>Technique</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Mono-ethanolamine</td>
<td>Uses existing technology</td>
<td>Expensive</td>
</tr>
<tr>
<td>2) Integrated Gasifier combined cycle</td>
<td>Cleaner</td>
<td>Expensive</td>
</tr>
</tbody>
</table>

After capture, the CO$_2$ must be stored. There are four main approaches:

**Table 1.4. - summary of CO$_2$ sequestration.**

<table>
<thead>
<tr>
<th>Technique</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Approx. capacity ($10^9$ t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Ocean injection</td>
<td>Long residence time</td>
<td>Immature technology</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>2) Oil/gas reservoir injection</td>
<td>Proven storage integrity</td>
<td>Limited capacity</td>
<td>&gt;100</td>
</tr>
<tr>
<td>3) Saline Aquifier injection</td>
<td>Large capacity</td>
<td>Unknown storage integrity</td>
<td>400 -1000</td>
</tr>
<tr>
<td>4) Coal mine injection</td>
<td>Low costs</td>
<td>Immature technology</td>
<td>10 - 100</td>
</tr>
</tbody>
</table>

1.9.1. Absorption in Oceans

CO$_2$ in seawater produces carbonates, and hence is used up in the process:
1. Introduction.

\[
\text{CO}_2 + H_2O \rightleftharpoons H^+ + HCO_3^-
\]

\[
\text{HCO}_3^- \rightleftharpoons H^+ + \text{CO}_3^{2-}
\]

Oceans are one of the largest carbon sinks, and it may be persuaded to take some more. Degassing of the gas may be avoided for up to a millennia by injecting CO\(_2\) into the oceans at depths of about 800 metres. This way, up to 250 billion tonnes of C could be captured from the atmosphere according to US officials.

1.9.2. Photosynthesis

Photosynthesis is carried out by many different organisms, ranging from plants to bacteria. The best known form of photosynthesis is the one carried out by higher plants and algae, as well as by cyanobacteria and their relatives, which are responsible for a major part of photosynthesis in oceans. All these organisms convert CO\(_2\) to organic material by reducing this gas to carbohydrates in a complex set of reactions:

\[
6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2
\]

The only other requirements are sunlight and chlorophyll in the leaves of plants. The 'waste' oxygen is useful for animal respiration, and hence the cycle naturally continues.

Sunlight plays a significant role in sustaining life: all the food consumed and all the fossil fuel used as energy is a product of photosynthesis. This is a natural process by which energy in sunlight is converted to chemical forms of energy that can be used by biological systems.

Electrons for this reduction reaction ultimately come from water, which is then converted to oxygen and protons. Energy for this process is provided by light, which is absorbed by pigments such as chlorophylls and carotenoids (found within plants). Figure 1.7 clearly shows how chlorophyll absorbs blue and red light and carotenoids absorb blue-green light, but green and yellow light are not effectively absorbed by...
photosynthetic pigments in plants; therefore, light of these colours are either reflected by leaves or passed through the leaves. This is why plants are green [77].

Fig. 1.7 - Absorption spectrum of isolated chlorophyll and carotenoid species. The colour associated with the various wavelengths is indicated above the graph [77].

Photosynthesis may be encouraged further by the plantation of more trees, crops and the restoration of forests etc, and hence the utilisation of more CO₂.

These forms of CO₂ sinks are natural and seek to provide a balance from the excess CO₂ in the atmosphere. The strategy means that these sinks are encouraged to accept more CO₂, but this is seen as a distraction by environmentalists from shifting to clean, renewable energy resources like wind or solar power and away from dirty fossil fuel like coal and oil. It is also seen as interfering with the natural balance since Man’s contribution to the problem in the first place makes it increasingly overwhelming for these natural processes to accommodate the excess demand.

Other ways of controlling CO₂ emissions include:

- Improving the efficiency of existing process technology, i.e. the novel application of existing technology (adaptation).
- Introducing new technology that deliberately minimises CO₂ emissions,
- Introducing an EU carbon tax as a deterrent to excess fuel use (see section 1.8),
- Introducing tighter EU CO₂ emissions legislation, and
• Finding new chemical or physical uses for CO$_2$ to syphon off by-product CO$_2$ and act as a disincentive to emit.

The last of these i.e. utilisation of CO$_2$ in the chemical industry [78] to produce CO/H$_2$ by dry reforming [79], CH$_3$OH by CO$_2$ hydrogenation [80] and DMC have been considered elsewhere, even though it is appreciated that the rates of CO$_2$ emission (i.e. 978 Mt CO$_2$ in Germany in 1990 rising to 987 Mt in 2010 [81]) is far in excess of rates of its consumption in commodity chemical production (i.e. 1.32 Mt CH$_3$OH in Germany in 1993 and 1.63 Mt in 1997 [82]). In general CO$_2$ is also used in carbonated drinks like coca cola, lemonade, fanta. etc.

1.9.3. New Uses such as in Oil Wells

The existence of CO$_2$ in oil wells allows for oil to flow more freely and loosens it from surrounding rocks, and hence increases oil production and output. So, CO$_2$ sequestration involving the pumping of CO$_2$ into deep, porous rocks may encourage the gas to be trapped underground for millions of years and curb a rise in global temperatures. The technique is said to raise oil production by 5 – 15 % [83]. This is not necessarily a new technique since oil firms such as in West Texas have for years piped CO$_2$ into oil wells to help raise production. Similar schemes have also been run in Hungary and Turkey.

1.9.4. Polycarbonates

Another use is in the formation and use of polycarbonates [84, 360]. These are a group of thermoplastics which are particularly known for their toughness. They are transparent and are resistant to heat and other chemicals. They have the general formula: H(OROC=O)$_n$-OROH and are usually polyesters of carbonic acid (H$_2$CO$_3$) with aliphatic or aromatic dihydroxy compounds. Industrial polycarbonates are typically formed from bisphenol A, [2,2-bis(4-hydroxyphenyl)propene,4,4'-isopropylidenediphenol] and phosgene (Cl$_2$CO). They are used in safety spectacles, baby’s bottles and lenses.
1.10. N$_2$O

Since N$_2$O contributes to the greenhouse effect (see section 1.5), its decomposition to relatively harmless nitrogen (N$_2$) and oxygen (O$_2$) is encouraged.

1.10.1. N$_2$O chemistry

Nitrous oxide (N$_2$O), sometimes known as dinitrogen monoxide is a colourless gas with melting point 182.15 K and boiling point 184.65 K. Structurally, N$_2$O is linearly unsymmetrical (with a bond angle of 180°) in the form N-N-O with bond lengths of 1.129 Å and 1.188 Å for N-N and N-O respectively [85-86]:

\[
\begin{array}{c}
\text{N} \quad 1.129 \text{Å} \quad \text{N} \quad 1.188 \text{Å} \\
\end{array}
\]

Fig. 1.8. – molecular structure for nitrous oxide

Chemically, it is isoelectronic with CO$_2$, NO$_2^+$ and NO$_3^-$ [87] with MO notation $1\sigma^2$, $2\sigma^2$, $1\pi^4$, $3\sigma^2$, $2\pi^4^*$, $4\sigma^2^*$. During the decomposition, the N-O bond from N$_2$O is broken and the O-O bond is formed. The O-O bond energy is $498.34 \pm 0.2$ kJmol$^{-1}$ [96-98] and the N-O bond in N$_2$O is $167 \pm 0.2$ kJmol$^{-1}$ [99-100].

N$_2$O is the third major contributor as a greenhouse gas [88] after CO$_2$ and CH$_4$ and has a global warming potential (GWP) of 290 [12, 89]. It is also an ozone (O$_3$) destroyer [90-93] implying that it has the potential of allowing harmful rays (like UV) from the sun to penetrate through the earth’s atmosphere and cause burns and potentially diseases such as skin cancer, etc. In terms of being an anthropogenic source, it is a by-product of coal combustion [94]. Vehicle emissions also contribute to a lesser extent [95].
1.10.2. Thermodynamics and calculations

The N\textsubscript{2}O decomposition reaction is thermodynamically feasible and spontaneous at any given temperature and atmospheric pressure since the change in Gibbs Free Energy is negative (i.e. \( \Delta G < 0 \)). The decomposition of N\textsubscript{2}O is known to be exothermic at standard conditions (i.e. 298 K and 101 kPa) and it is thermodynamically spontaneous over a large temperature range (i.e. \( \Delta G < 0 \)) with a large equilibrium constant, \( K \) (see Table 1.5). The equilibrium constant is a measure of whether the reaction is favourable at equilibrium. A large \( K \) (i.e. \( K > 1 \)) indicates that the products are favourable but a small value (i.e. \( K < 1 \)) favours the reactants.

\[
\text{N}_2\text{O} \rightarrow \text{N}_2 + \frac{1}{2} \text{O}_2 \quad \Delta H = -163 \text{ kJmol}^{-1} \quad \text{[101-102]}
\]

Considering:

\[
\Delta G = -RT \ln K \quad \text{(equation 1.1)}
\]

where \( \Delta G \) = change in Gibbs Free Energy, \( R \) = universal gas constant (8.314 JK\textsuperscript{-1}mol\textsuperscript{-1}), \( T \) = temperature (in K) and \( K \) = equilibrium constant.

Rearranging:

\[
- \frac{\Delta G}{RT} = \ln K \quad \text{(equation 1.2)}
\]

Table 1.5 summarises the AG and K values at selected temperatures. So plotting either \( \Delta G \) against \( \ln K \) or \( 1/T \) against \( \ln K \) gives a negative slope and an indication as to whether the reaction is feasible at a given temperature.

The \( \Delta G \) values can be plotted as a function of increasing \( T \) (i.e. an Ellingham diagram) \([104]\), and hence graphically show that the decomposition is thermodynamically spontaneous over the selected temperature range (see Figure 1.9). The negative slope implies that gas is being formed i.e. \( \text{N}_2 \) and \( \frac{1}{2} \text{O}_2 \).
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Table 1.5. – Free energy and K for N₂O decomposition tabulated with respect to T

<table>
<thead>
<tr>
<th>T (K)</th>
<th>ΔG (kJ mol⁻¹)</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>-103.8</td>
<td>1.18 x 10¹⁸</td>
</tr>
<tr>
<td>400</td>
<td>-111.3</td>
<td>3.45 x 10¹⁴</td>
</tr>
<tr>
<td>500</td>
<td>-118.9</td>
<td>2.60 x 10¹²</td>
</tr>
<tr>
<td>600</td>
<td>-126.4</td>
<td>1.00 x 10¹¹</td>
</tr>
<tr>
<td>700</td>
<td>-133.9</td>
<td>9.70 x 10⁹</td>
</tr>
<tr>
<td>800</td>
<td>-141.3</td>
<td>1.67 x 10⁹</td>
</tr>
<tr>
<td>900</td>
<td>-148.7</td>
<td>4.25 x 10⁸</td>
</tr>
<tr>
<td>1000</td>
<td>-156.0</td>
<td>1.14 x 10⁸</td>
</tr>
</tbody>
</table>

Fig. 1.9. – Gibbs free energy as a function of temperature for N₂O decomposition

Then one can plot ln K against 1/T:
Fig. 1.10. – Relationship between \( K \) and \( T \) for \( \text{N}_2\text{O} \) decomposition

The equation of the graph is

\[
y = 9.806x + 8.965 \quad \text{(equation 1.3)}
\]

Substituting \( y = \ln K \) and \( x = 1000/T \):

\[
\ln K = 9.806/T + 8.965 \quad \text{(equation 1.4)}
\]

\[
T = (9,806) / (\ln K - 8.965) \quad \text{(equation 1.5)}
\]

When \( T = 1073 \text{ K} \) (i.e. the temperature at which the continuous experiment was allowed to reach – see Chapter 3), the equilibrium constant \( K = 1.92 \times 10^8 \). This means that \( \text{N}_2\text{O} \) decomposition is feasible at this temperature. The equilibrium constant is very large throughout the temperature range used here (see Table 1.5). The fractional conversion, \( \alpha \) can therefore be confidently considered as \( \alpha = 1 = 100 \% \).
At 298 K the decomposition is however kinetically slow which is mainly attributable to the large activation energy, $E_a$, (see Chapter 2) which lies between 250 and 270 kJmol$^{-1}$ [101, 105-106].

$\text{N}_2\text{O}$ is used mainly as an anaesthetic in medicine [101] and in Internal Combustion Engines (ICE) to increase power output. It is also used as a dispersing agent in cream whippers. Here the application in terms of microsatellite propellants and reduction of emissions as a greenhouse gas are explored. It is justified therefore that it is a worthy cause to find ways of limiting the presence of this gas in the atmosphere. In this regard, catalytic decomposition of $\text{N}_2\text{O}$ has attracted much attention and has become a useful way to achieve this [102, 107-139].

$\text{N}_2\text{O}$ can be formed by surface NO$_2$-HC interactions and NO$_x$ is from car exhausts, but catalytic converters are useful in the sense that they convert them back to harmless N$_2$ and O$_2$.

$\text{N}_2\text{O}$ decomposition serves two very good purposes:

1) the conversion of $\text{N}_2\text{O}$ in the atmosphere over a suitable catalyst to harmless N$_2$ and O$_2$, and hence minimising the environmental impact of the greenhouse effect and ozone layer depletion.

2) interesting and exciting applications as a monopropellant for satellite microthruster fuel combustion.

1.10.3 $\text{N}_2\text{O}$ microthrusters in satellites

The decomposition of $\text{N}_2\text{O}$ and its use as a monopropellant fuel for satellite microthrusters is very useful technologically (e.g. orbital manoeuvring). In addition, satellites are in continuous demand with applications as diverse as communication, research and for military purposes [140]. The current use of hydrazine ($\text{N}_2\text{H}_4$) or hydrogen peroxide ($\text{H}_2\text{O}_2$) as fuel is unfavourable since they are hazardous, toxic and explosive. This is uneconomical due to high safety-related costs [101, 104, 141-142].
The use of mini, micro and nano-satellites has become possible in recent times as a result of the availability of miniature electronic hardware.

A microsatellite is shown in Figure 1.11 above and is designed to carry up to 35 kg space load, and weighs between 35 and 70 kg. Nanosatellites weigh less than 10 kg and minisatellites are capable of supporting missions of up to 400 kg.

These achievements provide opportunities for many new avenues of space exploration [143].

1.11. CH₄ Chemistry

As already mentioned CH₄ is the second major contributor to global warming (after CO₂). It is a colourless, odourless gas with a melting point of 89 K and boiling point of 109 K. It is the main constituent of natural gas associated with oil. It is formed by the decay of vegetable matter and occurs in coal mines. It is also obtained from the anaerobic digestion of sewage and it is produced by reacting CO and H₂ over a Ni catalyst at 503-523 K at atmospheric pressure:

\[ CO + 3H₂ \rightarrow CH₄ + H₂O \]

CH₄ is tetrahedral with H-C-H bond angles of 109.5°, in accordance to the VSEPR theory [144]. The frontier orbitals have C in its excited state where the 2s orbital is unpaired: 2s¹, 2px¹, 2py¹, 2pz¹. The four unpaired electrons overlap with singly
occupied \( s \) orbitals on the four \( H \) atoms. The mixing of these \( s \) and \( p \) orbitals results in four \( sp^3 \) hybrid orbitals which form stronger bonds than the original atomic orbitals. This also ensures that the molecule stabilises itself by conforming to a tetrahedral structure that maximises the bond angles.

\( \text{CH}_4 \) is also thermodynamically very stable with C-H bond energies of 414 kJmol\(^{-1} \) [145-146]. It does however react explosively with chlorine at 298 K and \( \text{CCl}_3 \) is formed at low temperatures. It is also used as a fuel and in the manufacture of chloro- and dichloromethane. Other uses include \( \text{H}_2 \), \( \text{NH}_3 \) and \( \text{CO} \) production.

1.12. Combined control of \( \text{CH}_4 \) and \( \text{CO}_2 \) (Dry reforming)

Since \( \text{CO}_2 \) and \( \text{CH}_4 \) are the two main gases that are responsible for global warming, it is a worthy cause to use these up. The main problem is that \( \text{CO}_2 \) is the final oxidation product for many chemical processes and is therefore of little value by itself. Dry reforming of \( \text{CH}_4 \) is a convenient means by which to use up \( \text{CO}_2 \) and \( \text{CH}_4 \) but it is very endothermic requiring a high energy input and costs (i.e. high temperature and/or pressure to make the reaction feasible):

\[
\text{CO}_2 + \text{CH}_4 \rightarrow 2\text{CO} + 2\text{H}_2 \quad \Delta H^\circ_{(298K)} = +247 \text{ kJmol}^{-1}.
\]

Despite the reaction having a considerable high \( \Delta H \) value in relation to the alternative technologies (see section 1.13), it nevertheless is still considered to be a convenient means by which to reduce the impact of \( \text{CO}_2 \) by its direct utilisation, especially in the presence of a suitably engineered catalyst. This aspect will be discussed in Chapters 2 and 4. To judge whether this technology is worth pursuing, one needs to consider the thermodynamics of the reaction, in terms of whether the reaction will become spontaneous at any given temperature and/or pressure (see section 1.12.1).

The production of synthesis gas, also known as syngas (2\( \text{CO} + 2\text{H}_2 \)) [147-148] via this reaction is an effective and convenient route by which to utilise both \( \text{CO}_2 \) and \( \text{CH}_4 \) (two of the major GHGs). For many, this has been one of the challenges with regards to reducing the environmental impact of the effects of the greenhouse effect.
Alternative technologies have been looked into, namely \textit{steam reforming} and \textit{partial oxidation} [149-153], but as will be shown in section 1.13, these are not as useful as the dry reforming route.

Research in this area is well documented in the literature indicating an enormous growth of interest in recent years, especially in the light of increasing environmental concerns [154-251]. A number of patents indicate a valuable application for this technology [252-254].

The \textit{syngas} can subsequently be used to give high value oxygenates, such as methanol (CH$_3$OH) [255] and dimethylcarbonates (DMC) [256-266]. The production of both CH$_3$OH and DMC uses up CO$_2$. CH$_3$OH itself is a very useful organic precursor used widely in both industry and academia. DMC has wide commercial applications, including as a fuel additive. High temperatures and pressures are normally required to convert the \textit{syngas} to CH$_3$OH and DMC. However, using a suitable designer catalyst/support, one may be able to compensate for these conditions. Hydrocarbons such as ethene [267] may be formed; these are useful as chemical intermediates. This area will however not be explored in the research but is suggested for future work (see Chapter 7).

1.12.1. Thermodynamics and calculations for dry reforming

As mentioned earlier a reaction is thermodynamically feasible at any given temperature and pressure when the change in \textit{Gibbs Free Energy} is negative (i.e. $\Delta G < 0$).

\textit{Table 1.5} summarises the $\Delta G$ and K values at selected temperatures. So plotting either $\Delta G$ against ln K or 1/T against ln K gives a negative slope and an indication as to whether the reaction is feasible at a given temperature.
Table 1.6. – Free energy versus equilibrium constant (K) with respect to temperature.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\Delta G$ (kJmol$^{-1}$)</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>+ 116.6</td>
<td>6.52 x 10$^{-13}$</td>
</tr>
<tr>
<td>800</td>
<td>+ 32.7</td>
<td>8.13 x 10$^{-3}$</td>
</tr>
<tr>
<td>900</td>
<td>+ 3.9</td>
<td>0.588</td>
</tr>
<tr>
<td>1000</td>
<td>- 24.6</td>
<td>19.22</td>
</tr>
</tbody>
</table>

Consequently, the $\ln K$ versus $1/T$ plot is:

![Graph showing $\ln K$ versus $1/T$]

Fig 1.12. – Temperature versus equilibrium constant (K) for the dry reforming of CH$_4$ reaction

The equation of the line is:

$$y = -30.978 x + 33.903$$  \hspace{1cm} \text{(equation 1.6)}

substituting for $y = \ln K$ and $x = 1000/T$:

$$\ln K = (-30.978 / T) + 33.903$$  \hspace{1cm} \text{(equation 1.7)}
1. Introduction.

\[ T = \frac{-30,978}{(\ln K - 33.903)} \]

(equation 1.8)

At 973 K, which was the upper temperature for pulse work (see Chapter 4), \( K = 7.88 \) implying that the reaction is feasible at that temperature.

Similarly, a plot for \( \Delta G \) against \( T \) can also be plotted:

![Graph showing the relationship between \( \Delta G \) and Temperature](image)

Fig. 1.13. – Gibbs free energy as a function of the temperature for the dry reforming of CH\(_4\) reaction.

An equation for a general reaction is:

\[ aA + bB \rightarrow cC + dD \]

the equilibrium constant, \( K \) can be expressed as:

\[ K = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]

For the dry reforming reaction:

\[ \text{CO}_2 + \text{CH}_4 \rightarrow 2\text{CO} + 2\text{H}_2 \]
K is thus expressed as:

$$K = \frac{[\text{CO}]^2[\text{H}_2]^2}{[\text{CO}_2][\text{CH}_4]} \quad (equation \ 1.9)$$

In terms of pressures in atmospheres (atmos.) this can be simplified to:

$$K = \frac{[\text{CO}]^4}{[\text{CO}_2]^2}$$

The units are therefore (atmos.)$^4$ / (atmos.$^2$) = (atmos.$^2$)

Now, if $\beta$ represents extent of reaction, so $\text{CO}_2 + \text{CH}_4 \rightarrow 2\text{CO} + 2\text{H}_2$ becomes:

$$(1-\beta) + (1-\beta) = \beta + \beta \quad (equation \ 1.10)$$

Substituting in equation 1.10 above:

$$K = \beta^2 \cdot \beta^2 / (1-\beta) (1-\beta)$$

$$\therefore \quad K = \beta^4 / (\beta^2 - 2\beta + 1) \quad (equation \ 1.11)$$

Hence, by substituting $\beta$ values from 0.1 to 0.9 for increasing relative fractional conversion, the $K$ values can be obtained. This can subsequently be substituted in equation 1.8 above to obtain $T$ (see Table 1.6). Then plotting $T$ against $\beta$ will give the relationship equation for the relative fractional conversion ($\beta$) expected with respect to a given $T$ (see Figure 1.14).

<table>
<thead>
<tr>
<th>$\beta$</th>
<th>$K$</th>
<th>$T$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.0001</td>
<td>722.1</td>
</tr>
<tr>
<td>0.2</td>
<td>0.0025</td>
<td>776.6</td>
</tr>
<tr>
<td>0.3</td>
<td>0.0165</td>
<td>815.2</td>
</tr>
<tr>
<td>0.4</td>
<td>0.0711</td>
<td>848.7</td>
</tr>
<tr>
<td>0.5</td>
<td>0.2500</td>
<td>879.3</td>
</tr>
<tr>
<td>0.6</td>
<td>0.8100</td>
<td>908.4</td>
</tr>
<tr>
<td>0.7</td>
<td>2.6678</td>
<td>941.0</td>
</tr>
<tr>
<td>0.8</td>
<td>10.240</td>
<td>980.9</td>
</tr>
<tr>
<td>0.9</td>
<td>65.610</td>
<td>1,042</td>
</tr>
</tbody>
</table>
From Figure 1.14, the equation of an approximate line was found to be \( y = 367.5x + 695.6 \) (equation 1.12) which equates to \( T = 367.5\beta + 695.6 \) (equation 1.13). Therefore at 973 K (i.e. conditions of pulse temperatures (see Chapter 4)), the maximum conversion that can be expected for this reaction in absolute terms is \( \beta = 0.8 \) or 80%.

\[ T (K) \]
\[ 1100 \]
\[ 1000 \]
\[ 900 \]
\[ 800 \]
\[ 700 \]
\[ 0.0 \]
\[ 0.2 \]
\[ 0.4 \]
\[ 0.6 \]
\[ 0.8 \]
\[ 1.0 \]

Fractional conversion, \( \beta \)

**Fig. 1.14.** - \( T \) as a function of the fractional conversion, \( \beta \) for dry reforming reaction.

1.13. Alternative technologies to syngas technology

Various technologies exist as an alternative to dry reforming of methane. These are steam reforming [190, 268-275], partial oxidation [269, 276-289] and the Fischer-Tropsch reaction [290-314].

Steam-reforming and partial-oxidation technologies have even been patented as recently as 1993, indicating a growing interest in this area [315]. Bearing in mind the present context, these were not as useful as the dry reforming of methane route. This is because steam reforming:

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad \Delta H^\circ_{\text{(298K)}} = + 206 \text{ kJmol}^{-1}
\]
produces synthesis gas but doesn’t use CO₂ as one of the reactants. Similarly partial oxidation:

\[ \text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \quad \Delta H^\circ_{(298 \text{K})} = -36 \text{kJmol}^{-1}. \]

produces syngas but does not consume CO₂. Both reactions do however have the advantage of using natural gas (i.e. CH₄). It is also worth noting that despite the steam reforming being the most dominant commercial process to produce syngas [269, 316-317], the partial oxidation route is more useful in the sense that the H₂/CO ratio is better. Partial oxidation is useful for the production of methanol and the Fischer-Tropsch synthesis [318], and the reaction is slightly exothermic, and hence the products are more easily formed.

In the case of the Fischer-Tropsch reaction, steam or oxygen and coal or coke (hydrocarbons) react to form a combination of methane, alkenes and gasolines. The disadvantage is that CO₂ is not consumed and methane (in certain cases) is being produced. It has the general formula:

\[ n\text{CO} + (2n+1)\text{H}_2 \rightarrow n\text{H}_2\text{O} + C_n\text{H}_{2n+2}. \]

Hence the limitation of the dry reforming reaction may be due to syngas products reacting further via the Fischer-Tropsch reaction or the reverse-water-gas-shift (RWGS) reaction [319]. The RWGS reaction occurs in certain cases when H₂ (the dry reforming product) and CO₂ (dry reforming reactant) react together to form CO and H₂O:

\[ \text{H}_2 + \text{CO}_2 \rightarrow \text{CO} + \text{H}_2\text{O}. \]

This can only happen however when there is enough product H₂ (since H₂ as reductant is flushed out of the system before the run begins – see Chapter 4) being formed with an excess CO₂ present in the stream. The presence of excess by-product CO and water may be due to this unwanted process occurring. Conversely however, the water-gas-shift (WGS) reaction may occur with CO products and H₂O as an impurity in the stream.
Catalytic combustion of methane \((\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}; \Delta H^\circ_{298 \text{ K}} = -801 \text{ kJmol}^{-1}\) as an alternative technology is mentioned in section 1.14 below. In this particular case, despite \(\text{CH}_4\) being consumed, the main problem is that \(\text{CO}_2\) is produced. Combustion and/or partial oxidation may also occur in the presence of oxygen as an impurity in the stream. Hence the need for reduced atmospheres during an experimental run (see Chapter 4). Despite the limitations, the dry reforming reaction is very selective (see Chapter 2) provided that the impurities in the stream are minimised as far as practically possible.

1.14. Other uses of \(\text{CO}_2\) and \(\text{CH}_4\)

From the above, there is much potential for a diversity of production of syngas, \(\text{CH}_3\text{OH}\) and DMC-type commodities. The conversion of alcohols to dialkylcarbonates (e.g. \(\text{CH}_3\text{OH}\) to DMCs) is promising [320-328]. The general reaction is of the form:

\[
\text{CO}_2 + 2\text{ROH} \rightarrow \text{CO(OR)}_2 + \text{H}_2\text{O};
\]

where \(\text{R}\) is an alkyl group.

The conversion of \(\text{CO}_2\) to dialkylcarbonates is thermodynamically feasible [256], but does not go to completion because of the unfavourable formation of water from the alcohol. The reaction itself is an endothermic one often requiring high temperature and/or pressure. It is hoped however that by the use of a catalyst such conditions would be compensated for, and hence economically cheaper to run (primarily on a small scale, and eventually to an industrial full-plant scale). This reaction will, however, not be the focus of the research project, and is suggested for future work (see Chapter 7).

\(\text{CH}_4\) and other hydrocarbons can also be used in other ways like catalytic combustion for energy production without the formation of pollutants like nitrogen oxides [209, 329-348].
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1.15. Aims of the research project

The aims of the research project were to:

- consider technologies for the control of two prominent greenhouse gas emissions (i.e. CO\textsubscript{2} and CH\textsubscript{4}).
- develop improved catalysts for CO\textsubscript{2}-CH\textsubscript{4} and N\textsubscript{2}O decomposition reactions.
- prepare effective catalysts for these reactions via sol gel and traditional impregnation routes.
- understand the modes of operation of these catalysts.
- explore the potential of heterogeneous photocatalysis for both the dry reforming and/or N\textsubscript{2}O decomposition.
- consider the potential of this catalytic technology to satellite propulsion.

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1. Introduction.

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1. Introduction.


1. Introduction.


2. Materials and Catalyst Preparations.

CHAPTER II:

Materials and Catalyst Preparations

2.1 Introduction

Catalysis is a unique and fascinating science because it addresses (and provides solutions to) many of society’s technological problems, without which the present day world would seem rather different [1-2]. Examples include catalytic converters for modern cars and catalytic oil cracking technology, which provided the Spitfires during World War II with an advantage over their opponents by using high octane fuel for faster acceleration. Other examples include many industrial processes such as (i) the Haber process for the production of ammonia using Fe as a catalyst, (ii) ethene and propene formation for polymer production from cracking naphtha, and (iii) margarine hydrogenation by saturating double bonds of unsaturated oils using Ni catalysts. In nature, enzymic catalysis is essential for all living matter (see section 1.9.2). Now catalysis provides “routes for the syntheses of energy sources and raw materials for chemical industries from alternative resources” [3].

2.2. Catalysis

Catalysis is not a new phenomenon. Davy [2] began experiments as early as 1815 with Pt gauzes catalysing combustion and oxidation. These gauzes were used in the Davy safety lamp for the use in mines that warned of dangerous atmospheres. The gauze would glow. Later in 1836, Berzelius [4] first coined the term ‘catalysis’ with the following definition:

“Many bodies... have the property of exerting on other bodies an action which is very different from chemical affinity. By means of this action they produce decomposition in bodies, and form new compounds into the composition of which they do not enter. This new power, hitherto unknown, I shall call it catalytic power. I shall also call catalysis the decomposition of bodies by this force.”

A more rigorous and scientifically precise definition was given by Ostwald, and to this day, it accurately describes this unique phenomenon:
2. Materials and Catalyst Preparations.

“A catalyst is defined as a substance, or a mixture of substances, which increases the rate of a chemical reaction by providing an alternative, quicker reaction pathway, without modifying the thermodynamic factors. The catalyst remains, in general, unaltered at the end of the catalytic process.”

In other words, a catalyst is “a substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction” [5], or “a substance that increases the rate at which a chemical reaction approaches equilibrium, without being consumed in the process” [6].

Hence, it is a substance that accelerates the rate of attainment of the equilibrium of a reaction, without itself being consumed in the process. It therefore does not appear in the stoichiometric equation for the overall reaction. Catalysis is therefore a kinetic phenomenon and is not concerned with the overall thermodynamics of the reaction (i.e. \( \Delta H \), \( \Delta G \) and \( \Delta S \) remain the same).

The catalyst also lowers the activation energy (\( E_a \), the energy barrier that needs to be overcome in order to convert the reactive species, or reactants to their respective products) of a process. The lower the \( E_a \) of the catalysed reaction (compared to the corresponding un-catalysed situation) the better the catalyst is. The catalytic reaction rate therefore needs to be very much greater than the non-catalysed reaction rate at the same temperature. This means that the throughput for a reactor is increased and therefore the reaction/reactor is more economical. Similarly, the temperature for a given rate over a catalyst should be lower than for a non-catalysed reaction.

The temperature for the thermal incineration of a hydrocarbon (HC) ranges from 1033 to 1255 K but with a catalyst, it is reduced to 533 to 755 K:

\[
HC + O_2 \rightarrow H_2O + CO_2
\]

Consequently, fuel and operating costs are decreased. Often the catalyst enables lower pressures to be used. This is economical as it lowers the reactor costs because the reactor walls are thinner.
2. Materials and Catalyst Preparations.

Major parameters that need to be considered when studying catalysed reactions are:

- the nature of the chemical bonds formed between the catalyst and the reactants;
- the energetics of the reaction over the catalyst; and
- the stereochemical requirements/restrictions of the catalysed reaction.

2.3. Activation Energy

The reaction energy path controls the speed of the reaction. The molecules follow the path of least resistance, but this path may still require a lot of energy. The energy requirement is called the activation energy, $E_a$. This $E_a$ is almost always positive, and if $E_a$ is higher then the reaction will be slower. This is different from the thermodynamic quantities like $\Delta H$ or $\Delta G$ which are defined by the thermodynamic differences between the reactants and products. Reactions often involve a transition state, TS. Figure 2.1 below illustrates the case for an exothermic reaction:

![E_a diagram for an exothermic process](image)

Fig. 2.1 – $E_a$ diagram for an exothermic process

For an endothermic reaction (see Figure 2.2 below) the energy for the products is higher than the energy for the reactants. The magenta curve shows the actual reaction pathway for an uncatalyzed reaction. The blue curve however shows what a catalyst does to the energy for the reaction path. Kinetically, the reaction is faster when the catalyst is present and the $E_a$ is lowered. The thermodynamics of the reaction however is unaltered, and hence the energies of the reactants and the products remain the same since $\Delta G$ stays the same. The relative amounts of reactants and products also stay the
The catalyst only allows the reaction to reach equilibrium faster (i.e. it alters the kinetics of the reaction).

![Diagram showing potential energy and reaction path.](image)

Fig. 2.2 – $E_a$ for an endothermic process

The reaction sequences can of course be much more complicated in the sense that there can be several activation energies associated with a particular reaction. In a simple reaction, there may only be one minimum, but in a complicated reaction there may be many local minima with one global minimum.

$E_a$ can be obtained from the Arrhenius equation [7]:

$$k = A \exp \left( - \frac{E_a}{RT} \right); \ln k = \ln A - \frac{E_a}{RT}$$

where $k$ = rate constant, $A$ = pre-exponential factor, $R$ = gas constant (8.314 J/K/mol) and $T$ is temperature in K.

Hence, by plotting $\ln k$ against $1/T$ over a certain temperature range, a straight line is obtained with the gradient equal to $- E_a/R$ and the intercept giving the value of $\ln A$. Compensation plots can also be plotted to show the compensation effect between the $\ln A$ term and the activation energy, $E_a$ (see Chapters 3 and 4). This effect is usually encountered in either of two situations:

- similar and related catalysts all being used for the same or similar reactions, or
- the same catalysts being used for different reactions.
2. Materials and Catalyst Preparations.

The first situation is relevant to the present investigation because similar and related catalysts are compared in the decomposition of N₂O (see Chapter 3) and dry reforming of methane (see Chapter 4). In A increases as Eₐ increases across a series and vice versa, and hence ‘compensation effect’.

2.4. Key properties of a catalyst

There are three main characteristics that indicate the properties of an ideal catalyst:

i) **High activity**: Activity determines how effective a particular catalyst is, so the higher the activity the more efficient the catalyst. A high surface area containing a well-dispersed active phase that is exposed to the reactants is often required. Surface area is largely dependent on the preparative method employed (see sections 2.9.4 and 2.9.5). In order to increase the rate of a reaction, a large number of active sites therefore must exist on the catalyst surface. A fast reaction rate and a short reaction time maximise product throughout.

ii) **High selectivity**: If a catalyst is selective, it yields a high proportion of the desired product with minimum amounts of by-products; hence there is a further economic incentive to develop selective catalysts. Consequently, the process efficiency is increased whilst pollution is decreased. Less waste implies less to dispose of or recycle. In essence therefore the yield of the desired product is maximised; the by-products ideally are eliminated and the purification costs are kept to a minimum.

So if several products are being formed during a reaction, the selectivity of the desired product can be defined as:

\[
S = \frac{\xi_i}{\sum \xi_i}
\]

where \( S = \text{selectivity}, \ i = \text{desired product} \) and \( \xi = \text{rate of reaction} \).

iii) **High recycling potential (regeneration)**: The catalyst lifetime must also be considered. This means that a small amount of catalyst must survive through a large number of cycles, if the process economics are to be most viable.
2. Materials and Catalyst Preparations.

2.5. Types of catalysis

There are principally three types of catalyst: homogeneous, enzymatic and heterogeneous.

2.5.1. Homogeneous catalysis.

Catalysed reactions that occur in a single phase are said to occur homogeneously. This means that the catalyst itself is in the same phase as the reactants; for example, the acid catalysed hydrolysis of an ester [8]. Recently, the term has been used more loosely to describe processes where the catalyst and one of the reactants are in the same phase, for example, the hydrogenation of liquid olefins catalysed by solutions of transition metal complexes. More generally, examples of such reactions are acid-base catalysis. There are two kinds of acid-base catalysis: specific and general. In specific acid-base catalysis, only H+ ions and OH− ions can effect catalysis. However, in general acid-base catalysis, acids and bases other than H+ and OH− ions effect catalysis. An example of acid-base catalysis is the reaction between acetone and iodine in aqueous solution:

$$\text{CH}_3\text{COCH}_3 + I_2 \rightarrow \text{CH}_3\text{COCH}_2I + HI$$

2.5.2. Enzymatic catalysis.

Enzymes, as proteins are in effect biological catalysts. Their action shows some resemblance to the catalytic action of acids and bases, but is considerably more complicated. They catalyse reactions with a high degree of specificity and efficiency. They are present in all living organisms and are responsible for catalysing most of the reactions that take place in a cell, e.g. the hydrolysis of fats, sugars and proteins.

One exceptional feature of enzymes is that they are often highly specific. Those that act on carbohydrates are particularly so that even the slightest change in the stereochemical configuration of the molecule is sufficient to make a particular enzyme incompatible and hence, unable to effect hydrolysis. Most enzymes work best within a narrow pH range and are susceptible to a wide variety of compounds which may
2. Materials and Catalyst Preparations.

inhibit or sometimes promote the activity. Most enzymes function well at around 313K, but are rapidly destroyed at higher temperatures. Enzymes are classified into divisions based on the type of reaction catalysed and the particular substrate. There are six main divisions, namely oxidoreductases, transferases, hydrolases, lyases, isomerases, and ligases. Catalytic sites in enzymes sit within a three-dimensional array of amino acids (hydrophobic) and are often coordinated with metal complexes, (e.g. those of Mg and Cu).

2.5.3. Heterogeneous catalysis.

In heterogeneous catalysis, the structure and geometry of the micro-environment in which the catalytic process takes place is important. Unlike the case for homogeneous catalysis, the catalyst is in a different phase from the reactants. The catalysed reaction is said to occur at an interface between two phases; for example, a solid catalyst in a reaction between liquid or gaseous reactants. Such reactions are generally considered to involve adsorption and reaction of the reactants at the catalytic surface. The major factors that affect the catalyst property are the active site chemistry, the support material and the location of the metal on and/or within the pore structure of the support e.g. TiO₂ and Al₂O₃ (see section 2.9.2.2).

2.6. Surface Science

In heterogeneous catalysis, reactions usually occur on the surface of a catalyst. Hence, the nature of the surface, as compared to the bulk, is a crucial factor in determining whether a particular catalyst is effective or not. Surfaces are generally unstable since the maximum coordination is not achieved. Hence it is a region of high energy. Consequently, there is a tendency to minimise this energy. Surface restructuring occurs in several ways to achieve this. These are:

- **Surface relaxation** – the surface atoms are drawn towards the bulk in such a way that it slightly increases the coordination of the surface atoms. The increased electron overlap from the layers below help to stabilize the surface.
2. Materials and Catalyst Preparations.

- **Surface reconstruction** – as an alternative to "relaxation", there is a reordering of the surface atoms to increase their coordination. This often means that as a result, there is a change in the number of atoms on the surface.

- **Sintering** – separate metal particles on the surface merge together to form fewer bigger ones in order to increase the average surface coordination. Even though this process stabilizes the surface, it is damaging to the catalyst and the reaction since the surface area is lowered causing a loss of the efficiency of the catalyst. The lifetime of the catalyst is therefore drastically reduced.

- **Adsorption** – this leads to chemisorption and reaction on the surface. This is the best way of stabilizing the surface and is ideal for catalysis (see section 2.7).

### 2.7. Adsorption and desorption

Central to heterogeneous catalysis is the concept of adsorption. Technically, there are two types of adsorption phenomena: **physical adsorption** (or physisorption) and **chemical adsorption** (or chemisorption). **Chemisorption** is when chemical bonds are formed between the adsorbate (the species undergoing adsorption) and the adsorbent (the surface at which adsorption is occurring).

If the chemisorption is weak then the reaction may not be efficient because the surface coverage (\(\theta\)) will be low, but with an increase in the strength of adsorption the activity will increase. However if the chemisorption is too strong, then subsequent reactions may be hindered because the surface will be fully covered (i.e. a poison). In this case, a decrease in the strength of adsorption will increase the activity.

Catalyst poisons are of two types: reversible and irreversible. In the case of reversible poisoning, the catalyst can be regenerated. In the case of irreversible poisoning, the catalyst cannot be regenerated and the poisoning is permanent (e.g. mercury or lead species on the surface). These can greatly reduce the activity of the catalyst.
2. Materials and Catalyst Preparations.

2.7.1. Physisorption

Physisorption or physical adsorption are not chemically specific and are therefore readily reversible. The forces of attraction between the adsorbate and adsorbent are usually weak *van der Waals* forces. As a result the formation of multiple layers is possible (e.g. N\textsubscript{2} adsorption for surface area analysis known as BET (see Chapter 6)).

2.7.2. Chemisorption

Chemisorption occurs when a substance adsorbs at a surface with the formation of chemical bonds between the adsorbate and adsorbent. Consequently the forces of attraction or the *heat of adsorption* are much stronger than in physisorption (i.e. 40 – 800 kJmol\textsuperscript{-1} for chemisorption and only 8–20 kJmol\textsuperscript{-1} for physisorption). This also means that multilayers are not possible because the surface is stabilised as a result of the adsorption [9]. This is very important in heterogeneous catalysis because it involves the reactants (in the gaseous phase for example) adsorbing on the active catalyst prior to further surface reactions and desorption of products. The strength of the adsorption will determine the activity of the catalyst. This is specific to the active catalytic site and not general like physisorption. *Table 2.1* below summarises the criteria for distinguishing between them.

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Chemisorption</th>
<th>Physisorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat of adsorption, $-\Delta H_{ads}$</td>
<td>40 – 800 kJmol\textsuperscript{-1}</td>
<td>8 – 20 kJmol\textsuperscript{-1}</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Usually small</td>
<td>Zero</td>
</tr>
<tr>
<td>Temperature of occurrence</td>
<td>Depends on $E_a$, but usually low</td>
<td>Depends on boiling point, but usually low</td>
</tr>
<tr>
<td>Number of layers adsorbed</td>
<td>Not more than 1</td>
<td>More than 1 is possible</td>
</tr>
</tbody>
</table>

The *Langmuir isotherm* is an example of chemisorption since the model explains how multilayers are not possible. The assumptions are:

1. the surface is intrinsically homogeneous;
2. Materials and Catalyst Preparations.

2. the surface consists of a specific number of sites. Each site can adsorb only one molecule after which no further adsorption is possible (i.e. multilayers are not allowed); and

3. all sites are equivalent and the presence of other molecules does not affect the energy of an adsorbed molecule.

Hence the Langmuir isotherm is derived [10]:

\[ \theta = \frac{bp}{1 + bp} \]

where \( \theta \) = surface coverage, \( b \) = Langmuir adsorption coefficient (i.e. rate constant of adsorption/ rate constant of desorption) and \( p \) = pressure. At low pressures, \( bp << 1 \) and \( \theta \propto p \); but at high pressures, \( bp >> 1 \) and \( \theta \to 1 \).

2.8. Types of heterogeneous catalysts

Two mechanisms exist to describe the surface reaction at the catalytic surface, or at the interface. Either one or both of the reactants are adsorbed on the surface followed by the reaction. Finally the product desorbs from the surface. These mechanisms are referred to as the Eley-Rideal and Langmuir-Hinshelwood mechanisms respectively. In both cases, adsorption coefficients representing the stabilities of the surface intermediates, and reaction rate constants representing the reactivity of the adsorbed intermediates are important parameters. The reactivity is therefore part influenced by the strength of adsorption.

The Langmuir-Hinshelwood mechanism has a number of assumptions [11]:

1. the surface reaction is the rate determining step;
2. the Langmuir isotherm describes the equilibrium between the gas phase and the adsorbed reactants;
3. the adsorbed reactants compete for surface sites; and
4. for bimolecular reactions the reaction is between two adsorbed species.
2. Materials and Catalyst Preparations.

I) In the unimolecular case there are two situations: i) decomposition of a single species where products are not adsorbed and ii) decomposition of a single species where products are adsorbed. For N₂O decomposition, the latter is experienced (see Chapter 7). The general reaction scheme is:

\[ \text{A} \rightarrow \text{B} \rightarrow \text{B}_{\text{gas}} \]

where A is the adsorbed single species and B is the adsorbed product prior to desorption.

For two competing species the Langmuir isotherm modifies to:

\[ \theta_A = \frac{b_A p_A}{1 + b_B p_B + b_A p_A} \]

where \( \theta_A \) is the surface coverage with respect to species A; \( b_A \) and \( p_A \) are the Langmuir adsorption coefficients for reactant A and its pressure respectively. \( b_B \) and \( p_B \) are the equivalent terms for product B. The rate, \( r \) is given by:

\[ r = \frac{k b_A p_A}{1 + b_B p_B + b_A p_A} \]

where \( k \) is the rate constant. At low pressure of A where \( b_A p_A \ll 1 \),

\[ r = \frac{k b_A p_A}{1 + b_B p_B} \]

and when the product is strongly adsorbed so that \( b_B p_B \gg 1 \) and \( b_B p_B \gg b_A p_A \),

\[ r = \frac{k b_A p_A}{b_B p_B} \]
II) Similar situations are experienced for a bimolecular reaction. For dry reforming both reactants and products adsorbing on the surface also need to be considered (see Chapter 7). The reaction scheme is:

\[ \text{A} \rightarrow \text{B} \rightarrow \text{C} \rightarrow \text{C}_{\text{gas}} \]

where A and B are the adsorbed reactants and C is the adsorbed product prior to desorption. The Langmuir isotherm therefore modifies to:

\[ \theta_A = \frac{b_A p_A}{1 + b_A p_A + b_B p_B + b_C p_C} \]

Similarly \( \theta_B \) is given by an analogous expression. The rate of the reaction is given by

\[ r = k \theta_A \theta_B \]

Or

\[ r = \frac{k b_A p_A b_B p_B}{(1 + b_A p_A + b_B p_B + b_C p_C)^2} \]

For strongly adsorbed products where \( b_C p_C \gg 1 + b_A p_A + b_B p_B \),

\[ r = \frac{k b_A p_A b_B p_B}{b_C^2 p_C^2} \]

The *Eley-Rideal* mechanism however considers the possibility that an adsorbed species has a gas molecule collide directly with it to cause the reaction. One atom in the gas molecule interacts with the surface leaving the other end available to react with other atoms in the layer, and hence the collision. This mechanism was not relevant here and therefore not discussed further.
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2.9. Materials and preparation of catalysts

2.9.1. Metal oxides

An oxide may be ionic (e.g. CaO), complex transition metal oxides (TiO$_2$) and group III and IV metal oxides (e.g. Al$_2$O$_3$ and SiO$_2$ respectively). TiO$_2$, Al$_2$O$_3$ and SiO$_2$ are complex because depending on the conditions (i.e. at atmospheric pressure but varying temperatures), they can exhibit many polymorphic structures (see section 2.9.2.2) with each having their own chemistry and applications.

In oxidative catalysis metal oxides (e.g. Rh$_2$O$_3$) play a crucial part because it is these that determine how well a reaction proceeds on the surface. The surface of oxides “contain dangling bonds or defects whose valency requirements are usually satisfied by a chemical reaction” or “reconstruction of the near surface atoms” [12]. In catalysis therefore, most oxide surfaces contain a variety of sites ranging from hydroxyl groups, Lewis acid/basic sites and Bronsted acid/basic sites. A Lewis acid is a substance that is an electron pair acceptor (e.g. Ti$^{4+}$ cation) and a Lewis base is one that donates an electron pair (e.g. NH$_3$). A Bronsted acid is a compound that donates an H$^+$ ion (proton) to another compound (e.g. H$_2$O, H$_3$O$^+$, HSO$_4^-$), whereas a Bronsted base is one that accepts an H$^+$ ion (e.g. OH$^-$ and CH$_3$COO$^-$). It is these that interact with the d-orbital electrons of transition metal cations. As an example, Figure 2.3 below shows a schematic energy level diagram indicating how a first row transition metal ‘M’ in octahedral coordination interacts with an oxygen anion that may be on the surface. Oxygen is an electron pair accepter and hence behaves as a Lewis acid site.

The exact nature of the sites depend upon the preparative method used, the presence of foreign species (as impurities or promoters), and the pre-treatment conditions (see Chapters 3 and 4) employed prior to a catalytic experiment. Transition metal oxides often display nonstoichiometric behaviour (variable composition) and these often lead to binary and tertiary phase systems. These phases have uses in heterogeneous catalysis and in semiconductor devices.
Fig. 2.3 - Schematic energy level diagram for transition metal 'M' (e.g. row 1 transition metals) in octahedral coordination with oxygen anion [13].

i) Binary and tertiary oxide systems – Structurally, these are considerably more complicated. In the binary case, two oxides are combined together into one. In the case of a sol-gel derived binary oxide, an extensive polymeric structure is intertwined in both (see section 2.9.5). The advantage of these systems is that the second oxide system can stabilize the first (e.g. TiO₂ in SiO₂-TiO₂). Often the second oxide is added as a modifier to the first, hence enhancing the properties of the catalyst to facilitate a particular reaction (e.g. yttria stabilised zirconia, YSZ [14]). Tertiary oxide systems are even more complicated with three oxide phases combined into one [15]; their chemistry will not be discussed here.

2.9.2. Materials chemistry

Here the materials that were used for the preparation of catalysts and used for the decomposition of N₂O (see Chapter 3) and the dry reforming of methane (see Chapter 4) are described.
During Stage I Ag (as Ag\textsuperscript{+NO}_3\textsuperscript{-} precursor) was used for the preparation of Ag/SiO\textsubscript{2}-TiO\textsubscript{2} because it was thought to be active in the take-up and release of CO\textsubscript{2}. It can also be used for the epoxidation of ethene to ethylene oxide at 523- 573 K [16-17]. Even though the product can form explosive mixtures with air, it is a useful organic intermediate since it allows for routes into the production of valuable oxygenates such as ethylene glycol, ethers of glycol, ethylene chlorohydrin, ethanolamines, monoesters of ethylene glycol, di-esters, ethanol, ethanal, 1,2-epoxide polymers, etc. It was prepared as a result of various investigations that were done to find the ideal method by which to introduce the metal ‘M’ to the sol-gel matrix (see section 2.9.5.1-4). This was used as a base for further preparations (i.e. Stages III and IV).

Ag: Silver (Ag) has the following properties: electronic configuration: [Kr]4d\textsuperscript{10}5s\textsuperscript{1}, atomic number: 47, atomic weight: 107.87 gmol\textsuperscript{-1}, density: 10.49 g cm\textsuperscript{-3}, melting point: 1235 K, boiling point: 2485 K. It’s relative abundance in the Earth’s crust compared to other elements is 0.08 ppm. The metal is a pure white ductile material with a cubic close packing (ccp) structure and is used extensively in jewellery, electrical components (conductors, dental and surgical equipment), in mirrors, photography and catalysis. It exists as the pure metal and as an impurity in sulphide ores. It shows +4, +3, +2 and +1 oxidation states.

Silver nitrate (Ag\textsuperscript{+NO}_3\textsuperscript{-}) is obtained by dissolving the metal in dilute HNO\textsubscript{3}. On heating it decomposes to Ag, N\textsubscript{2}O\textsubscript{4} and O\textsubscript{2}. Ag\textsuperscript{+NO}_3\textsuperscript{-} was used as a precursor in loading the support (SiO\textsubscript{2}-TiO\textsubscript{2}) with Ag (see section 2.9.5.2-4).

2.9.2.1. Group VIII metals

Group VIII metals were shown to have activity for dry reforming as early as 1928 [18]. Environmental concerns like global warming have meant that the problem has been recently revisited. Group VIII metals include the Pt metals (comprising the elements Ru, Rh, Pd, Os, Ir and Pt). These six elements are grouped together due to their similarities. With the exception of the lanthanides, these similarities are greater than anywhere else in the Periodic Table. The Pt metals are widely used as catalysts in chemical processes for reactions ranging from gas phase oxidation through selective hydrogenation of chemical, petrochemical and pharmaceutical feedstocks to fuel cell
for power generation. Despite these rare metals being expensive, they are often more reactive and selective because they require milder reaction conditions. An added advantage of their use is that the spent catalyst can be reprocessed and the precious metal can be regenerated into fresh catalyst.

Rh, Ru, and Ir upon SiC\(^{\text{2}}\) as support (see Chapter 4) were the catalysts used in Stage II for developing the experimental methodology. Rh, Ru, Ir and Ni are well known to be good catalysts for dry reforming of methane [19-22]. Rh was chosen because it was shown to be active for decomposition of N\(_2\)O [23-36] and dry reforming of methane [37-44]. Although Rh is mentioned here, other metal catalysts could be used in its place, for example, Pd or Pt. From an economic viewpoint, it would be advisable to consider a metal such as Pd instead of Rh. This is because Rh is more expensive (since it is rarer than both Pd and Pt). Pd is more abundant than both Pt and Rh, and hence due to it’s availability, it is much cheaper, and also possesses similar chemistry, but obviously not the same. It has been reported however that in terms of catalytic activity, Rh is the best with the actual sequence being Rh > Pt ~ Cu > Pd > Au [45]. Therefore, despite controversial debates “about the most suitable metal, Rh was unanimously observed to be among the most stable and active of group VIII metals” [46]. Furthermore, Rh was chosen in place of Ru and Ir as the main metal in catalysts because it was most effective in terms of producing the syngas (see Chapter 4). Hence Rh was considered to be the ideal choice.

Ir: Iridium was discovered by Tenant in 1803 and is the heaviest member of the Co group and it is one of the Pt group metals with the following properties: electronic configuration \([\text{Xe}]5\text{d}^7\text{6s}^2\), atomic number: 77, atomic weight: 192.9 g mol\(^{-1}\), density: 22.65 g cm\(^{-3}\), melting point: 2716 K and boiling point: 4,403 K. It is a rare element comprising only 0.001 ppm of the earth’s crust. It is a silvery white metal with a ccp structure and it shows variable oxidation states from +6 (IrF\(_6\)) right through to -1 [Ir(CO)\(_4\)]. The +6 and +5 oxidation states are strongly oxidizing and +4 and +3 are stable. The +4 oxidation state is more stable than Rh. The +2 oxidation state is not very common and +1 generally exists as square planar molecules such as with phosphines and carbonyls. Ir(0) exists in the form of carbonyls for example, e.g. Ir\(_2\)(CO)\(_8\).
Its high melting point is associated with very good mechanical properties above 1873 K. It is used as a hardening agent for Pt and to encapsulate radioactive fuels in space. It also has uses in electrochemistry (25%), catalysis (8%) and in crucibles (11%).

**Ru:** Ruthenium was discovered by Klaus in 1844 and it is also a Pt group metal and a member of the Fe group with electronic configuration [Kr]4d⁷5s¹ and atomic number: 44; atomic weight: 101.07 gmol⁻¹; density: 12.45 g cm⁻³; melting point 2583 K and boiling point: 4173 K. Ru is a very rare element; relative abundance in the earth’s crust is estimated to be only 0.0001 ppm. It is a hard, grey-white metal with a hexagonal close packed (hcp) structure. It is very stable and resistant to most acids although it reacts with O₂ and F₂ at high temperatures. It shows variable oxidation states ranging from +8 to −2. The +8 oxidation state is strongly oxidizing and the most common oxidation states are those of +3 and +2. N-bonded complexes are particularly stable and many ammines, dinitrogen and nitrosyl complexes (NO bonded to the metal through N) are known. Phosphine (PH₃) complexes are also known with lower oxidation states. The chloride and hydride complexes are good hydrogenation catalysts. Ru compounds have uses in catalysis, anode plating in chlorine production, alloys and in electrical applications.

**Rh:** Rhodium was discovered by Wollaston in 1803. It is also a Pt group metal and like Ir, it is a member of the Co group. It has the electronic configuration [Kr]4d⁸5s¹ and atomic number: 45; atomic weight: 102.9055 gmol⁻¹; density: 12.4 g cm⁻³; melting point: 2239 K and boiling point: 4000 K. It is found with other Pt metals often in Ni-Cu deposits and heavy metal sulphide ores. The mixed metals are reduced and the Rh is extracted from the insoluble aqua-regia material with fused KHSO₄; and then extracted with H₂O and precipitated out as hydrated Rh₂O₃. This is dissolved in HCl to give (NH₄)₃RhCl₆. The metal is subsequently obtained by reduction with H₂. It is a silvery white metal with a ccp structure and is very inert. Due to its rarity (only 0.0001 ppm of the earth’s crust), it is also rather expensive. It shows variable oxidation states ranging from +6 (RhF₆) to −1 [Rh(CO)₄]⁺. The +6, +5 and +4 oxidation states are strongly oxidizing and +3 is the most common and most stable state. The +2 oxidation state is not very well known but square planar complexes of the +1 state are very well known, including that of Wilkinson’s catalyst, [RhCl(PPh₃)₃] [47-48].
2. Materials and Catalyst Preparations.

**Ni:** Nickel catalysts are used in many industrial processes including hydrogenation, hydrogenolysis of hydrocarbons and steam reforming [49]. Ni was used and chosen here as a comparison catalyst to Rh during Stage III because it was shown to have activity for the dry reforming reaction [50-77] and the decomposition of N₂O [78-85]. The use of Rh and Ni catalysts in dry reforming of methane is also supported by the work of Kumarasamy [86].

Nickel was discovered by Cronstedt in 1751 and it is a transition metal of Group VIII with the following properties: electronic configuration [Ar]3d⁸4s², atomic number: 28, atomic weight: 58.69 g mol⁻¹, density: 8.90 g cm⁻³, melting point: 1726 K and boiling point: 3005 K. It’s relative abundance in the Earth’s crust is 99 ppm making it the seventh most abundant transition metal and the twenty-second most abundant element in the Earth’s crust.

The most stable oxidation state is +2 (e.g. NiCl₂.6H₂O). The +3 and +4 oxidation states are known for fluorides and oxides. Ni(I) e.g. Ni(PPh₃)₃Cl is fairly stable and Ni(0) compounds are known such as nickel carbonyls, Ni(CO)₄. These in particular are toxic, so in the investigations that follow, care had to be taken to prevent the occurrence of this material. Its melting point is 298 K and boiling point is 341 K and so it exists as a liquid at room temperatures. Ni is a cheaper option but the health risks mean that the Pt group metals are worth considering. Fortunately, the experiments required the decomposition of N₂O to occur at high temperatures, which meant that any Ni(CO)₄ forming would decompose to pure Ni (the Mond process for purifying Ni) [87].

2.9.2.2. Support materials

The following are descriptions of elements and associated compounds that were eventually used as supports.

**Si:** Silicon was discovered by Berzelius in 1824. It is a group IV element and has the following properties: electronic configuration [Ne]3s²3p², atomic number: 14, atomic weight: 28.0855 g mol⁻¹, density: 2.33 g cm⁻³, melting point: 1683 K and boiling point: 2628 K. It is the most abundant element (27.2 %) in the Earth’s crust after oxygen.
2. Materials and Catalyst Preparations.

(45.5 %). It is normally in the +4 oxidation state although +2 species are known because of their importance as reactive intermediates. Like carbon, catenation and bridging (with C, N and O for example) is possible so that there is an extensive range of Si chemistry. These include SiC (carborundum – a hard refractory material used for bricks, fibres in metals and crucibles), SiF₄, SiCl₄ and higher chlorides such as Si₂Cl₆ and Si₆Cl₁₄. Crude Si is obtained by reduction of SiO₂ with C in an electric furnace. Pure Si is then obtained by converting to SiCl₄ or other halide which is then purified by fractional distillation and reduced to Si on a hot wire. Si, like C has a characteristic diamond lattice and is oxidised on strong heating in air. It reacts with F₂ or Cl₂ and gives silicates with fused alkalis. The pure material, doped with B or P is used in transistors.

Silica: It is one of the most important constituents of the Earth’s crust and many polyforms of SiO₂ exists across a wide temperature range at atmospheric pressure. Figure 2.4 shows some of the different forms such as quartz (to 846 K), tridymite (to 1743 K) and cristobalite (to 1986 K) [88-89] and Figure 2.5 shows a phase diagram of the various regions as a function of temperature and free energy.

<table>
<thead>
<tr>
<th>β-quartz</th>
<th>β-tridymite</th>
<th>β-cristobalite</th>
<th>liq SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>fast 846 K</td>
<td>fast 393-533 K</td>
<td>fast 473-550 K</td>
<td>Sluggish 1986 K</td>
</tr>
<tr>
<td>slow 1140 K</td>
<td>slow 1743 K</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2.4 – Some of the different forms of SiO₂
There are two modifications of each type: glass and high pressure forms. All consist of the SiO$_4$ tetrahedra. Naturally occurring SiO$_2$ is amorphous and slightly coloured by Fe. SiO$_2$ can also be synthesised under laboratory conditions using tetraethoxysilane (TEOS) as a precursor for example. It is one of the "simplest of oxides with relatively unreactive siloxane, Si-O-Si, bridges and surface hydroxyl groups" [90-91]. It usually has high surface areas ranging from 100m$^2$/g to 600m$^2$/g making it suitable to act as supports for heterogeneous catalysts. On exposure to air (or water), it can become fully hydroxylated (or hydrolysed) forming Si-OH bonds, hence its use as a drying agent. Other uses include sensors, novel coatings, process chemistry and pharmaceutical applications [92]. It was used during Stage II (see Chapter 4) and during the Rh and Ni catalyst preparations (see section 2.11)

Silica gel: Amorphous form of hydrated silica produced by precipitation, flocculation or coagulation of silica sol or decomposition of some silicates. When freshly prepared it has a gelatinous appearance and upon heating, it cannot be reconverted to the sol.
Dehydrated SiO\(_2\) gel is commercially used as an absorbent in the recovery of solvents, for drying air, dehydrating gases, for filtration and as a support for catalyst. Some gels are inert but hygroscopic, and hence have uses in chromatographic columns. Co(II) compounds are often incorporated into the gel and used as moisture detectors; upon moisture absorption, the colour is pink and blue when it is re-heated.

Silicates: These are an extensive group of substances, minerals and derivatives of SiO\(_2\). They are a major constituent of most rocks. All silicates are based on a [SiO\(_4\)] tetrahedron. Simple minerals are like ZrSO\(_4\) with [SiO\(_4\)]\(^{4-}\) anions. Elements like Al, B and Be can replace Si in the anion and cations are in the holes of the lattice. Typical silicates are feldspar, mica, zeolites and aluminasilicates.

Ti: Titanium was discovered by Gregor in 1791. It is a Group IV transition element with the following properties: electronic configuration [Ar]3d\(^{2}\)4s\(^{2}\), atomic number: 20, atomic weight: 47.88 g mol\(^{-1}\), density: 4.5 g cm\(^{-3}\), melting point: 1933 K and boiling point: 3560 K. It comprises 0.63 % of the Earth’s crust making it a very abundant element – ninth of all elements and second of the transition metals. Its principal minerals are ilmenite, FeTiO\(_3\) and rutile, TiO\(_2\). The metal is obtained by reducing TiCl\(_4\) with Mg and it has a protective layer of oxide in air. It is as strong as steel, but 45 % lighter and 60 % heavier than Al but twice as strong. It has uses as a lightweight construction material, as a white pigment in paint and in catalysis. Ti alloys are used in the aircraft industry, lightweight sports gear (e.g. squash and badminton rackets), engines and chemical plants. The most stable oxidation state is +4 (e.g. TiO\(_2\)) and is largely covalent. Ti(III) is more ionic and and its compounds are reducing agents. Ti(II) is strongly reducing and Ti(0) and Ti(-1) are generally octahedral.

Titanium occurs primarily in the minerals anatase, brookite, ilmenite, leucoxene, perovskite, rutile, and sphene. Of these minerals, only ilmenite, leucoxene, and rutile have significant economic importance. As a metal, titanium is well known for corrosion resistance and for its high strength-to-weight ratio. Approximately 95% of titanium is consumed in the form of titanium dioxide (TiO\(_2\)), a white pigment in paints, paper, and plastics. TiO\(_2\) pigment is characterized by its purity, refractive index, particle size, and surface properties. To develop optimum pigment properties, the particle size is controlled within the range of about 0.2 to 0.4 micrometer. The
superiority of TiO₂ as a white pigment is due mainly to its high refractive index and resulting light-scattering ability, which impart excellent hiding power and brightness. TiO₂ and its semi-conductor properties also makes it ideal in photocatalysis (see Chapter 5) [93-96] and as a catalyst support [97-101].

TiO₂: It occurs naturally in three modifications: anatase, rutile and brookite. Anatase and rutile share the same crystal system: tetragonal, and rutile is the most common whilst brookite is the least. Figure 2.6 shows the respective structures of anatase and rutile. Each oxygen has three planar near neighbour Ti cations. In rutile, hcp means that the three Ti-O-Ti angles are equal to 120°, whilst in anatase one Ti-O-Ti angle is at 180° and the other two are at 90°. Figure 2.7 shows a phase diagram of anatase and rutile regions as a function of temperature and pressure. At constant pressure and high temperature anatase converts (as expected) to the rutile structure; but at low temperatures and high pressure anatase converts to an αPbO₂ structure, known as TiO₂ II [102]. At the crucial temperature of 757 K and pressure of 9.5 kbars, all three phases co-exist.

Fig. 2.6 – Rutile: hcp with respect to O and anatase: ccp with respect to O [103].
2. Materials and Catalyst Preparations.

Fig. 2.7 – A schematic transition phase diagram for TiO$_2$ [88].

**Anatase:** The white pigment is formed by hydrolysis of purified TiOSO$_4$ or TiCl$_4$ or heating TiCl$_4$ and O$_2$. It is used as a white pigment in paint, paper, rubber, fabrics, plastics, leather and printing inks. It has the structure:

Fig. 2.8. – Illustration of the (111) plane of anatase. The red and green balls are oxygen and titanium ions respectively.
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It exists at relatively lower temperatures, and rutile forms at higher temperatures, typically above 773 K (see Chapter 6). The (111) plane and other associated miller indices are explained in Chapter 6.

Rutile: This is naturally a reddish brown material and is a source of Ti and ceramics. It has a tetragonal structure whereby each Ti is octahedrally coordinated by O and each O is coordinated by 3 Ti. The structure is adopted by other oxides and fluorides e.g. PbO₂ and MnO₂. It can be represented as:

![Rutile Structure](image)

**Fig. 2.9.** - Illustration of the (110) plane of rutile

The structure appears trivial at first sight, but from a different plane the structure is slightly more complex:

![Rutile Structure](image)

**Fig. 2.10.** – Illustration of the (011) plane of rutile.

*Figure 2.9 above shows the rutile structure via the 110 plane. The Ti-O-Ti angle at 120° due to hexagonal close packing (hcp) can clearly be seen, whereas in the anatase structure this cannot be seen because it has a ccp structure. The hcp structure is more favoured at the higher temperatures (i.e. bond angles increase from 90° to 120° to*
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stabilise the system). Structural differences between anatase and rutile in particular can be observed by using experimental techniques like X-ray diffraction (XRD) and Raman (see Chapter 6).

**Brookite:** This is a less common form of TiO$_2$ but it shares many of the same properties as rutile such as chemistry, colour and lustre. It has nearly the same hardness and density as rutile and at about 1023 K, it automatically reverts to the rutile structure. Unlike rutile though, its crystal system is orthorhombic. Other compounds with this structure include tellurite, TeO$_2$.

**SiO$_2$-TiO$_2$:** This is a binary oxide system and a combination of the SiO$_2$ and TiO$_2$ oxide systems above. This support system was explored during Stage I (see section 2.9.5) and used during the Rh and Ni catalyst preparations during Stage III (see section 2.11). SiO$_2$-TiO$_2$ systems prepared by the sol-gel method are widely reported in the literature to be stable, inert supports [104-106].

**Al:** Aluminium is the most abundant metal in the Earth's crust (8.3 wt. %) and exceeded only by O (45.5 %) and Si (25.7 %) [107]. It was discovered in 1827 by Oersted and has the following properties: electronic configuration [Ne]3s$^2$3p$^1$, atomic number: 13, atomic weight: 26.98 g mol$^{-1}$, density: 2.702 g cm$^{-3}$, melting point: 933.52 K and boiling point: 2740 K. It is normally present in ground water but acid rain increases it's concentration. It is manufactured by electrolysis of Al$_2$O$_3$ dissolved in Na$_3$AlF$_6$. Al reduces many oxides and is unattacked by water, but is corroded by salt or seawater and dissolved by acids. The metal and its alloys are used in applications requiring lightweight and strength: engineering, aircraft, kitchen utensils and overhead cables. Al film is used as mirror coating and as wrapping material. Al salts are important in H$_2$O purification and as catalysts.

**Al$_2$O$_3$:** Alumina is a well known refractory (materials that are not damaged by heating to at least 1773 K in a clean oxidised atmosphere) and has uses in abrasive cement, ceramics, anti-perspirants and gemstones. It is also widely used as catalysts and catalyst supports [108-110], and it exists in a variety of micro-crystalline forms with high surface areas. Al$_2$O$_3$ is formed by heating Al(OH)$_3$ or Al salts of oxy acids. It occurs naturally as the $\alpha$-form, corundum, obtained by heating $\alpha$-AlO(OH) and it is
used as an abrasive and polishing agent. Ruby, sapphire and emery are mineral varieties of corundum. The corundum structure has close packed oxygen with Al in octahedral holes (i.e. hexagonal close packing, hcp). Moderate heat on aluminium hydroxides produces $\gamma$-$\text{Al}_2\text{O}_3$ with a defect spinel structure (Al in both tetrahedral and octahedral coordination). It is a very important catalyst because of its adsorptive power, and is therefore used as an effective support (see section 2.12.1.3). $\beta$-$\text{Al}_2\text{O}_3$ is an aluminate (see ‘Aluminates’ section below).

This was used during Stage IV preparations after collaboration with Surrey Satellite Technology Ltd. (SSTL - see section 2.12.1.3) and used during the final analysis during Stage V (see Chapters 3 and 4).

**Aluminium hydroxides:** These are a source of $\text{Al}_2\text{O}_3$ and are amphoteric. They have a white or yellowish gel-like appearance and are precipitated from solutions of Al salts by $\text{NH}_3$; and exist as minerals. $\text{Al(OH)}_3$ has two forms: $\alpha$-bayerite and $\gamma$-gibbsite. $\text{Al(OH)}$ also exists in two forms: $\alpha$-diaspore and $\gamma$-boehmite. $\alpha$-diaspore gives $\alpha$-$\text{Al}_2\text{O}_3$ and other hydroxides initially give $\gamma$-$\text{Al}_2\text{O}_3$, but on strong heating, $\alpha$-$\text{Al}_2\text{O}_3$ results. Aluminium hydroxide gels give $\gamma$-$\text{Al}_2\text{O}_3$ which are valuable drying agents, catalysts and absorbents (alumina gel). It is also used medicinally as an antacid.

**Aluminates:** These are a group of compounds consisting of an $\text{Al}^{3+}$ ion in an anionic hydroxy- or oxo- complex. Species containing $[\text{Al(OH)}_x]^{-}$ and higher polymers are formed from $\text{Al}^{3+}(\text{aq})$ solutions at high pH. Aluminates formed by fusing together $\text{Al}_2\text{O}_3$ and a mixed metal oxide with the $\text{Al}^{3+}$ ion in tetrahedral and octahedral coordination gives a spinel structure e.g. $\text{MgAl}_2\text{O}_4$ and $\text{NaAl}_2\text{O}_4$. $\beta$-$\text{Al}_2\text{O}_3$ is an aluminate of composition $\text{Na}_2\text{O}.11\text{Al}_2\text{O}_3$ and is an ionic conductor. The variable amounts of $\text{Na}^+$ can be replaced by other cations.
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2.9.2.3. Other materials

**Ar**: Argon was used as the *carrier gas* during all of the catalytic experiments. It was discovered by *Cavendish* in 1785 and it has the electronic configuration [Ne]3s^23p^6; atomic number: 18; atomic weight: 39.948 g mol⁻¹; melting point: 84 K and boiling point: 87 K. It is the most abundant of the noble or inert gases (0.93 % of dry air) [111]. *Noble or inert* implies the tendency to be unreactive because the electronic configuration is very stable (i.e. energy levels are full). Hence it was ideally used as the carrier gas. Ar is separated by fractionation from liquid air and has uses in light bulbs and as an inert shield in arc welding. It also has uses in metal production (Ti, Si). It forms no true compounds although it is soluble in H₂O and forms some clathrates and excited state derivatives.

**Mn**: Manganese in its oxide form was used as the O₂ trap for the catalytic experiments (see *Chapters 3, 4 and 5*). It was discovered by Scheele in 1774 and is a group VII transition metal with electronic structure [Ar]3d^54s^2; atomic number: 25; atomic weight: 54.938 g mol⁻¹; density: 7.2 g cm⁻³; melting point: 1517 K and boiling point: 2235 K. It is the twelfth most abundant metal (1060 ppm of the earth's crust) [112] and is found naturally as the principal ore, pyrosulite (MnO₂). The metal can be extracted by electrolysis of the sulphate and is mostly used in alloys (e.g. steels and bronzes). It also has uses in dyes, paints, batteries, fertilizers, herbicides, fungicides and chemical processes. It exhibits variable oxidation states of which +4 (MnO₂) and +7 (KMnO₄) are most common. MnO₂ is used in batteries, as a catalyst and oxidising agents. KMnO₄ is a dark purple oxidising agent that has uses in titrations and antiseptic medicines. Its compounds also have importance in photosynthesis.

2.9.2.4. Precursors and gases used

*Table 2.2* provides a list of all the precursors that were used to prepare all the catalysts. *Table 2.3* shows all the gases used together with their composition and purities.
2. Materials and Catalyst Preparations.

Table 2.2 - Material precursors and purities

<table>
<thead>
<tr>
<th>Precursor</th>
<th>FW (g/mol)</th>
<th>purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RhCl₃·H₂O</td>
<td>209.25</td>
<td>99.98</td>
</tr>
<tr>
<td>NiCl₂·6H₂O</td>
<td>237.71</td>
<td>98</td>
</tr>
<tr>
<td>TiOP</td>
<td>284.26</td>
<td>97</td>
</tr>
<tr>
<td>TEOS</td>
<td>208.33</td>
<td>98</td>
</tr>
<tr>
<td>HCl</td>
<td>36.46</td>
<td>37</td>
</tr>
<tr>
<td>Dytech (CF)</td>
<td>101.96</td>
<td>99.8</td>
</tr>
<tr>
<td>Ethanol</td>
<td>46.07</td>
<td>96</td>
</tr>
<tr>
<td>TiO₂ (Degussa, P25)</td>
<td>79.90</td>
<td>99</td>
</tr>
<tr>
<td>H₂O</td>
<td>18.02</td>
<td>Deionised</td>
</tr>
</tbody>
</table>

*Dytech (CF)* was the alumina ceramic foam (CF) supplied by Dytech. In addition the densities of TiOP and TEOS were 0.955 g cm⁻³ and 0.934 g cm⁻³ respectively. The amounts used are mentioned where appropriate. The gases used were obtained from British Oxygen Company (BOC) and they are mentioned in the relevant experimental sections (see *Chapters 3, 4 and 5*). For convenience a complete list is provided in *Table 2.3* below:

Table 2.3 - Gases used and their composition and purities

<table>
<thead>
<tr>
<th>Gas</th>
<th>FW(g/mol)</th>
<th>% Composition</th>
<th>Purity grade</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>44</td>
<td>100</td>
<td>99.98 %</td>
<td>neat</td>
</tr>
<tr>
<td>CH₄</td>
<td>16</td>
<td>10 % in Ar</td>
<td>-</td>
<td>specialist gas</td>
</tr>
<tr>
<td>N₂O</td>
<td>44(31)</td>
<td>100</td>
<td>99.9 %</td>
<td>neat</td>
</tr>
<tr>
<td>Ar</td>
<td>40</td>
<td>100</td>
<td>99.9 %</td>
<td>neat</td>
</tr>
<tr>
<td>H₂</td>
<td>2</td>
<td>100</td>
<td>99.9 9%</td>
<td>neat</td>
</tr>
<tr>
<td>CO</td>
<td>28</td>
<td>6</td>
<td>-</td>
<td>specialist gas</td>
</tr>
</tbody>
</table>

N.B. - The formula weight in brackets, e.g. (31), is the secondary m/e peak for N₂O since the primary m/e peak is also shared by CO₂.

CO₂ and CH₄ were used for the dry reforming reaction (see *Chapters 1 and 4*). N₂O was used for its decomposition (see *Chapters 1 and 3*). Ar was used as the carrier gas and H₂ was used as pre-reductant (i.e. to activate the catalyst surface). CO was used as
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2.9.2.5. Impregnation techniques

Various methods exist by which to load the metal, M onto the support. Usually the metal catalyst is in an inorganic salt precursor form (e.g. AgNO₃). Impregnation is the most widely practiced method. Three particular variations exist:

- **Direct solution** – In this case the support is added directly to a solution of the active phase precursor. This effectively means that the catalyst adsorbs onto the support directly.
- **Precipitation impregnation** – The catalyst precursor is precipitated onto the support (often by a sudden pH change).
- **Incipient wetness technique** – the catalyst precursor is dissolved in a minimum volume of the solvent (e.g. ethanol) and the support is in powder form. The solution is added directly onto the support whilst observing continuous stirring until the mixture turns slightly tacky. This happens because the pores are filled with the liquid.

The impregnated material is then dried to remove the solvent and calcined to decompose the catalyst precursor to produce the catalyst. Before actual use, it is often reduced as a pre-treatment to activate the catalyst (see Chapters 3 and 4).

Other methods exist but they will not be discussed here. Many, like washcoating for example, have important industrial relevance. These include slurry precipitation, co-precipitation, fusion, the Raney Method, physical mixing and washcoating [113].

2.9.2.5. Support and its effects

The nature of the support can tailor the performance of a catalyst. Since the active phase is normally dispersed on the support, its surface area can determine the surface area of the catalyst itself. Impurities on the support can either facilitate (promote) a particular reaction or inhibit it. Many supports are inert (e.g. SiO₂) but some are...
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reducible (e.g. TiO₂). The reduced form of these supports are often labile and can enhance the catalytic activity by diffusing onto the metal. The support in this case is said to have SMSI (strong metal support interactions – see Chapters 3 and 4) [114].

2.9.3. Sol-gel Science and Technology

The sol-gel process is a versatile solution process for making ceramic and glass materials. It is also a useful route to making catalysts and their supports. In general, the sol-gel process involves the transition of a system from a solution to a liquid "sol" (mostly colloidal) into a solid "gel" phase. A sol is defined as “a stable suspension of colloidal solid particles within a liquid” [115-116], and a gel is defined as “a porous 3-dimensionally interconnected solid network that expands in a stable fashion throughout a liquid medium and is only limited by the size of the container” [116]. By applying the sol-gel process, it is possible to fabricate ceramic or glass materials in a wide variety of forms: ultra-fine or spherical shaped powders, thin film coatings, ceramic fibers, microporous inorganic membranes, monolithic ceramics and glasses, or extremely porous aerogel materials. An overview of the sol-gel process is presented in Figure 2.11. It shows the many routes that are available to tailor the desired material.

The starting materials used in the preparation of the "sol" are usually inorganic metal salts or metal organic compounds such as metal alkoxides, M(OR)ₙ, where M is a metal atom with oxidation state z and R is usually an alkyl group (e.g. CH₃). In a typical sol-gel process, the precursor is subjected to a series of hydrolysis, condensation and polymerisation reactions to form a colloidal suspension, or a "sol". Further processing of the "sol" enables one to make ceramic materials in different forms. Thin films can be produced on a piece of substrate by spin-coating or dip-coating. When the "sol" is cast into a mold, a wet "gel" will form. With further drying and heat-treatment, the "gel" is converted into dense ceramic or glass articles. If the liquid in a wet "gel" is removed under a supercritical condition, a highly porous and extremely low density material called "aerogel" is obtained.
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**Sol-Gel method**

- Hydrolysis
- Condensation
- Ageing (maturing)
- drying
- calcining
- pre-treatment

- Step 1:
  - \( \text{H}_2\text{O}, \text{HCl}, \text{EtOH}, \text{TEOS} \)

- Step 2:
  - TiOP, EtOH

- Step 3:
  - EtOH, \( \text{H}_2\text{O} \)
  
  - 'M' (e.g. \( \text{RhCl}_3\cdot\text{H}_2\text{O} \) or \( \text{NiCl}_2\cdot6\text{H}_2\text{O} \)) added during step 3

**Fig. 2.11.** - Schematic diagram showing the sol-gel process

**Fig. 2.12.** - The above sequence represents the process by which the conventional sol-gel process occurs, where TiOP = titanium isopropoxide, TEOS = tetraethoxysilane and EtOH = ethanol. TiOP and TEOS are the metal alkoxide precursors for TiO\(_2\) and SiO\(_2\) synthesis respectively (see methods of preparations at section 2.9.5.1-4). The different types of gels can be briefly classified as:
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- **Aquagel**: The pores of the gel are filled with water.
- **Alcgel**: The pores are filled with alcohol e.g. ethanol
- **Xerogel**: The liquid medium is removed often by gentle heating and hence the structure is compressed. As a result the porosity is decreased by at least some degree by the surface tension forces as the liquid is removed.
- **Aerogel**: This is a special type of xerogel from which the liquid has been removed in such a way as to prevent any form of structural collapse. In essence, this is done by heating the gel above the critical point of the liquid i.e. supercritical drying.

### 2.9.4. Stage I - Preparative routes

Three methods have been outlined [117-120] for the preparation of the aforementioned support, namely pre-hydrolysis, the reflux technique, and preparation via the non-hydrolytic route. Each procedure is briefly described below:

#### 2.9.4.1. Pre-hydrolysis:

This is the conventional method of producing metal oxides and the reaction occurs at room temperature: Absolute ethanol (Hayman 99.99%), distilled water and hydrochloric acid (Aldrich 36%) is added to a closed reaction vessel, then shaken to ensure homogeneity. Tetraethoxysilane (TEOS; Aldrich 97%) is then added to the vessel slowly. A mixture of ethanol and titanium isopropoxide (TiOP; Aldrich 97%) is then added slowly. The mixture is left to stir for approximately 15 h. The remaining mixture of water and ethanol is then added. The final resulting mixture is allowed to mix for about 24 h. The resulting product has a clear, colourless and homogeneous appearance. The reason why TEOS is added first and TiOP is added second is due to their respective rates of hydrolysis. Generally, transition metal alkoxides (such as TiOP) have lower electronegativities than silicon alkoxides (such as TEOS) which makes them more reactive to nucleophilic reactions like hydrolysis and condensations [121]. Thus, TiOP has a much faster relative hydrolysis rate to the extent that if it was added first then it “would lead to the precipitation of TiO₂” [122] meaning that the gel process cannot occur. Hence the TEOS is first added and allowed to stabilize for
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about 2 h. This ensures that the TEOS has sufficiently hydrolysed but not to the extent of condensation. The amount of water and solvent therefore need to be carefully judged in order to strike this balance. When the TiOP/EtOH mixture is thus slowly added, the hydrolysis rate is controlled by the presence of the stabilised reaction mixture ensuring that the TiO₂ does not precipitate out of solution. The condensation and polymerisation process continues as described in section 2.9.5.1.

2.9.4.2. The Reflux method:

This is an alternative method to the pre-hydrolysis route whereby the reaction occurs at high temperature. The TEOS and TiOP are usually mixed together and the reaction mixture is allowed to reflux at 353 K for 15 h. The resulting mixture is then allowed to cool to room temperature. A mixture of HCl and 50% ethanol (of total concentration) is then added slowly. This is left to stir for five hours before the remaining ethanol and water is added dropwise. The final reaction mixture is allowed to stir for about 15 h in order to ensure the maximum level of mixing. The principal advantage of the pre-hydrolysis over the reflux route is that it can occur at room temperature and also precipitation is less likely because the reactive TiOP is added after the TEOS has stabilised. In the case of reflux, both alkoxides are mixed together for refluxing.

2.9.4.3. Non-hydrolytic route

The third method of sol-gel preparation is via the non-hydrolytic route which is a relatively new area. As the name suggests, there is no hydrolysis step and essentially comprises a direct one-step poly-condensation reaction involving a metal alkoxide (e.g. TiOP) as the oxygen donor and a metal halide (m M'Xₙ) to give an oxide and an alkyl halide (nm RX) as by-product:

\[ n \text{M(OR)}_m + m \text{M'X}_n \rightarrow \text{M}_n\text{M'}_n\text{O}_{nm} + nm \text{RX} \]

Metal oxides are known to be prepared via this route [123-127].
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*Table 2.4* below summarises the main differences between the pre-hydrolysis and non-hydrolysis routes:

**Table 2.4 — comparison of pre-hydrolysis and non-hydrolysis methods for sol-gel preparations**

<table>
<thead>
<tr>
<th></th>
<th>pre-hydrolysis</th>
<th>non-hydrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>low temperature</td>
<td>low temperature</td>
<td>no solvent</td>
</tr>
<tr>
<td>water</td>
<td>no water</td>
<td>no solvent</td>
</tr>
<tr>
<td>solvent</td>
<td>no solvent</td>
<td>no solvent</td>
</tr>
<tr>
<td>fast reaction</td>
<td>slow reaction</td>
<td>reaction control</td>
</tr>
<tr>
<td>little reaction control</td>
<td>reaction control</td>
<td>low surface areas</td>
</tr>
<tr>
<td>high surface areas</td>
<td>low surface areas</td>
<td>biomimetics application</td>
</tr>
<tr>
<td>catalyst use</td>
<td></td>
<td>biomimetics application</td>
</tr>
<tr>
<td>possible precipitation</td>
<td></td>
<td>no precipitation</td>
</tr>
</tbody>
</table>

Clearly, the *non-hydrolytic* route has many advantages. These include simpler preparations, but in terms of application, the *pre-hydrolysis* route is favoured because it has applications in catalysis and despite the reaction being relatively fast with little reaction control, it produces oxides with high surface areas (typically 50 m²/g for TiO₂ as compared to < 5 m²/g for the non-hydrolysis route). Hence the pre-hydrolysis route was employed.

2.9.5. Sol-gel synthesis of silica-titania (SiO₂-TiO₂)

As mentioned in *Chapter 1*, SiO₂-TiO₂ was synthesised via the sol-gel route in order to gain an understanding of the sol-gel process and an understanding of the various stages involved for metal loading into the sol-gel matrix. This allowed a knowledge base that was used later to prepare materials for the practical applications of catalytic testing. From previous work in the research group [128], it is known that sol-gel derived silica-titania (SiO₂-TiO₂) materials are effective supports for catalytic metals such as Rh, Ru, Ir and Pd. etc.

The following methods show four different ways of preparing silica-titania gels. The first is a blank SiO₂-TiO₂ gel; the remaining three contained 2% Ag on SiO₂-TiO₂ gel, but in each case the Ag was introduced via a slightly different technique. During the second case the 2% Ag was introduced via the incipient wetness technique. During
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the third method, the Ag was introduced as a one-step sol-gel method (i.e. the Ag was introduced with the reactants). Finally, in the fourth method, the Ag was impregnated during the sol-gel stage (further explanations provided below). Six ratios of silica:titania gels were considered: (100%:0%), (0%:100%), (50%:50%), (90%:10%), (10%:90%) and (80%:20%). It was found that the 80%:20% or 4:1 ratio gave the most suitable clear homogeneous gel.

2.9.5.1. Method of preparation 1: Blank SiO\textsubscript{2}-TiO\textsubscript{2} gel

This method was executed in accordance with the general procedure described in section 2.9.4.1 above. The amounts used were determined after careful investigations based on the work of Leadley [117].

Absolute ethanol (13.50 cm\textsuperscript{3}, 0.2316 mol, Hayman 99.99 %), distilled water (0.3 cm\textsuperscript{3}, 0.0166 mol) and hydrochloric acid (two drops, Aldrich 36 %) were added to a closed reaction vessel, and then shaken to ensure homogeneity. Tetraethoxysilane (15 cm\textsuperscript{3}, 0.0672 mol, TEOS; Aldrich 97 %) was added to the reaction mixture slowly. The mixture was left to stir for 2 h in order to allow the hydrolysis of the TEOS to occur, after which a mixture of ethanol (2.95 cm\textsuperscript{3}, 0.0506 mol) and titanium isopropoxide (4.95 cm\textsuperscript{3}, 0.0166 mol, TiOP; Aldrich 97 %) was then added slowly to the above reaction mixture. The mixture was then left to stir for approximately 15 h.

The remaining mixture of water (2.10 cm\textsuperscript{3}, 0.1166 mol) and ethanol (3.75 cm\textsuperscript{3}, 0.6435 mol) was then added. The resulting mixture was then allowed to mix for 24 h in order to ensure a clear, colourless and homogeneous appearance. The sol was then allowed to ‘age’ during which stage the gel is formed. This occurs since during the condensation reactions, extensive cross-linking and polymerisation occur, which eventually allow for Si-O-Ti cross-linking “bridges” to form [129]. This gives rise to the extensive three-dimensional polymeric and tetrahedral SiO\textsubscript{2}-TiO\textsubscript{2} structural framework across the entire gel. The TiO\textsubscript{2} is added as a modifier and thermally stabilises the SiO\textsubscript{2}. It can therefore be used at considerably higher temperatures than SiO\textsubscript{2} itself. SiO\textsubscript{2} prefers tetrahedral coordination whilst TiO\textsubscript{2} normally prefers octahedral coordination [104]. The SiO\textsubscript{2}-TiO\textsubscript{2} structure is stabilised by assuming a tetrahedral coordination. The increased bond angles in the tetrahedral (as compared to
the octahedral) coordination stabilises the whole system [104]. The presence of TiO₂ also increases the selectivity of ethene formation. A metal in the form of an ‘M’ precursor (e.g. RhCl₃.H₂O) can then be added via one of the routes such as impregnation, precipitation, washcoating, etc. (see section 2.9.2.5). SiO₂-TiO₂ was also chosen since it is technologically very useful and its use in this area of work is quite novel.

The clear wet gel was then allowed to dry at 373 K in order to allow the ethanol solvent and water to evaporate. The resulting white solid was then crushed, and calcined at 973 K. This produced a black powdered solid that was ready for catalytic testing.

2.9.5.2. Method of preparation 2

During this method, the metal ‘M’ was introduced via an incipient wetness technique. The gel was prepared, dried and crushed to produce a white powdered solid (as explained above). Ag⁺NO₃⁻ (0.1671 g, 5.9 mmol) was dissolved in water (5 ml, 0.278 mol). The crushed white solid was added to the solution. The mixture was stirred vigorously to ensure all the components were mixed well. The water was evaporated off as the mixture was allowed to dry at 373 K. The white powder was then calcined at 973 K in order to dispose of nitrate substances. The resulting dark brown solid was then ready for catalytic testing.

2.9.5.3. Method of preparation 3

During this procedure, the Ag⁺NO₃⁻ is introduced with the water during the final stage when the ethanol/water mixture is added to the SiO₂-TiO₂ sol (see section 2.9.5.1). This technique will be termed the ‘one-step sol-gel preparation’ since the Ag⁺NO₃⁻ is introduced with the reactants. This results in a brown sol, and upon ageing, a brown gel results. However, after drying at 373 K followed by crushing, a pale purple powdered solid is produced. When this is calcined at 973 K, it turns to a greyish-black solid, which is then ready for catalytic testing.
The Ag\(^{+}\)NO\(_3\)\(^{-}\) in this case, is added during the sol-gel stage of the preparation; hence this procedure will be termed the ‘sol-gel stage impregnation’ technique. The method was followed as indicated in procedure 1 except that during the gelling stage, the Ag\(^{+}\)NO\(_3\)\(^{-}\) was added. The typical gelling time, \(g_t\) was between four to seven days. The Ag\(^{+}\)NO\(_3\)\(^{-}\) was therefore added directly to the sol-gel typically after one or two days whilst continuous stirring was observed. This was to ensure the highest level of mixing at the molecular scale. The resulting grey-white wet gel was then treated as above. Upon drying at 373 K, the greyish white colour remained. After crushing and calcining at 973 K, a greyish black solid was produced, which was then ready for catalytic testing.

2.9.6. R\(_{W}\).R\(_{A}\) ratios and pH factors

The determination of the ideal, clear homogeneous gel was dependent upon certain parameters. These include the acidity of the reaction mixture, and in particular, the \(R_W\) and \(R_A\) values. According to Gaboiaoud and Co. [130], “the degree of polymerization” and therefore gellation, “depends on the pH of the solution”. Furthermore, “the decrease in pH induces the formation of cyclic oligomers in the solution followed by the growth of primary particles”. If the concentration of the particles is high enough, then “the growing aggregates percolate and form a gel”. Brinker et al. [121] suggest a pH of 2 is required for effective hydrolysis and condensation in order to allow for the gel to form.

The \(R_W\) value indicates the water:alkoxide (TEOS) ratio, and the \(R_A\) indicates the alcohol:alkoxide (TEOS) ratio. Brinker et al. [121] also indicate that the shortest gelation time, \(g_t\) of approximately 100 hours occurs when \(R_W = 4\) and \(R_A = 1\), or when \(x = 4\) in the following equation:

\[
\text{Si(OEt)}_4 + x\text{H}_2\text{O} \rightarrow \text{Si(OH)}_x(\text{OEt})_{4-x} + x\text{EtOH}
\]

This implies that full hydrolysis of TEOS occurs:
2. Materials and Catalyst Preparations.

\[
\text{Si(OEt)}_4 + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4\text{EtOH}
\]

However, Brinker recommends these ratios when considering SiO\textsubscript{2} systems only. For SiO\textsubscript{2}-TiO\textsubscript{2} systems, Leadley [117] suggests ratios of R\textsubscript{W} = 2, R\textsubscript{A} = 7, and SiO\textsubscript{2}-TiO\textsubscript{2} ratio of 4:1. These conclusions were derived by varying R\textsubscript{W} and keeping the other parameters constant. However, investigations were carried out by varying R\textsubscript{A}, and keeping R\textsubscript{W} constant at R\textsubscript{W} = 2, and SiO\textsubscript{2}-TiO\textsubscript{2} ratio constant at 4:1. It was found that clear homogeneous SiO\textsubscript{2}-TiO\textsubscript{2} gels were formed when the SiO\textsubscript{2}-TiO\textsubscript{2} ratio was 4:1, R\textsubscript{W} = 2 and R\textsubscript{A} = 5 or 6. If however R\textsubscript{A} << 5, the solution precipitates out and no gel is formed. On the other hand, if R\textsubscript{A} >> 6, either the gel time, g\textsubscript{t} dramatically increases or in extreme cases, no gel results i.e. it remains as a sol. Furthermore, Brinker [121] adds that even though the increase of R\textsubscript{W} is generally favoured in terms of promoting hydrolysis, “when R\textsubscript{W} is increased while maintaining a constant ethanol:TEOS ratio”, the concentration of TEOS is reduced. By implication, this means a reduction in the rates of hydrolysis and condensation, and hence an increase in the gel time, g\textsubscript{t}.

In addition, it is interesting to note that the SiO\textsubscript{2}-TiO\textsubscript{2} ratio of 4:1 agrees with Mountjoy and Co [104], who recommend that the TiO\textsubscript{2} should have a low content of x << 1 in the formula, (SiO\textsubscript{2})\textsubscript{1-x}(TiO\textsubscript{2})\textsubscript{x}.

Titanium isopropoxide, [Ti(OPr)\textsubscript{4}] is similarly hydrolysed:

\[
\text{Ti(OPr)}_4 + \text{x.H}_2\text{O} \rightarrow \text{Ti(OH)}_4(\text{OPr})_{4-x} + \text{x.PrOH}
\]

However, full hydrolysis can occur when x < 4 since during the condensation reactions, water is eliminated enabling the alkoxides to further hydrolyse:

\[
\text{Si(OH)}_4 + \text{Ti(OH)}_4 \rightarrow (\text{OH})_3-\text{Si-O-Ti-(OH)}_3 + \text{H}_2\text{O}
\]

It is also possible to expect other reactions to occur. These include transesterification and reesteterification reactions. Transesterification involves the displacement of an alkoxide group by an alcohol to produce an alcohol molecule:

\[
\text{R'}\text{OH} + \text{Si(OR)}_4 \rightarrow \text{Si(OR)}_3\text{OR'} + \text{ROH}
\]
2. Materials and Catalyst Preparations.

Reesterification is simply the reverse of hydrolysis reactions:

\[ x \cdot \text{ROH} + \text{Si(OR)}_4 \cdot (\text{OH}) \rightarrow \text{Si(OR)}_4 + x \cdot \text{H}_2\text{O} \]

There are also effects due to the solvent (which is used to reduce viscosity and achieve homogeneity of the system), catalyst (see section 2.9.7) and steric and inductive effects [131]. All these parameters need to be controlled and balanced in order to give the most effective and efficient synthetic process by which to produce gels that will have the potential of being used in a catalytic system.

2.9.7. Mechanisms

The hydrolysis steps follow a bimolecular nucleophilic substitution (S\(_\text{N}2\) - type) mechanism with the inversion of either the Si- or Ti- tetrahedra. In the acid catalysed case, the alkoxide group is protonated in a rapid first step before the substitution occurs [121, 132], e.g.

\[
\text{HOH} + (\text{OR})_3\text{Si} \rightarrow \text{O}^+\text{R(H)} \quad \text{HO}^\delta^-(\text{H}) \rightarrow \text{Si(OR)}_3 \rightarrow \text{O}^\delta^+\text{R(H)}
\]

\[
\text{HO}^\delta^+\text{Si(OR)}_3 + \text{ROH} + \text{H}^+
\]

However in the base-catalysed case [132] the water dissociates in a rapid first step. The resulting hydroxyl ion (OH\(^-\)) then takes part in the nucleophilic substitution with the alkoxide group:

\[
\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-
\]

\[
\text{HO}^- + (\text{OR})_3\text{Si} \rightarrow \text{HO}^\delta^- \rightarrow \text{Si(OR)}_3 \rightarrow \text{O}^\delta^+\text{R} \rightarrow \text{HO}^\delta^-\text{Si(OR)}_3 + \text{OR}^-
\]

Acid catalysts are chosen to give more linear or polymer-like chain growth which form high density materials upon drying [132] whilst base-catalysed conditions tend to produce highly branched chains that eventually give particulate-like structures. This is because the reactions are directed towards the middle instead of the ends of chains [118, 133].
2. Materials and Catalyst Preparations.

During the condensation stage and under acid catalysis, the $H^+$ ion attacks the silantriol group (hydrolysed alkoxide) to form a $R\text{-Si(OH}_2\text{(OH)}_2$ species in a fast step:

$$R\text{-Si(OH}_3 + H^+ \rightarrow R\text{-Si(OH}_2\text{(OH)}_2$$

The rate constant of the forward reaction is $k_1$ and that of the reverse reaction is $k_{-1}$. This activated species reacts with a titanetriol group, $R\text{-Ti(OH}_3$ in the slow rate determining step, polymerising to form the Si-O-Ti link bridge:

$$R\text{-Si(OH}_2\text{OH}_3 + R\text{-Ti(OH)_3 \rightarrow R(OH)_2Si-O-Ti(OH)_2R + H}_3\text{O}^+$$

The rate constant of the forward reaction is $k_2$ and that of the reverse is $k_{-2}$. The order of the overall reaction is 3 with the rate equation being:

$$-d[\text{silanetriol}][\text{titanetriol}] / dt = k_1k_2/k_{-1}[R\text{Si(OH}_3][R\text{Ti(OH)}_3][H^+]$$

In the base catalysed case, the $OH^-$ attacks a silanetriol group to form a $R\text{-Si(OH}_2\text{O}^-$ species in a fast step. The resulting species then reacts with a titanetriol group in a slow rate determining step to form the polymerised Si-O-Ti link bridge:

$$R\text{-Si(OH}_3 + OH^- \rightarrow R\text{-Si(OH}_2\text{O}^- + H}_2\text{O}$$

The rate constant of the forward reaction is $k_1$, and that of the reverse is $k_{-1}$. The slow rate-determining step:

$$R\text{-Si(OH}_2\text{O}^- + R\text{-Ti(OH)_3 \rightarrow R(OH)_2Si-O-Ti(OH)_2R + OH}^-$$

The rate constant of the forward reaction is $k_2$, and that of the reverse is $k_{-2}$. The overall order of the reaction is 3 with the overall rate equation being:

$$-d[\text{silanetriol}][\text{titanetriol}] / dt = k_1k_2/k_{-1}[R\text{Si(OH}_3][R\text{Ti(OH)}_3][OH^-]$$
2. Materials and Catalyst Preparations.

The formation of Si-O-Ti link-bridges and further condensation reactions eventually cause the sol to transform into a homogeneous gel with a SiO_2-TiO_2 structure. This is known as a wet-gel. However, when this is dried under supercritical conditions, an *Aerogel* is formed. If the wet-gel is dried sufficiently to solidify and allow for structure collapse, a *Xerogel* is formed typically with an internal microporous (<2 nm diameter) structure. The pores of these gels have very high surface areas making them ideal to act as supports for precious metal catalysts, such as group VIII metals.

2.10. Stage II

*Stage II* didn't require preparations since existing catalysts were used in catalytic work (see *Chapter 4*).

2.11. Stage III preparations - Initial preparations of Rh/S & Ni/S

In terms of catalyst preparations, Wang *et al* argued that [134] increased Rh loading reduces the effect of O assisted dissociation of CH_4, and therefore, on the basis of previous experimental work and suggestions from the literature, it was decided that it would be fruitful to prepare the following 9 selected catalyst materials (0.5 wt % metal loading):

<table>
<thead>
<tr>
<th>Material</th>
<th>SiO_2</th>
<th>SiO_2-TiO_2</th>
<th>TiO_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh/SiO_2</td>
<td></td>
<td>Rh/SiO_2-TiO_2</td>
<td>Rh/TiO_2</td>
</tr>
<tr>
<td>Ni/SiO_2</td>
<td></td>
<td>Ni/SiO_2-TiO_2</td>
<td>Ni/TiO_2</td>
</tr>
</tbody>
</table>

It is worth noting that the SiO_2 system was chosen as a result of indications from previous work (see *Chapter 4*). The SiO_2-TiO_2 system was chosen to add stability to the system. The TiO_2 system was added for completion and its known activity for SMSI [113].

The SiO_2, SiO_2-TiO_2 and TiO_2 supports alone would be the blanks in terms of the absence of the metal catalyst. These were chosen because of the already known properties of SiO_2-TiO_2 in terms of being an inert support (see *Stage I*), the TiO_2 having a stabilising effect on the SiO_2 and the support being rather novel in the
2. Materials and Catalyst Preparations.

The SiO_2 was used as the support as an alternative to the SiO_2-TiO_2 system. For completion, it was logical to complete the series by also considering the TiO_2 system. In any case, the TiO_2 does have a considerable effect in terms of contributing to the stability of the SiO_2-TiO_2 system [104].

The SiO_2-TiO_2 based materials consisted of the following parameters: SiO_2 : TiO_2 ratio of 4 : 1, R_w = 2, R_A = 5 and pH = 2. Furthermore the method of preparation of SiO_2 based and SiO_2-TiO_2 catalysts (SiO_2, Rh/SiO_2, Ni/SiO_2, SiO_2-TiO_2, Rh/SiO_2-TiO_2 and Ni/SiO_2-TiO_2) was the ‘sol-gel stage impregnation’ technique (see method of preparation 4 earlier – section 2.9.5.4). This involved the metal precursor (0.5 wt %) being introduced during the ‘sol-gel stage’ of the preparation which is the period at which the gelling itself occurs after all the constituents have been added (see method of preparation 1 and 4 at section 2.9.5.1 and 2.9.5.4). The metal precursors were obtained as inorganic salts from the supplier (Aldrich), namely rhodium(III) chloride hydrate (RhCl_3.H_2O, 99.98 %) and nickel(II) chloride hexa-hydrate (NiCl_2.6H_2O, 98 %)

However for the TiO_2 based system (TiO_2, Rh/TiO_2 and Ni/TiO_2), the ‘one-step sol-gel preparation’ (see method of preparation 3 at section 2.9.5.3) was employed. This involved the metal precursor (0.5 wt % metal) being introduced with the water during the final stage when the ethanol/water mixture is added to the appropriate sol. This particular method was adopted for the TiO_2 systems due to the considerably faster rate of hydrolysis and gelling times (g_t) with regards to the addition of the final stage of the preparation, typically 5-10 minutes. It can therefore be understood that if the method prior to this (sol-gel stage impregnation) was adopted then the gel would have resulted before an opportunity to add in the metal precursors. The sequence for the observed typical g_t (in brackets) of the relevant systems in order of fastest first was as follows:

\[
\text{TiO}_2 (5-10\text{mins}) >> \text{SiO}_2-\text{TiO}_2 (1-2 \text{ weeks}) >> \text{SiO}_2 (\sim 4 \text{ weeks})
\]

As mentioned at section 2.9.4.3, better reaction control may be achieved for TiO_2 (SG) via the non-hydrolytic route [118], but this would give low surface areas (1-5
m²/g as compared to 50 m²/g), so preparation via the hydrolytic route is considered to be better in comparison.

The effects of the metals on these systems need to be more closely observed although the experiments so far have indicated that in terms of the rate of gelation, it is not significantly affected by the introduction of the metal precursors. This is because in each case, the $g_t$ was within the above-indicated timescales. For reproducibility, the blank supports of all three types were prepared again and as a result the $g_t$ was consistent with the above timescales.

Each of the catalyst materials was dried overnight at 373 K to allow for volatile compounds (e.g. ethanol, propanol etc) and water to evaporate off. The samples were then crushed and ready for testing.

The blank SiO₂-TiO₂ (A) appeared to have clear glassy look after drying, and upon crushing it was a white powdery material. Similarly, the Rh/SiO₂-TiO₂ (B) was a black glassy like material. However, during the gelling stage, it was a rich red colour. The Ni/SiO₂-TiO₂ (C) was a light green glassy material. The green colour was considerably more intense during the gelling stage. The Rh/SiO₂ (D) was similar to (B) in the sense that it too appeared to be a black glassy material. The Ni/SiO₂ (E) was a light green glassy solid. The blank SiO₂ (F) was similar to (A) in the sense that it too was a clear glassy material after drying overnight. The blank TiO₂ (G) was a clear powdery material after drying, and was white powder after crushing. The Rh/TiO₂ (H) was a black powdery material and was different in texture relative to the corresponding SiO₂ and SiO₂-TiO₂ cases. This difference was also observed in the case of Ni/TiO₂ (I) which was a light green powdery material as opposed to being glassy both in appearance and texture.

2.12. Stage IV - Modified Rh/TiO₂ catalysts

As a result of scanning N₂O decomposition work it was found that ½ wt % Rh/TiO₂ (SG) was the best catalyst (see Chapter 3). This was now used as the basis for preparing other modified catalysts. In addition, collaboration with SSTL meant additional sample catalysts for testing (Shell 405; CRI Fine Chemicals [135]) and V-
2. Materials and Catalyst Preparations.

Rh/Al₂O₃, where V = Vadim (see below). SSTL were interested in making satellite microthrusters more efficient by the use of a better catalyst. Commercially, 36 wt. % Ir/Al₂O₃ (Shell 405) was being used, but it proved difficult to regenerate since most of the Ir was lost in the process (see SEM results in Chapter 6). A Rh/Al₂O₃ support was provided by V. Zakirov [136] but the challenge was to produce a more efficient catalyst that had potential to be regenerated and also to have activity for dry reforming of methane. Subsequently, investigations on commercial Shell 405 and Rh/Al₂O₃ (Vadim) lead to the catalyst development of 5 wt % Rh/Al₂O₃ pellets (IMP) and 5 wt % Rh/TiO₂ (Degussa, P25). Furthermore, the literature suggests that the most effective catalyst for the H₂ formation is Rh/Al₂O₃ [42] followed by Rh/TiO₂, Rh/SiO₂ and Rh/MgO. This may relate to the similarity between Rh₂O₃ and Al₂O₃.

These catalysts were tested for N₂O decomposition by SSTL (for satellite microthruster applications) and also in the catalytic rig (see Chapter 3) for reduction of GHG (N₂O decomposition and dry reforming of methane). Al₂O₃ pellets (2.5 mm) was commercially available from CONDEA and provided by SSTL. TiO₂ (Degussa, P25) was commercially available from Degussa. It was in fine powder form, so suitable inhalation protection was used.

2.12.1. Methods of preparation:

2.12.1.1. 5 wt % Rh/TiO₂ (SG IMP):

Absolute ethanol (53.8 cm³, 1.168 mol, Hayman 99.99 %), distilled water (1.2 cm³, 0.067 mol) and concentrated hydrochloric acid (6 drops, 0.12 cm³, Aldrich 36 %) to acidify the solution to pH 2, were added to a closed reaction vessel and stirred for about 10 minutes to ensure homogeneity at the molecular level. The second stage involved the addition of a mixture of ethanol (11.8 cm³, 0.256 mol) and titanium isopropoxide (19.8 cm³, 0.07 mol, Aldrich 97 %). The reaction mixture was left to stir for 15 hours. The third stage required the remaining mixture of distilled water (8.4 cm³, 0.466 mol) and ethanol (15 cm³, 0.326 mol, Hayman 99.99 %) to be added and left to stir until the resulting sol gelled within 5 min.
2. Materials and Catalyst Preparations.

RhCl₃·H₂O (0.0520 g, 0.23 mmol, Aldrich 99.98 %) was dissolved in ethanol (11.6 cm³, 0.25 mol, Hayman 99.99 %) in order to equate to ½ wt % of Rh metal particles loaded onto sol-gel derived TiO₂ (as prepared above) via the incipient wetness impregnation technique. This had to be done within the 5 minutes gelation time. The resulting sticky orange-red mixture was stirred vigorously and left to dry at 343 K overnight, followed by further drying at 373 K. The orange coloured glass-like material was gently ground and then was ready for characterisation and catalytic experiments.

2.12.1.2. ½ wt % Rh/TiO₂ (P25 Degussa IMP)

TiO₂ (5.0012g, 0.0626 mol, Degussa AG, P25) was titrated with ethanol (15 cm³, 0.326 mol, Hayman 99.99 %) to attain the minimum volume of ethanol required to produce the mixture required for incipient wetness impregnation.

RhCl₃·H₂O (0.0553 g, 0.24 mmol, Aldrich 99.98 %) was dissolved in ethanol (15.00 cm³, 0.326 mol, Hayman 99.99 %) and the resulting solution was added to TiO₂ (5.0012 g, 0.0626 mol, degussa AG, P25). The resulting sticky pink mixture was stirred vigorously as part of the incipient wetness impregnation method which ensured a 0.5 wt % loading of Rh metal. The mixture was then dried at 343 K overnight, followed by further drying at 373 K. The resulting solid had a pink surface with a deep blue underlay. The material was fluffy and fine compared to the glass-like material derived via the sol-gel route. This was gently ground and dried further at 373 K and was ready for characterisation and catalytic work.

2.12.1.3. 5 wt.% Rh/Al₂O₃ pellets

Initially a titration was performed with the Al₂O₃ pellets and ethanol to determine the critical volume required that would be considered as the minimum volume for the incipient wetness slurry mixture for the metal impregnation. It was found to be 26 cm³ for 20 g of Al₂O₃ pellets.

RhCl₃·H₂O (2 g, 9.56 mmol, Aldrich) was dissolved in ethanol (26 cm³). The resulting solution was added slowly to Al₂O₃ pellets (20 g), whilst the mixture was stirred
2. Materials and Catalyst Preparations.

vigorously. The resulting red impregnated solution was then dried at 373 K overnight to allow excess ethanol to be evaporated from the surface. This had a red-orange appearance. The dried catalyst was then reduced at 673 K using pre-reductant H\textsubscript{2} (neat, 20 cm\textsuperscript{3} min\textsuperscript{-1}) for 1 h, upon which it changed to grey-black in appearance. 15g of this was kindly donated to SSTL for the testing of N\textsubscript{2}O decomposition. The remaining 5 g was reserved for use in the Chemistry Department, namely for N\textsubscript{2}O decomposition experiments and comparative testing for dry reforming.

It is worth noting that not all pellets were uniform in colour due to variance in surface level Rh concentration (see SEM pictures in Chapter 6).

2.12.1.4. 5 wt\% Rh/TiO\textsubscript{2} (Degussa P25, IMP)

This was prepared to provide a comparison with the previous catalyst. As in the previous case RhCl\textsubscript{3}.H\textsubscript{2}O (2g, 9.56 mmol, Aldrich) was dissolved in ethanol (26 cm\textsuperscript{3}) and the mixture was slowly added with stirring to the TiO\textsubscript{2} Degussa P25 (25g, 0.31 mol) until a tacky-sticky mixture was produced. Upon further vigorous stirring, the resulting mixture was left to dry at 373 K overnight. The dark reddy-brown coloured solid was then ready for catalytic testing.

2.12.2. Ceramic (cellular foams - CF)

Al\textsubscript{2}O\textsubscript{3} CF are known to have moderate surface areas [137], so in order to increase activity and facilitate the reaction, the following materials were prepared. The blank Al\textsubscript{2}O\textsubscript{3} CF was characterised by SEM (see Chapter 6) before and after acid-etching for 15 hrs. This was done to see how the surface would change. These preparations were similar to the sol-gel impregnation methods.

Four types of sol-gel (SG) derived TiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} CF were prepared simultaneously. These were ½ wt % Rh/TiO\textsubscript{2} (SG-100 %)/Al\textsubscript{2}O\textsubscript{3} CF, ½ wt % Rh/TiO\textsubscript{2} (SG-80 %)/Al\textsubscript{2}O\textsubscript{3} CF, ½ wt % Rh/TiO\textsubscript{2} (SG-30 %)/Al\textsubscript{2}O\textsubscript{3} CF and ½ wt % Rh/TiO\textsubscript{2} (SG-0 %)/Al\textsubscript{2}O\textsubscript{3} CF. In each case, the appropriate amount of RhCl\textsubscript{3}.H\textsubscript{2}O/EtOH solution (totalling 20 cm\textsuperscript{3}) was added:
2. Materials and Catalyst Preparations.

2.12.2.1. ½ wt % Rh/TiO$_2$ (SG-100 %)/Al$_2$O$_3$ (CF, IMP)

The Al$_2$O$_3$ cellular foam (CF) ceramic was acid etched (HNO$_3$, 200 cm$^3$, 3 M) three times for 15 h each time. TiO$_2$ (SG, 20 cm$^3$) was coated on the surface of the alumina block (1 cm x 1 cm x 3 cm). This ensured a surface relative composition of 100 % (i.e. neat) sol-gel derived TiO$_2$. The TiO$_2$ was allowed to gel on the surface overnight.

RhCl$_3$.H$_2$O (0.0270 g, 0.118 mmol, Aldrich 99.98 %) was dissolved in ethanol (20 cm$^3$, 0.434 mol, Hayman 99.99 %). The resulting solution was added to the TiO$_2$ (SG-100 %)/Al$_2$O$_3$ ceramic block. This was allowed to gently dry at subsequently elevated temperatures of 313, 333 and 343 K. The reddish-pinky coloured ceramic block was then dried at 373 K for 24 h and was then ready for characterisation and catalytic work.

2.12.2.2. ½ wt % Rh/TiO$_2$ (SG-80 %)/Al$_2$O$_3$ (CF, IMP)

As before, the Al$_2$O$_3$ ceramic was acid etched (HNO$_3$, 200 cm$^3$, 3 M) three times for 15 hours each time. However, this time a mixture of TiO$_2$ (SG, 16 cm$^3$) and ethanol (4 cm$^3$, 0.087 mol, Hayman 99.99 %) was coated on the surface of the alumina block (1 cm x 1 cm x 3 cm). This ensured a surface relative composition of 80 % sol-gel derived TiO$_2$. The TiO$_2$ as before was allowed to gel on the surface overnight.

The addition of RhCl$_3$.H$_2$O (0.0270 g, 0.118 mmol, Aldrich 99.98 %) involved the steps as indicated in the above synthesis.

2.12.2.3. ½ wt % Rh/TiO$_2$ (SG-30 %)/Al$_2$O$_3$ (CF, IMP)

The Al$_2$O$_3$ ceramic was treated as above. A mixture of TiO$_2$ (SG, 6 cm$^3$) and ethanol (14 cm$^3$, 0.3045 mol, Hayman 99.99 %) was coated on the surface of the alumina block (1 cm x 1 cm x 3 cm). This ensured a relative surface composition of 30 % sol-gel derived TiO$_2$. As before, the TiO$_2$ was allowed to gel on the surface overnight.

The addition of RhCl$_3$.H$_2$O (0.0270 g, 0.118 mmol, Aldrich 99.98 %) involved the steps as indicated in the first of these syntheses.

---

2. Materials and Catalyst Preparations.

2.12.2.4. \( 0.5 \) wt % Rh/TiO\(_2\) (SG-0 %)/Al\(_2\)O\(_3\) (CF, IMP)

In the final case, the Al\(_2\)O\(_3\) ceramic was acid etched (HNO\(_3\), 200 cm\(^3\), 3 M) and treated as above. Ethanol (20 cm\(^3\), 0.435 mol, Hayman 99.99 %) was added to the alumina block (1 cm x 1 cm x 3 cm).

RhCl\(_3\).H\(_2\)O (0.0270 g, 0.118 mmol, Aldrich 99.98 %) treatment involved the steps as indicated in the first of these syntheses.

2.13. Stage V

Stage IV N\(_2\)O decomposition results (see Chapter 3) clearly showed that the CF catalysts were not very effective, hence the final five catalysts (together with their corresponding supports) for dry reforming were (see Chapter 4):

\[
\frac{1}{2} \text{wt} \% \text{Rh/TiO}_2 \ (\text{SG}) \\
\frac{1}{2} \text{wt} \% \text{Rh/TiO}_2 \ (\text{SG IMP}) \\
\frac{1}{2} \text{wt} \% \text{Rh/TiO}_2 \ (\text{Degussa, P25}) \\
5 \text{wt} \% \text{Rh/Al}_2\text{O}_3 \text{ pellets (IMP)} \\
5 \text{wt} \% \text{Rh/TiO}_2 \ (\text{Degussa, P25}) \\
\text{TiO}_2 \ (\text{SG}) \\
\text{TiO}_2 \ (\text{Degussa P25}) \\
\text{Al}_2\text{O}_3 \text{ pellets (CONDEA, 2.5 mm)}
\]

The best of these were used in photocatalytic experiments (see Chapter 5). Stage V therefore didn’t require any preparations since it used the final selection of catalysts for N\(_2\)O decomposition (see Chapter 3) and dry reforming catalytic testing (see Chapter 4).

2.14. Conclusions

- The ‘sol-gel stage impregnation’ technique of introducing the metal ‘M’ to the support (Method of Preparation 4 at section 2.9.5.4) is the most effective technique.
2. Materials and Catalyst Preparations.

- For blank SiO₂-TiO₂, it was found that the clearest, most homogeneous gels are formed when $R_w = 2$, $R_A = 5$ or 6 and SiO₂: TiO₂ ratio is 4:1. (low pH). This also provides for the shortest $t$, typically 4-5 days, which is in agreement with Babonneau et al [138].
- Modified versions of $\frac{1}{2}$ wt. % Rh/TiO₂ (SG) was prepared after results from Stage III (see Chapter 3).
- Collaboration work with SSTL led to the preparations of 5 wt. % Rh/Al₂O₃ pellets (IMP) and 5 wt. % Rh/TiO₂ (Degussa, P25, IMP) catalysts during Stage IV.

2.15. References

2. Materials and Catalyst Preparations.


2. Materials and Catalyst Preparations.


2. Materials and Catalyst Preparations.

2. Materials and Catalyst Preparations.


CHAPTER III
Catalysis I : Nitrous oxide decomposition.

3.1. Introduction

The decomposition of nitrous oxide was justified in Chapter 1 as fulfilling two useful objectives:

i) the reduction of a prominent GHG, and

ii) as a monopropellant for satellite microthruster fuel combustion (this aspect was particularly useful for SSTL).

In this chapter details of the experimental set up and their results is provided. In this regard, the strategy focussed on three main areas:

i) scanning temperature-programmed (TP) continuous $N_2O$ decomposition to establish a pecking order of all existing and prepared catalysts, the preparations of which are described in Chapter 2. This provided an indication as to the development of further catalysts and aided in evolving the experimental design for final catalysts.

ii) TP continuous and pulse analysis on selected final catalysts.

iii) the testing of Shell 405 (36 wt % Ir/Al$_2$O$_3$) and the development of an alternative catalyst, 5 wt % Rh/Al$_2$O$_3$ pellets (IMP) (see Chapter 2) and testing for N$_2$O decomposition.

3.2. Types of experiments

Two types of experiments were used to achieve and monitor the decomposition of $N_2O$. These were i) temperature-programmed (TP) continuous and ii) pulse mode experiments.
TP continuous experiments showed in real time when and to what extent the decomposition occurred. Furthermore, for the active catalysts it provided information relating to activation energies, $E_a$ (see Chapter 2) and an indication of how good a catalyst is as a function of temperature. It also shows whether a catalyst will deactivate at a particular temperature. Pulse experiments are useful as they provide information relating to the mechanisms of a particular process. A combination of these two approaches provides a powerful tool for the study of surface catalytic phenomena.

During a continuous type experiment, all the reactant gases including the carrier (i.e. Ar) pass through the rig system (see section 3.3 and Appendix II) either through the reactor or bypass it to the Residual Gas Analysor, RGA (see section 3.7). During the pulse type experiments however, only the carrier gas passes through the rig system and the N$_2$O is pulsed into the stream just before the reactor. The RGA is only required as the main detector. The bypass is useful in the sense that it provides useful comparative information as a blank run.

3.3. Experimental rig design

These experiments required the need to design and construct an experimental rig system. The system was constructed from PTFE tubing and stainless steel because these were less reactive than Cu. This was designed to accommodate heterogeneous catalytic reactions at the gas-solid interface. The experimental set up is shown in Appendix II (see Chapter 8). The design also had the added advantage of switching between pulse and continuous flow experiments.

The appropriate gases were controlled by the respective taps of the relevant gas cylinders, and their flow rates are controlled by the appropriate valves. The gases pass through the flow meters and through into the mixer which ensures that the gases are adequately mixed. At this juncture, there is a choice. The gases, depending on the particular experiment being conducted, either bypass the reactor and go straight through the various analysers and out to the exhaust; or they may pass through the reactor which is conveniently placed in the furnace. The reactor contained the sample
material under investigation supported on some silica wool. This sample can be any of the catalyst/support materials resting on some silica wool in a bed reactor.

The biggest problem with the rig was to eliminate impurities from the stream. For both dry reforming and N₂O decomposition, the presence of O₂ can ruin the experiments. In the case of dry reforming in particular, it affects the mechanism (see Chapter 4 and 7) and in N₂O decomposition it can hinder O₂ production (by Le Chatelier's principle). In this regard, an effective O₂ trap had to be used. MnOₓ/Celite (approx. 20 g, Phasep N, 60-85 mesh, Phase Separations Ltd.) (see Chapter 2) provided the answer. It was reduced at 523 K for an hour before a run and displayed a characteristic green colour in its reduced form (MnO) [1]:

\[
\text{Mn(IV)O}_2 + \text{H}_2 \rightarrow \text{Mn(II)O} + \text{H}_2\text{O}
\]

brown \hspace{1cm} green

It therefore captures O₂ from the stream by oxidising from Mn(II)O to Mn(IV)O₂, and in the process, it turns back to brown. In addition, the need to remove O₂ from a stream prior to introducing H₂ as reductant is significantly important from a safety perspective since a mixture of O₂ and H₂ is potentially explosive [2]:

\[
\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}
\]

It was therefore justified to use MnOₓ/Celite to reduce the levels of O₂ in the stream. Hence, the O₂ as an impurity level with respect to the levels of atmospheric Ar was reduced to 100 ppm corresponding to a p₁₀₂ of 10.13 Pa. The water levels with respect to atmospheric Ar was 5280 ppm corresponding to p₁H₂O of 535 Pa. The saturation vapour pressure of water at 298 K (SVP₂₉₈K) is 77.5 kPa and at 773 K and 1073 K, it is 420.9 kPa and 566.4 kPa respectively [3].

3.3.1. Furnace

The furnace was an integral part of the experimental rig system, as it provided the energy required for the catalytic reactions. It was a Lenton "Pyro therm" furnace
equipped with a type K (chrome-alumel) thermocouple (BSEN 60584.1; Ø 1 mm; (Ni-10%/Cr positive node and Ni + 2% Al + 2% Mn + 1%, negative node)) that has maximum and minimum working temperatures between 73 K and 1400 K [4-6]. This made it suitable for the experiments described. Figure 3.1 below shows the temperature versus response time when the ramp rate (r.r.) was set to 10 K/min. The straight line shows the ideal theoretical situation of exactly 10 K/min. As can be seen, the response is almost linear and has excellent agreement with the ideal case, especially up to 900 K where the maximum error is only ± 1 %. At higher temperatures, the errors increase to ± 2.4 % as the response deviates from the ideal case. On average therefore, the errors associated with the temperature programming was ± 10 K. The furnace temperature can therefore be reliably used for the experiments described here.

3.3.2. Reactors

A full-scale industrial plant may use up to 50 tonnes of catalyst in order to maximise productivity and profitability. However, from an academic and research perspective industrial plants are often inflexible in the sense that they operate in a narrow range of temperature, pressure and flow rate. The catalyst cannot also be readily changed. For
research purposes microreactors (usually accommodating less than 1 g of catalyst) often need to be used. The scale-up for catalyst testing follows the scheme:

\[
\text{Microreactor (1 g catalyst)} \rightarrow \text{Large-scale reactor (1 kg catalyst)} \rightarrow \text{Pilot plant (100 kg catalyst)} \rightarrow \text{Full-scale plant (50 tonne catalyst)}
\]

Fig. 3.2 – Industrial scale-up of catalyst testing.

Industrial reactors come in various forms depending on the applications required. They include fixed bed reactors, multi-tubular reactors, fluidised bed reactors, batch reactors and flowing bed reactors [7]. Their differences are not discussed here.

The small-scale microreactor is a small, fixed-bed reactor which uses about 1 g of catalyst at a time. The catalyst (often in powder form) is usually supported on some silica wool to prevent it from flowing through the reactor with the gaseous flow. Silica wool is a thermally stable and inert material that is suitable for this purpose. The reactor is placed in a furnace (see Appendix II) for the TP experiments. Microreactors are of two main types: fused-silica wool and pyrex. In this case, fused-silica reactors were used instead of pyrex reactors. This was because a fused silica reactor can withstand a maximum temperature of 1678 K whereas a pyrex reactor would start melting from 723 K which was clearly inappropriate for the purposes of the investigations concerned. The use of the silica reactors were therefore justified and fulfilled the requirements to carry out the TP work and pulse work up to at least 973 K. Appropriately, the melting point of these silica reactors are 2126 K [8], which was well above the desired experimental conditions.

3.3.3. Residence time in the reactor

The residence or contact time, which is said to be the average time a molecule remains in the catalyst bed, is defined as:

\[
\text{Contact time} = \frac{\text{free volume in bed (inc. pore volume)}}{\text{flow rate of gas}}
\]
The reciprocal of contact time (i.e. 1/contact time or flow rate of gas/free volume in bed) is the space velocity or volume of gas flowing through free volume of the bed in unit time. The contact time with regards to the above is 20 cm$^3$/100 cm$^3$min$^{-1} = 0.2$ min = 12 s, which by definition implies that the space velocity = 5 min$^{-1} = 300$ h$^{-1}$.

Consequently, space velocity is directly proportional to the flow rate, i.e. the higher the flow rate the higher the space velocity. Graphically, the linear relationship is shown in Figure 3.3 below:

![Fig. 3.3 - Space Velocity as a function of Flow Rate.](image)

From the RGA software, the cycle number and time (in seconds) at the point of injection, $t_{inj}$, for a particular pulse was noted. Furthermore, careful attention was given to the $t_{max}$ value, i.e. the time it takes from $t_{inj}$ to the maximum position of the peak to be attained after the pulse. The $t/t_{max}$ is the ratio of normalisation where $t$ is the time in seconds from the point of injection, $t_{inj}$ (equivalent to $t/t_{max} = 0$), whereas $t_{max}$ signifies the time at which the maximum of the injected peak is detected after $t_{inj}$. This was plotted against $p/p_{max}$ (the ratio of normalisation for pressure) where $p$ is the measured pressure and $p_{max}$ is the maximum pressure of the injected peak in the bypass stream and the blank reactor. Molecular residence time ($t_{res}$, i.e. the amount of

time a molecule stays in the catalytic bed) it will be dependent upon the type of fluid flow (i.e. whether the flow is laminar or turbulent). Reynold's number is relevant in this context. It is defined as the ratio of the flow speed to the viscosity of the fluid:

\[ N_{Re} = \frac{LV\rho}{\mu} \]

where \( N_{Re} \) = Reynold's number; \( L \) = Characteristic dimension, e.g. length; \( V \) = Fluid Velocity; \( \rho \) = density of Ar at T and \( \mu \) = viscosity of Ar at T. The formula is valid for a planar surface, however for a fluid in a pipe, the term \( L \) is substituted with \( d \) (the cross-sectional diameter of the piping). Hence, the equation becomes:

\[ N_{Re} = \frac{dV\rho}{\mu} \]

When \( N_{Re} \) is less than 2000, the flow is usually laminar. For \( N_{Re} \) above 4000, there is turbulent flow. There is no sharp change from laminar to turbulent flow, only a gradual change as the velocity of the fluid within a given system is increased. When the Reynold's number is lying in between 2000 and 4000, the flow will be changing rapidly from laminar to turbulent [9]. So when the flow is laminar, the \( t_{res} \) is higher as compared to when the flow is turbulent. This is because during laminar flow, the molecules in the gas stream are travelling slower (compared to the corresponding turbulent flow). This means that the gaseous molecules spend a longer time period on the catalytic bed, and therefore the \( t_{res} \) is higher. Hence at 101kPa and 298 K Ar in the present reactor has an \( N_{Re} \) given by \( d = 0.65 \text{ cm (0.0065m)} \), \( V = 319 \text{ms}^{-1} \), \( \rho = 1.783 \text{gdm}^{-3} \) and \( \mu = 22.9 \times 10^{-6} \text{Pa s} \) [3]. From this \( N_{Re} \) is 161,443, and so is very much greater than 4000. Therefore the flow must be turbulent. At increasingly higher temperatures the flow becomes increasingly more turbulent.

3.3.4. Gases

During the experiments the gases that were employed were Ar (neat) as the carrier gas (flow rate 80±1 cm³min⁻¹) and N₂O (neat) (20±1 cm³min⁻¹) for TP continuous mode experiments. The pulse work required Ar flow as above and N₂O (neat) pulses of

0.1 cm$^3$ (2.24 mmol) at 523 K and 973 K. H$_2$ (neat) was also used as pre-reductant (50±1 cm$^3$ min$^{-1}$).

3.4. Materials

The materials used were those that were prepared in Chapter 2. These included the supports: SiO$_2$ (SG) (0.0560 g, 939 μmol), SiO$_2$-TiO$_2$ (SG) (0.0545 g, 389 μmol), TiO$_2$ (SG) (0.0521 g, 652 μmol), TiO$_2$ (Degussa, P25) (0.0565 g, 707 μmol), Al$_2$O$_3$ pellets (CONDEA,) (0.2150 g, 2.11 mmol), Al$_2$O$_3$ (CF) (1.5395 g, 0.015 mol); the Ni samples: 0.5 wt % Ni/SiO$_2$ (SG) (0.0519 g, 4.42 μmol. Ni cat.), 0.5 wt % Ni/TiO$_2$ (SG) (0.0494 g, 4.21 μmol. Ni cat.), 0.5 wt % Ni/SiO$_2$-TiO$_2$ (SG) (0.0512 g, 4.36 μmol. Ni cat.); the Rh samples: 0.5 wt % Rh/SiO$_2$ (SG) (0.0521 g, 2.53 μmol. Rh cat.), 0.5 wt % Rh/SiO$_2$-TiO$_2$ (SG) (0.0512 g, 2.49 μmol. Rh cat.), 0.5 wt % Rh/TiO$_2$ (SG) (0.0590 g, 2.87 μmol. Rh cat.); and the modified Rh/TiO$_2$ samples: 0.5 wt % Rh/TiO$_2$ (SG IMP) (0.0575, 2.79 μmol. Rh cat.), 0.5 wt % Rh/TiO$_2$ (Degussa, P25, IMP) (0.0656 g, 3.19 μmol. Rh cat.), 0.5 wt % Rh/TiO$_2$ (SG-100 %/Al$_2$O$_3$ (CF) (2.4551 g, 119.0 μmol. Rh cat.), 0.5 wt % Rh/TiO$_2$ (SG-80 %/Al$_2$O$_3$ (CF) (2.4777 g, 120.0 μmol. Rh cat.), 0.5 wt % Rh/TiO$_2$ (SG-30 %/Al$_2$O$_3$ (CF) (2.8464 g, 138.3 μmol. Rh cat.), 0.5 wt % Rh/TiO$_2$ (SG-0 %/Al$_2$O$_3$ (CF) (2.3928 g, 116.3 μmol. Rh cat.). Also used were the commercial 36 wt % Ir/Al$_2$O$_3$ (Shell 405; CRI Fine Chemicals) (0.0979 g, 183.3 μmol. Ir cat.) and V-Rh/Al$_2$O$_3$ (0.0515 g, 10.0 μmol. Rh cat.) which were both kindly supplied by SSTL. 5 wt % Rh/Al$_2$O$_3$ pellets (IMP) (0.0526 g, 25.6 μmol. Rh cat.) and 5 wt % Rh/TiO$_2$ (Degussa, P25, IMP) (0.0508 g, 24.7 μmol. Rh cat.) were prepared (see Chapter 2) and tested as alternatives to the commercial Shell 405 catalyst.

3.5. Conditions

The catalyst/support (0.05 g, either 0.5 or 5 wt. % loading) was placed on the catalyst bed in the reactor (volume = 20 cm$^3$). The sample was pre-reduced with H$_2$ up to 723K. The carrier gas was Ar (neat), (80±1 cm$^3$ min$^{-1}$) and depending on the nature of
the experiment i.e. pulse or TP continuous the appropriate method of analysis was employed (see section 3.6).

3.5.1. Pre-treatment

Initially, the flow rate of the Ar as carrier gas was checked and confirmed to be 80±1 cm³ min⁻¹. A blank reactor was first used as a control in a TP and pulse mode. The flow rate was checked again to maintain a constant flow of 80±1 cm³ min⁻¹. The catalyst/support was then introduced into the reactor and the flow rate was adjusted to maintain the constant value. This was followed by the pre-treatment under H₂ atmosphere (neat, 50±1 cm³ min⁻¹) to reduce the MnOₓ/celite and catalyst (if required). The experiment continued with either a TP continuous or pulse experiment.

3.5.2. TP Continuous

This involved the N₂O (neat, 20±1 cm³ min⁻¹) and Ar (neat, 80±1 cm³ min⁻¹) stream to be continuously monitored by the RGA. This was followed by analysis of the supports and catalysts in a TP continuous mode as the temperature was increased from 523 K to 923 K (following Method of Analysis A below). The experiment was terminated but the stream was switched to bypass to check the observations were real.

3.5.3. Pulse methods

In this case, the experiment is performed isothermally first at 523±5 K and then again at 973±5 K) at a pressure of 101.3 kPa. It also involved the use of a continuous flow of Ar (neat, 100±1 cm³ min⁻¹) as the carrier gas with N₂O (neat, 0.1 cm³, 2.24 mmol) pulses initially as blanks to show experimental reproducibility. This is followed by at least two N₂O pulses at each temperature over one of the prepared catalysts monitored by the use of RGA. Therefore, the number of moles of reactive gas per mole of Rh₆ in Rh/TiO₂ in N₂O pulse was \( n_{N_2O}/n_{Rh_6} = 2.24/2.87 \times 10^{-3} \).

3.5.4. Independent testing by SSTL

Independent testing was carried out by SSTL on the Shell 405 and 5 wt % Rh/Al₂O₃ pellets (IMP). This was done on their N₂O decomposition prototype thruster which was designed to simulate a lightweight flight thruster of a microsatellite. The decomposition of N₂O is used as a monopropellant fuel. The problem with commercial Shell 405 is that Ir is rapidly lost from the surface (see SEMs in Chapter 6). The challenge was to design a catalyst that would show evidence of being retained on the surface whilst showing activity. Figure 3.4 below shows the experimental set-up of the prototype thruster. The flow rate of the N₂O was measured by a pressure gauge and controlled by a flow control valve. The catalyst was contained in the thruster which sat in a vacuum chamber and the energy to activate the catalyst was provided by an external electrical power supply [10].

![Schematic diagram of test set-up for N₂O prototype thrusters](image)

Fig. 3.4 - Schematic diagram of test set-up for N₂O prototype thrusters [10].

The operating conditions for the prototype thruster are shown in Table 3.1.

### Table 3.1 - N₂O monopropellant thruster design parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thrust</td>
<td>100 mN</td>
</tr>
<tr>
<td>Specific impulse</td>
<td>150 s</td>
</tr>
<tr>
<td>Flow rate of N₂O</td>
<td>4 cm³ min⁻¹</td>
</tr>
<tr>
<td>Chamber temperature (max./min./average)</td>
<td>1191 K/ 956 K / 1073 K</td>
</tr>
<tr>
<td>Operating pressure</td>
<td>3x10⁵ Pa</td>
</tr>
<tr>
<td>Power input to initiate decomposition</td>
<td>30 W</td>
</tr>
<tr>
<td>Heating time to initiate decomposition</td>
<td>300-420 s</td>
</tr>
</tbody>
</table>

3.6. Data Acquisition

#### 3.6.1. Method of analysis A

A method of experimentation and analysis (data acquisition) is described here for N₂O decomposition TP continuous analysis:

1) The catalyst was reduced (plus MnOₓ trap) with pre-reductant H₂ at 723 K for about 1 h. The RGA capillary was removed from reaction stream, otherwise the RGA was affected and hence data output will not make sense.

2) The Ar was switched on as the carrier gas for 10 min to flush out excess H₂ and allow time for the furnace to cool. The RGA capillary was re-attached.

3) The Ar bypass was allowed for 5 min for equilibration, then the bypass data was recorded with Ar flowing for 5 min. This was then switched to N₂O for 5 min recording. The gas levels were noted on the RGA.

4) The reaction stream was switched from bypass and the data was recorded on the RGA in TP mode when the furnace reached 523 K. The data was recorded in the temperature range: 523 - 1073 K.

5) At 1073 K, the reaction stream was switched back to bypass to confirm that the observed reaction was real. The cycle number on the RGA was noted for reference since this would help with data manipulation later.

This procedure was useful for scanning the range of catalysts in order to determine a pecking order, and also for activity measurements, $E_a$ etc.

3.6.2. Method of analysis B

Similarly, the procedure for the pulse mode:

1) The catalyst was pre-reduced with $H_2$ at 723 K for about 1 h. Care had to be taken to remove the RGA capillary from the reaction stream, otherwise the RGA would have been affected.
2) $Ar$ was switched on bypass for 10 min flushing. The RGA capillary was reattached.
3) The reaction stream was switched on and left to stabilise for 10 min.
4) Data acquisition was allowed to start on the RGA.
5) Two $N_2O$ pulses were undertaken for a blank reactor and a reaction. This was compared with the bypass.
6) The data was recorded as

$$
\begin{array}{cccc}
t(min) & t(s) & t_{max} & t/t_{max} \\
\end{array}
$$

special note was taken care of $t_{max}$ (i.e. the time it takes from $t_{inj}$ to the time of maximum RGA response).

These results helped to give information about mechanisms.

3.7. Instrumental method – the RGA-MS

The analysis was carried out using an “ESS VG Quadrupole, Sensorlab” Residual Gas Analyser (RGA) with a built-in mass spectrometer. It measures gaseous effluent of a reaction using partial pressures. It does this by separating ions according to their mass to charge ratio ($m/e$). The instrument was fitted with a quadrupole detector (see Figure 3.5) which involved the application of alternating electric fields across four poles to allow the separation of ions to their respective $m/e$ ratios. Furthermore, it was important that the instrument operated under vacuum in order to maximise the mean free path of the ions reaching the detector. Otherwise, ion recombination will mean
that they will not be detected. As an illustration, the measured internal pressure of the RGA was typically $3 \times 10^{-4}$ Pa (i.e. about $3 \times 10^{-9}$ atm.)

Helium gas was originally used as an inert carrier gas for the RGA, but its low relative atomic mass (RMM = 2) interferes with the vacuum pump that is used for the RGA instrument. Hence Ar (RMM = 40) was used instead. The RGA provides a convenient on-line view of production/consumption of major products/reactants and other chemicals. It can be used in two modes: i) as a pulse technique or ii) as a continuous mode of detecting reactants and products.

![Schematic diagram of an RGA quadrupole filter](image)

Fig. 3.5 - Schematic diagram of an RGA quadrupole filter

The instrument can be set to look for ions in two modes, namely multiple ion monitoring (molecular ion peaks) and isotope patterns.

Multiple ion monitoring involves the accurate measurement of the relative molecular mass of molecules (e.g. CO = 28).

Isotope patterns clearly indicate that certain elements exist as isotopes and hence produce distinct isotopic patterns based on their natural relative abundance. As an example Br can exist as $^{79}$Br (50.7% relative abundance) and $^{81}$Br (49.3% relative abundance). Both of these can be seen in the form of [M+1 (H)] in the mass spectra.
of HBr. Hence, two lines of similar intensity are produced at m/e 80 and m/e 82 respectively.

The RGA is a versatile instrument that can be set up to be used for TP continuous or pulse type experiments. It was used to detect these species with the following m/e values: 32 (O\(_2\)), 31 (N\(_2\)O), 44 (N\(_2\)O), 28 (N\(_2\)) and 40 (Ar) for continuous TP and pulse work. The N\(_2\)O with m/e at 31 is a secondary peak and is used to distinguish from 44 (residual CO\(_2\)) that may be in the stream. Blank runs (i.e. reactor only containing silica wool) of N\(_2\)O pulses were initially performed to check the instrument and the experimental set-up gave reproducible results.

The results show N\(_2\)O and \(\frac{1}{2}\) O\(_2\) only because the decomposition of N\(_2\)O was the main objective and the production of O\(_2\) is easily measured. N\(_2\) was not used since it is a major component of air and in case of confusion with CO (an impurity that was thought to be originating from the N\(_2\)O cylinder). It was later determined that the presence of CO would be unavoidable in the RGA since carbon compounds would react with oxygen at the heated filament of the mass spectrometer (MS) ion source and filaments of the ion gauges. The use of MnO\(_x\)/Celite is therefore of utmost importance.

3.8. Results

The results are first shown for the TP continuous work and then the pulse work. In each case the bypass/blank results were compared with the catalyst results.

3.8.1. TP continuous results

In terms of N\(_2\)O conversion 0.20 atmospheres is 0 % conversion tending to 100 % conversion towards 0 atmospheres. Conversely, in terms of oxygen production 0 atmospheres is 0 % production and 0.20 atmospheres is 100 % production. A factor of 2 was included for oxygen production.

3.8.1.1. Blank reactor
The extent of reaction in the blank reactor was considered first:

![Graph showing TP N₂O decomposition through blank reactor](image1)

**Fig. 3.6** - TP N₂O decomposition through blank reactor

The blank reactor shows less than $10\pm 3\%$ N₂O conversion and $0\pm 1\%$ $\frac{1}{2}$ O₂ production below 1000 K.

3.8.1.2. Supports.
Now consider TP results for the supports alone:

![Graph showing TP N₂O decomposition over SiO₂ (SG)](image2)

**Fig. 3.7** – TP N₂O decomposition over SiO₂ (SG)


Fig. 3.8 – TP N₂O decomposition over SiO₂-TiO₂ (SG)

Fig. 3.9 – TP N₂O decomposition over TiO₂ (SG)

Fig. 3.10 – TP N₂O decomposition over TiO₂ (Degussa, P25)

Fig. 3.11 – TP N₂O decomposition over Al₂O₃ ceramic foam (CF)

![Graph](image)

Fig. 3.12. – TP N₂O decomposition over Al₂O₃ pellets (2.5 mm diameter)

SiO₂ (SG), SiO₂-TiO₂ (SG) and Al₂O₃ (CF) showed no activity i.e. they are inert supports in N₂O decomposition. TiO₂ (SG) on the other hand showed the most activity above 800 K followed by Al₂O₃ pellets and TiO₂ (Degussa, P25). Table 3.2 below shows a comparison of % N₂O conversion and % ½ O₂ production for the active supports at 1000 K.

<table>
<thead>
<tr>
<th></th>
<th>% N₂O conversion at 1000 K</th>
<th>% ½ O₂ production at 1000 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ (SG)</td>
<td>25± 3</td>
<td>50± 3</td>
</tr>
<tr>
<td>Al₂O₃ pellets</td>
<td>25± 3</td>
<td>5± 3</td>
</tr>
<tr>
<td>TiO₂ (Degussa P25)</td>
<td>10± 3</td>
<td>10± 3</td>
</tr>
</tbody>
</table>

Thus the order of activity was

TiO₂ (SG) > Al₂O₃ pellets > TiO₂ (Degussa P25), where > = more active than.

3.8.1.3. Ni catalysts

Now consider TP N₂O decomposition over Ni catalysts.

Fig. 3.13. – TP N₂O decomposition over 0.5 wt. % Ni/SiO₂ (SG)

Fig. 3.14. – TP N₂O decomposition over 0.5 wt. % Ni/SiO₂-TiO₂ (SG)
Table 3.3 shows a comparison of % N₂O conversion and % N₂O production for the Ni catalysts at 1000 K. Clearly, the presence of Ni had no real effect on the rate of N₂O decomposition above that shown for the supports alone. Thus 0.5 wt. % Ni/TiO₂ (SG) (Figure 3.15) was similar to TiO₂ (SG) on its own. This could possibly be due to Ni being sintered or oxidised [11]. Ni was therefore not pursued further in the research.

Table 3.3. - % N₂O conversion and % N₂O production at 1000 K for Ni catalysts.

<table>
<thead>
<tr>
<th>Ni Catalyst</th>
<th>% N₂O conversion at 1000 K</th>
<th>% N₂O production at 1000 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 wt. % Ni/SiO₂ (SG)</td>
<td>4± 3</td>
<td>2± 1</td>
</tr>
<tr>
<td>0.5 wt. % Ni/SiO₂–TiO₂ (SG)</td>
<td>5± 3</td>
<td>2± 1</td>
</tr>
<tr>
<td>0.5 wt. % Ni/TiO₂ (SG)</td>
<td>13± 3</td>
<td>13± 3</td>
</tr>
</tbody>
</table>

Fig. 3.15. – TP N₂O decomposition over 0.5 wt. % Ni/TiO₂ (SG)

3.8.1.4. Rh and Ir catalysts:

Chapter 4 shows that the existing Rh/SiO$_2$ was the most active catalyst in dry reforming out of Rh/SiO$_2$, Ru/SiO$_2$ and Ir/SiO$_2$. It was also found that Rh/SiO$_2$ was the most active catalyst for N$_2$O decomposition. Hence, investigations on Ru/SiO$_2$ and Ir/SiO$_2$ were not pursued further. Early TP continuous N$_2$O decomposition runs on 0.5 wt % Rh/SiO$_2$ (SG) and 0.5 wt % Rh/SiO$_2$-TiO$_2$ (SG) did not show any appreciable activity, but 0.5 wt % Rh/TiO$_2$ (SG) showed marked activity. This was therefore a catalyst of immense interest. TiO$_2$ appears to aid in the decomposition process and this is perhaps due to its strong metal support interaction (SMSI) [12]. This significant result provided the basis for further development, modification and preparation of modified Rh/TiO$_2$ catalysts (see Chapter 2). Figures 3.16-3.23 show the extent of N$_2$O decomposition for the Rh and commercial Shell 405 catalysts over various supports. Figure 3.24 shows a comparison of Shell 405, 5 wt % Rh/Al$_2$O$_3$ pellets (IMP) and the previously prepared V-Rh/Al$_2$O$_3$ catalyst.

![Fig. 3.16. – TP N$_2$O decomposition over 0.5 wt. % Rh/TiO$_2$ (SG).](image-url)

Fig. 3.17. — TP N₂O decomposition over 0.5 wt. % Rh/TiO₂ (SG IMP).

Fig. 3.18. — TP N₂O decomposition over 0.5 wt. % Rh/TiO₂ (Degussa, P25).


Fig. 3.19. – TP N₂O decomposition over 0.5 wt. % Rh/TiO₂ (SG-80%)/Al₂O₃ (CF, IMP).

Fig. 3.20. – TP N₂O decomposition over V-Rh/Al₂O₃ pellets.

Fig. 3.21. – TP N₂O decomposition over 36 wt. % Ir/Al₂O₃ pellets (Shell 405).

5 wt % Rh/Al₂O₃ pellets (IMP) and 5 wt % Rh/TiO₂ (Degussa, P25, IMP) were prepared (see Chapter 2) to compare against Shell 405:

Fig. 3.22. – TP N₂O decomposition over 5 wt. % Rh/Al₂O₃ pellets (IMP).

Fig. 3.23. - TP N₂O decomposition over 5 wt. % Rh/TiO₂ (Degussa, P25, IMP).

Fig. 3.24. - Comparison for TP N₂O decomposition over V–Rh/Al₂O₃, Shell 405 and 5 wt % Rh/Al₂O₃ pellets.

Table 3.4 below shows the extent of N₂O decomposition in terms of % N₂O conversion and % ½ O₂ production for the various catalysts.

Table 3.4. - % N₂O conversion and % ½ O₂ production at 1000 K for Rh and Ir catalysts

<table>
<thead>
<tr>
<th></th>
<th>% N₂O conversion</th>
<th>% ½ O₂ production</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30±3</td>
<td>30±3</td>
</tr>
<tr>
<td>2</td>
<td>62±5</td>
<td>70±3</td>
</tr>
<tr>
<td>3</td>
<td>85±3</td>
<td>80±3</td>
</tr>
<tr>
<td>4</td>
<td>95±3</td>
<td>97±3</td>
</tr>
<tr>
<td>5</td>
<td>80±3</td>
<td>97±3</td>
</tr>
<tr>
<td>6</td>
<td>92±3</td>
<td>97±3</td>
</tr>
<tr>
<td>7</td>
<td>78±4</td>
<td>75±3</td>
</tr>
<tr>
<td>8</td>
<td>84±3</td>
<td>48±3</td>
</tr>
</tbody>
</table>

where 1 = 0.5 wt % Rh/TiO₂ (SG); 2 = 0.5 wt % Rh/TiO₂ (SG IMP); 3 = 0.5 wt % Rh/TiO₂ (Degussa, P25); 4 = 0.5 wt % Rh/TiO₂ (SG-80%)/Al₂O₃ (CF, IMP); 5 = V-Rh/Al₂O₃ pellets; 6 = 36 wt % Ir/Al₂O₃ pellets (Shell 405); 7 = 5 wt % Rh/Al₂O₃ pellets (IMP) and 8 = 5 wt % Rh/TiO₂ (Degussa, P25, IMP).

3.8.1.5. Continuous TP observations

Figure 3.16 shows that 0.5 wt % Rh/TiO₂ (SG) catalyst allows N₂O decomposition above 650K but it deactivated above 860 K, possibly due to sintering. It was shown that at 1000 K, there was 30±3 % N₂O conversion and 30±3 % ½ O₂ production. Figure 3.17 shows that 0.5 wt % Rh/TiO₂ (SG IMP) catalyst does not deactivate at high temperatures but no activity was observed below 790 K. Here 62±5 % N₂O conversion and 70±3 % ½ O₂ production was achieved. Activity for 0.5 wt % Rh/TiO₂ (Degussa P25) catalyst however begins above 690 K but deactivation occurs above 950 K (see Figure 3.18) with 85±3 % N₂O conversion and 80±3 % ½ O₂ production. For 0.5 wt. % Rh/TiO₂ (SG-80%)/Al₂O₃ (CF, IMP) catalyst there was no activity below 825 K and it was stable beyond 1000 K (see Figure 3.19) with 95±3 % N₂O conversion and 97±3 % ½ O₂ production. Figure 3.20 shows that for V-Rh/Al₂O₃ pellets catalyst, there was activity above 650 K and it appeared to be stable at high temperatures. Here N₂O conversion was 80±3 % and ½ O₂ production was 97±3 %. Shell 405 catalyst showed activity above 590 K and sustained its activity steadily up.

to 1000 K (see Figure 3.21) where % N₂O conversion was 92±3 % and ½ O₂ production was 97±3 %. For 5 wt. % Rh/Al₂O₃ pellets (IMP) catalyst N₂O decomposition occurred above 615 K but it deactivated above 1000 K (see Figure 3.22), at which point there was 78±4 % N₂O conversion and 75±3 % ½ O₂ production. Figure 3.23 showed that for 5 wt. % Rh/TiO₂ (Degussa, P25, IMP) catalyst, activity was only seen above 590 K but it rapidly deactivated above 850 K. Here there was 84±3 % N₂O conversion and 48±3 % ½ O₂ production at 1000 K. Figure 3.24 showed a comparison plot for TP N₂O decomposition over V–Rh/Al₂O₃, Shell 405 and 5 wt % Rh/Al₂O₃ pellets (IMP). It seemed that weight for weight %, 5 wt % Rh/Al₂O₃ decomposed N₂O to a further extent than Shell 405 and V-Rh/Al₂O₃ (see Table 3.4).

Thus the order of activity in terms of % N₂O conversion at 1000 K (see Table 3.4) was:

0.5 wt % Rh/TiO₂ (SG-80%)/Al₂O₃ (CF) > Shell 405 > 0.5 wt % Rh/TiO₂ (Degussa P25) > 5wt % Rh/TiO₂ (Degussa P25) > V-Rh/Al₂O₃ > 5 wt % Rh/Al₂O₃ pellets (IMP) > 0.5 wt % Rh/TiO₂ (SG IMP) > 0.5 wt % Rh/TiO₂ (SG).

3.8.1.6. Mass Balance

In order to determine whether the experiments were carried out properly and therefore whether the results were true, mass balance calculations and profiles are provided. Simply, the amount of substance reacting must in effect produce the same output. Since the decomposition has a 2:1 ratio with respect to N₂O and O₂:

\[ \text{N}_2\text{O} \rightarrow \text{N}_2 + \frac{1}{2} \text{O}_2 \]

the mass balance was given by:

\[ \frac{\text{the change in pressure of N}_2\text{O consumption over the temperature range}}{\text{twice the change in pressure of O}_2 \text{ production over the temperature range}} \]

or mathematically represented as:


\[-\Delta P_{\text{N}_2\text{O}}\]
\[+ 2\Delta P_{\text{O}_2}\]

The consumption and production are represented by the ‘minus’ (-) and ‘plus’ (+) signs respectively. This was plotted against the temperature range concerned, and if mass balance is obeyed then there should be an averaging around the origin since overall, no real net gain or loss is made.

Mass balance profiles are now shown for a selection of the catalysts used:

Fig. 3.25 – Mass balance for 0.5 wt % Rh/TiO₂ (SG)

Fig. 3.26. – Mass balance for Shell 405

Fig. 3.27 – Mass balance for 5 wt % Rh/Al₂O₃ pellets (IMP)

As expected, a good mass balance exists for all these results. Small deviations are noticeable, but this is simply attributed to inherent experimental errors. The results therefore are very useful for interpreting the extent of N₂O decomposition on these catalysts.

3.8.1.7. Activation Energies

Activation energies ($E_a$) were worked out for the catalytic results with respect to N₂O decomposition/conversion and $\frac{1}{2}$ O₂ production using the procedure described in Chapter 2. As an example, Figure 3.28 below shows an Arrhenius plot for 5 wt % Rh/Al₂O₃ pellets (IMP) with respect to % N₂O conversion. The gradient gave an $E_a$ of 29.4±1.0 kJmol⁻¹ with the intercept giving a ln A value of 8.40±0.3. Similarly Figure 3.29 shows a corresponding Arrhenius plot for % $\frac{1}{2}$ O₂ production. Here the $E_a$ was found to be 70±2.5 kJmol⁻¹ and ln A value of 15.9±0.6. $E_a$s and corresponding ln As for the other catalysts are shown in Table 3.5 for both $\frac{1}{2}$ O₂ production and N₂O consumption. % N₂O conversion and % $\frac{1}{2}$ O₂ production after 900 K is provided in Table 3.4.

Fig. 3.28 - Arrhenius plot for 5 wt % Rh/Al₂O₃ pellets (IMP) with respect to % N₂O conversion. \( E_a = 29.4 \pm 1.0 \text{ kJ mol}^{-1} \) and \( \ln A = 8.4 \pm 0.3 \)

Fig. 3.29 - Arrhenius plot for 5 wt % Rh/Al₂O₃ pellets (IMP) with respect to % \( \frac{1}{2} \) O₂ production. \( E_a = 70.0 \pm 2.5 \text{ kJ mol}^{-1} \) and \( \ln A = 15.9 \pm 0.6 \)


Table 3.5 – comparison of $E_a$ and $\ln A$ terms for different catalysts

<table>
<thead>
<tr>
<th>$\frac{1}{2}O_2$ production</th>
<th>N$_2$O decomposition</th>
<th>$E_a$ T range</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$ (kJ/mol)</td>
<td>$\ln A$</td>
<td>$E_a$ (kJ/mol)</td>
</tr>
<tr>
<td>1</td>
<td>104±3.6</td>
<td>21.5±0.8</td>
</tr>
<tr>
<td>2</td>
<td>207±7.2</td>
<td>34.7±1.2</td>
</tr>
<tr>
<td>3</td>
<td>127±4.4</td>
<td>23.7±0.8</td>
</tr>
<tr>
<td>4</td>
<td>249±8.7</td>
<td>39.0±1.3</td>
</tr>
<tr>
<td>5</td>
<td>412±14.4</td>
<td>78.4±2.7</td>
</tr>
<tr>
<td>6</td>
<td>249±8.7</td>
<td>52.6±1.8</td>
</tr>
<tr>
<td>7</td>
<td>70.0±2.5</td>
<td>15.9±0.6</td>
</tr>
<tr>
<td>8</td>
<td>80.5±2.8</td>
<td>18.5±0.6</td>
</tr>
</tbody>
</table>

where 1 = 0.5 wt. % Rh/TiO$_2$ (SG); 2 = 0.5 wt. % Rh/TiO$_2$ (SG, IMP); 3 = 0.5 wt. % Rh/TiO$_2$ (Degussa, P25, IMP); 4 = 0.5 wt. % Rh/TiO$_2$(SG-80%)/Al$_2$O$_3$ (CF, IMP); 5 = V-Rh/TiO$_2$; 6 = 36 wt. % Ir/Al$_2$O$_3$ pellets (Shell 405); 7 = 5 wt. % Rh/Al$_2$O$_3$ pellets and 8 = 5 wt. % Rh/TiO$_2$ (Degussa, P25, IMP). $E_a$s were taken at the temperature range of the greatest rate of change of conversion for each catalyst, hence the temperature of $E_a$ of any given catalyst was different from other catalysts.

The order of activity in terms of $E_a$s for N$_2$O decomposition (see Table 3.5) was:

5 wt % Rh/Al$_2$O$_3$ pellets (IMP) > 0.5 wt % Rh/TiO$_2$ (Degussa P25) > 0.5 wt. % Rh/TiO$_2$ (SG) > 5 wt. % Rh/TiO$_2$ (Degussa, P25, IMP) > 0.5 wt. % Rh/TiO$_2$ (SG, IMP) > 0.5 wt. % Rh/TiO$_2$(SG-80%)/Al$_2$O$_3$ (CF, IMP) > 36 wt. % Ir/Al$_2$O$_3$ pellets (Shell 405) > V-Rh/Al$_2$O$_3$.

3.8.1.8. Compensation plots

For related catalysts, the compensation effect is often experienced whereby the $\ln A$ term increases as the $E_a$ term increases across a series and vice versa, and hence ‘compensation effect’ (see Chapter 2).

$E_a$ is plotted against $\ln A$ for N$_2$O decomposition (see Figure 3.30) and $\frac{1}{2}O_2$ production (see Figure 3.31):

Fig. 3.30. – $E_a$ versus $\ln A$ term for $N_2O$ decomposition over selected catalysts.

Fig. 3.31. – $E_a$ versus $\ln A$ term for $\frac{1}{2} O_2$ production over selected catalysts.
There is therefore a correlation between the $E_a$ and the $\ln A$ terms for both decomposition of $N_2O$ and $\frac{1}{2} O_2$ production, hence compensation effect \[13\] exists between these catalysts. There was however no real relationship between surface area ($S_{BET}$) and $E_a$ (see Chapter 6).

Thus the order of activity (taking into account % $N_2O$ conversion at 1000 K and $E_a$s) was:

0.5 wt % Rh/TiO$_2$ (Degussa P25) > 5 wt % Rh/TiO$_2$ (Degussa P25) > 5 wt % Rh/Al$_2$O$_3$ pellets (IMP) ~ 0.5 wt % Rh/TiO$_2$ (SG-80%)/Al$_2$O$_3$ (CF) > Shell 405 > 0.5 wt % Rh/TiO$_2$ (SG) > 0.5 wt % Rh/TiO$_2$ (SG IMP) > V-Rh/Al$_2$O$_3$.

3.8.2. Low Temperature (523 K) & High Temperature (973 K) pulse results

Now $N_2O$ pulse results are considered; first the blank reactor followed by the support results and finally the catalysts (in conjunction with Chapter 4).

3.8.2.1. Blank reactor results:

![Fig. 3.32. - Duplicate $N_2O$ pulses as bypass for blank reactor.](image)

Duplicate $N_2O$ pulses through the blank reactor show good reproducibility and hence give an indication that the pulse data were reliable.

Fig. 3.33. – N₂O pulses through blank reactor at (a) 523 K and at (b) 973 K.

At 523 K (Figure 3.33(a)) and 973 K (Figure 3.33(b)) there is no N₂O decomposition in the blank reactor. This is consistent with TP data in Figure 3.6.

3.8.2.2. Support results

Fig. 3.34. – N₂O pulses for TiO₂ (SG) support at (a) 523 K and at (b) 973 K.

Figure 3.34 appears to show slight N₂O adsorption but no ½ O₂ production in N₂O pulses at 523 K and 973 K. This compares with TP results in Figure 3.9.

Fig. 3.35. – N₂O pulses for TiO₂ (Degussa, P25) at (a) 523 K and (b) at 973 K.

Figure 3.35(a) shows no activity at 523 K for TiO₂ (Degussa, P25) in N₂O pulsing, but decomposition was noted at 973 K. This was consistent with the TP continuous result (see Figure 3.10).

Fig. 3.36. – N₂O pulses for Al₂O₃ pellets at (a) 523 K and at (b) 973 K.

No activity in N₂O pulsing was seen for Al₂O₃ pellets at 523 K but N₂O decomposition was noted at 973 K (see Figure 3.36(a)-(b)). This is consistent with the TP continuous result (see Figure 3.12).

Table 3.6 below shows a comparison of % N₂O pulse decomposition and % ½ O₂ production at 973 K over various supports.

Table 3.6.- % N₂O pulse decomposition and % ½ O₂ production at 973K for various supports

<table>
<thead>
<tr>
<th>Support</th>
<th>% N₂O pulse decomposition</th>
<th>% ½ O₂ production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank reactor</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TiO₂ (SG)</td>
<td>10±2</td>
<td>0</td>
</tr>
<tr>
<td>TiO₂ (Degussa, P25)</td>
<td>90±5</td>
<td>5±3</td>
</tr>
<tr>
<td>Al₂O₃ pellets</td>
<td>20±3</td>
<td>20±5</td>
</tr>
</tbody>
</table>

N₂O adsorption and decomposition occurred mostly over TiO₂ (Degussa, P25) at 973K. However there appeared to be very little ½ O₂ production. Al₂O₃ pellets decomposed N₂O to a lesser extent but there appeared to be up to 20±5 % ½ O₂ production.

3.8.2.3. Catalysts

Fig. 3.37. – N₂O pulse at (a) 523 K and (b) 973 K for 0.5 wt % Rh/TiO₂ (SG).

For 0.5 wt % Rh/TiO₂ (SG), no adsorption or decomposition at 523 K was observed but significant adsorption at 973 K was noticed (see Figure 3.37(a)-(b)). This was consistent with the first step of the mechanism (see Chapter 7) [14, 16]. There was very little ½ O₂ production at 973K because the catalyst was already deactivating by this stage. Nevertheless, N₂O still seemed to be adsorbing on the surface.

Fig. 3.38. - N$_2$O pulse at (a) 523 K and (b) 973 K for 0.5 wt % Rh/TiO$_2$ (SG, IMP).

Here also the same observation was made as 0.5 wt % Rh/TiO$_2$ (SG) above (see Figure 3.37). The catalyst was deactivating at 973 K, hence there was limited N$_2$O adsorption.

Fig. 3.39. - N$_2$O pulse at (a) 523 K and (b) 973 K for 0.5 wt % Rh/TiO$_2$ (Degussa, P25).

No N$_2$O decomposition was seen at 523 K but significant N$_2$O adsorption and $\frac{1}{2}$ O$_2$ production was seen at 973 K (see Figure 3.39(a)-(b)). There was very little $\frac{1}{2}$ O$_2$ production because the catalyst was beginning to deactivate at that temperature, perhaps due to sintering.

Fig. 3.40. – N2O pulse at (a) 523 K and (b) 973 K for 5 wt % Rh/Al2O3 pellets (IMP).

Figure 3.40(a) and (b) also showed that there was no N2O decomposition at 523 K but N2O adsorption and ½ O2 production was noted at 973 K. There was little ½ O2 production due to deactivation.

Fig. 3.41. – N2O pulse at (a) 523 K and (b) 973 K for 5 wt % Rh/TiO2 (Degussa, P25).

Similarly, Figure 3.41(a) showed that there was no N2O adsorption or decomposition at 523 K but ½ O2 production was seen at 973 K with complete uptake of N2O at the surface (see Figure 3.41(b)). Despite deactivation at 973 K (see Figure 3.22), there was still activity perhaps due to more Rh available (since 5 wt % loading) even after sintering.

Table 3.7 shows a comparison of % N2O pulse decomposition and % ½ O2 production at 973 K over the final five catalysts.

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| Table 3.7 - %N₂O pulse decomposition and % V₂O₂ production at 973K over various catalysts |
|-----------------------------------------------|-------------------|------------------|
| Support                                      | % N₂O pulse decomposition | % V₂O₂ production |
| 0.5 wt % Rh/TiO₂ (SG)                        | 37±5              | 0                |
| 0.5 wt % Rh/TiO₂ (SG, IMP)                   | 15±5              | 0                |
| 0.5 wt % Rh/TiO₂ (Degussa, P25)              | 55±5              | 40±5             |
| 5 wt % Rh/Al₂O₃ pellets (IMP)                 | 50±5              | 25±5             |
| 5 wt % Rh/TiO₂ (Degussa, P25)                | 97±3              | 38±5             |

% N₂O pulse decomposition and % V₂O₂ pulse production in the N₂O pulse were worked out in terms of peak heights and areas in relation to those obtained for the respective bypass data.

5 wt % Rh/TiO₂ (Degussa, P25) catalyst was most impressive in terms of decomposing 97±3 % N₂O and producing 38±5 % V₂O₂. Both 0.5 wt % Rh/TiO₂ (SG) and 0.5 wt % Rh/TiO₂ (SG, IMP) catalysts decomposed N₂O moderately but produced no V₂O₂. The order of activity was therefore:

5 wt % Rh/TiO₂ (Degussa, P25) > 0.5 wt % Rh/TiO₂ (Degussa, P25) > 5 wt % Rh/Al₂O₃ pellets (IMP) > 0.5 wt % Rh/TiO₂ (SG) > 0.5 wt % Rh/TiO₂ (SG, IMP).

These results were in general agreement with TP work except that here 5 wt % Rh/TiO₂ (Degussa, P25) was the best catalyst but 0.5 wt % Rh/TiO₂ (Degussa, P25) was the best in TP work.

3.8.3. Independent results by SSTL

Now the independent work by SSTL is considered. These experiments were carried out as explained in section 3.5.4. SSTL used the Shell 405 catalyst and the 5 wt % Rh/Al₂O₃ pellets (IMP) catalyst in their prototype thruster to test the extent of decomposition. The results are shown in Figures 3.42 and 3.43. 5 wt % Rh/Al₂O₃ pellets (IMP) was used by SSTL in their prototype thruster and was able to be used successfully twice and surprisingly retained a significant amount of Rh on the surface (see SEM/EDAX in Chapter 6). It was also used the third time (see SEMs in Chapter 6 for variance in surface morphology) to achieve the required temperature for N₂O decomposition but took twice as long, and hence was less successful. The colour


Shell 405 cat.

Fig. 3.42(a).

5% Rh cat, Uni. Surrey

Fig. 3.42. (a). Shell 405 showed effective decomposition, but initial run on 5 wt % Rh/Al₂O₃ [Fig. 3.42. (b)] was unsuccessful.
Fig. 3.43 (a), (b) and (c) – showing three subsequent runs on 5 wt. % Rh/Al₂O₃. Each time the activity is retained, but takes slightly longer in each case to achieve the same level of activity i.e. deactivating slowly. The yellow lines show the extent to which the decomposition occurs after the heater is switched off.

changed from red to orange to white on progressive use in the thrusters. In comparison, the conventional Shell 405 loses most surface Ir (see SEMs in Chapter 6), perhaps from sintering. 36 wt % Ir on the surface for a short lifetime can be very costly in the long term. Rh however may be expensive, but in the long term, that can be compensated for since it was proven to be used more than once successfully in an independent SSTL thruster. Its effectiveness has been separately proven on the current rig system in chemistry (see Figure 3.21 and Table 3.2).

The TP continuous work was complementary to SSTL’s approach in the sense that no pulses are used and the N₂O continuously exists in the reaction stream as the temperature is raised. In SSTL’s case the temperature was first raised and then the N₂O was introduced into the thruster at a steady flow rate (i.e. “N₂O flow start”), and eventually switched off (“N₂O purge”). This compares to the pulse work in the sense that a large pulse of N₂O is introduced at an elevated temperature. The errors associated with this approach are larger than the author’s pulse work. This is because SSTL, in principle, had an engineering approach that was semi-quantitative but the author had a chemical approach that was quantitative.

3.10. Results summary 1:

In terms of activity, for N₂O decomposition (where > = more active than, therefore better than):

\[
0.5 \text{ wt } \% \text{ Rh/TiO}_2 \text{ (SG)} > 0.5 \text{ wt } \% \text{ Rh/SiO}_2 \text{ (SG)} > 0.5 \text{ wt } \% \text{ Rh/SiO}_2-\text{TiO}_2 \text{ (SG)}
\]
\[
0.5 \text{ wt } \% \text{ Ni/TiO}_2 \text{ (SG)} > 0.5 \text{ wt } \% \text{ Ni/SiO}_2 \text{ (SG)} > 0.5 \text{ wt } \% \text{ Ni/SiO-TiO}_2 \text{ (SG)}
\]
and
\[
0.5 \text{ wt } \% \text{ Rh/TiO}_2 \text{ (SG)} > 0.5 \text{ wt } \% \text{ Ni/TiO}_2 \text{ (SG)} > \text{ TiO}_2 \text{ (SG)}
\]

In terms of supports:

\[
\text{TiO}_2 \text{ (SG)} > \text{SiO}_2-\text{TiO}_2 \text{ (SG)} > \text{SiO}_2 \text{ (SG)} \text{ and hence } \text{TiO}_2 \text{ (SG)} \text{ can be used as a good support due to its strong metal-support interaction (SMSI) which enhances the activity and hence facilitates the reaction.}
\]
In collaboration with SSTL and the results above inspired the preparation of the catalyst preparations described in Chapter 2. 0.5 wt % Rh/TiO₂ (SG) was therefore justified to be used as a basis for further preparations.

3.11. Results summary 2:

In terms of removal of a prominent GHG (weight for weight %) 0.5 wt % Rh/TiO₂ (Degussa, P25) catalyst is the best catalyst for N₂O decomposition. This is because it is effective at relatively low temperatures (from 680 K). All other catalysts with similar Rh loading become active at considerably higher temperatures. It also has a very favourable Eₐ (127± 4.4 kJmol⁻¹ for ½ O₂ production and only 69.6± 2.4 kJmol⁻¹ for N₂O decomposition; (see Table 3.5 and Figures 3.28-3.29). This is much lower than the typical literature value of 245-264 kJmol⁻¹ [15]. It was also shown that 85± 3 % N₂O is converted and 80± 3 % ½O₂ is produced at 1000 K (see Table 3.5)). Furthermore 25 % N₂O decomposition occurs at 730± 10 K over this catalyst. Table 3.8 shows temperatures at which 25 % N₂O decomposition occurs for other catalysts, and also the minimum temperature at which a particular catalyst becomes active. Two SSTL runs are also shown for completion.

Table 3.8. – T (25 % N₂O decomposition) and T(min.) for various catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T (K)_{25 % N₂O}</th>
<th>T (K)_{min}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 wt % Rh/TiO₂ (SG)</td>
<td>740±10</td>
<td>650±10</td>
</tr>
<tr>
<td>0.5 wt % Rh/TiO₂ (SG IMP)</td>
<td>830±10</td>
<td>790±10</td>
</tr>
<tr>
<td>0.5 wt % Rh/TiO₂ (Degussa, P25)</td>
<td>730±10</td>
<td>590±10</td>
</tr>
<tr>
<td>0.5 wt % Rh/TiO₂ (SG-80%)/Al₂O₃ (CF)</td>
<td>850±10</td>
<td>830±10</td>
</tr>
<tr>
<td>V-Rh/Al₂O₃</td>
<td>680±10</td>
<td>640±10</td>
</tr>
<tr>
<td>commercial Shell 405</td>
<td>630±10</td>
<td>590±10</td>
</tr>
<tr>
<td>5 wt % Rh/Al₂O₃ pellets (IMP)</td>
<td>700±10</td>
<td>620±10</td>
</tr>
<tr>
<td>5wt % Rh/TiO₂ (Degussa, P25)</td>
<td>640±10</td>
<td>590±10</td>
</tr>
<tr>
<td>SSTL – Shell 405</td>
<td>573±30</td>
<td></td>
</tr>
<tr>
<td>SSTL – 5wt % Rh/Al₂O₃ pellets (IMP)</td>
<td>973±30</td>
<td></td>
</tr>
</tbody>
</table>

In terms of the temperature required to reach 25 % N₂O decomposition (T (K)_{25 \% N₂O}) and the minimum temperature required to activate the catalysts (T (K)_{min}), Table 3.8 suggests that the activity order is:

Commercial Shell 405 > 5 wt % Rh/TiO$_2$ (Degussa, P25) > 5 wt % Rh/Al$_2$O$_3$ pellets (IMP) > V-Rh/Al$_2$O$_3$ > 0.5 wt % Rh/TiO$_2$ (Degussa, P25) > 0.5 wt % Rh/TiO$_2$ (SG > 0.5 wt % Rh/TiO$_2$ (SG IMP) > 0.5 wt % Rh/TiO$_2$ (SG-80%)/Al$_2$O$_3$ (CF).

However the overall order of activity (taking into account % N$_2$O conversion at 1000K, $E_a$, $T_{25\%}$ N$_2$O and $T_{\text{min}}$) seems to be:

0.5 wt % Rh/TiO$_2$ (Degussa, P25) > 5wt % Rh/TiO$_2$ (Degussa, P25) > commercial Shell 405 > 5 wt % Rh/Al$_2$O$_3$ pellets (IMP) > 0.5 wt % Rh/TiO$_2$ (SG-80%)/Al$_2$O$_3$ (CF) > 0.5 wt % Rh/TiO$_2$ (SG) > 0.5 wt % Rh/TiO$_2$ (SG IMP) > V-Rh/Al$_2$O$_3$.

For the applications of decomposing N$_2$O as a fuel for satellite microthrusters, 5 wt % Rh/Al$_2$O$_3$ pellets (IMP) has been shown (on a % weight to weight basis) to compare favourably with Shell 405. Independent testing on a SSTL prototype thruster (see section 3.9) has confirmed that supported Rh can be retained for 3 uses (before regeneration) as compared to only once for Ir. As mentioned in Chapter 1 satellites use N$_2$O as fuel for orbital manoeuvring. They need to use the fuel quickly to generate the required energy for the motion. The lower the temperature at which this begins the better because the energy is released quicker. Once generated, the energy must be sustained (see section 3.9). The minimum temperature of activation for commercial Shell 405 was found to be 590± 10 K (by the author) and 573± 30 K (independently by SSTL). The corresponding values for 5 wt % Rh/Al$_2$O$_3$ pellets (IMP) catalyst were 620± 10 K and 973± 30 K respectively (see Table 3.8). Therefore despite Rh (from 5 wt % Rh/Al$_2$O$_3$ pellets (IMP) catalyst) being retained for 3 uses, commercial Shell 405 activated at the lowest temperature and provided the required energy at the expense of Ir volatilising from the catalyst surface. This aspect will be returned to in the conclusions of the thesis (see Chapter 7). Pulse work was therefore ideal in this context because satellites require occasional power for orbital manoeuvring. Most of the time is spent orbiting above the Earth’s atmosphere, but N$_2$O pulse is required (as described in section 3.9) to provide the necessary fuel and energy to help it to move. N$_2$O pulse work therefore has a very important application in this area. The TP continuous work complemented this (see section 3.9).
3.12. Conclusions

Rh/TiO$_2$ (SG) was found to have more activity than Rh/SiO$_2$ (SG) and Rh/SiO$_2$-TiO$_2$ (SG) in terms of N$_2$O decomposition. This important finding hence led to the catalyst development by making various modifications based on the original 0.5 wt. % Rh/TiO$_2$ (SG) prepared by the acid catalysed sol-gel route. These included corresponding preparations for Rh impregnations using TiO$_2$ (Degussa, P25) and Al$_2$O$_3$ pellets (which was compared to the Shell 405). These newly developed materials were subsequently used in this context and the dry reforming of methane reaction (see Chapter 4).

It was also found that Rh upon TiO$_2$ (Degussa, P25) based catalysts were the most effective for the decomposition of N$_2$O. This served the purpose of reducing GHGs and as a mono-propellant for satellite microthrusters; even as far as being a competitor of commercial Shell 405. 5 wt % Rh/Al$_2$O$_3$ pellets (IMP) catalyst compared favourably with commercial Shell 405. Finally, SSTL’s N$_2$O pulse approach was similar to the author’s pulse work, and the TP work was not comparable but complemented their approach.

3.13. References


CHAPTER IV

Catalysis II : Dry reforming of methane

4.1. Introduction

Dry reforming of methane was justified in Chapter 1 as being a convenient means by which to reduce the environmental impact of two major GHGs i.e. CO₂ and CH₄.

The experimental set up and results obtained are linked through the strategy:

i) developing the experimental methodology using traditional catalysts.
ii) optimising catalysts using TP continuous and pulse analysis.

4.2. Types of experiments

TP (temperature-programmed) continuous experiments showed in real time when and to what extent the reaction occurred as a function of temperature in terms of CO₂/CH₄ consumption, rates of CO/H₂ production, activation energies, Eₐ (see Chapter 2) and deactivation. Pulse experiments (see Chapter 3) were also useful as they provided information relating to the mechanisms of the reaction.

4.3. Experimental rig design

The experimental set-up was the same as in the case of N₂O decomposition experiments, except that the reactant gases used were CO₂ and CH₄. The experimental rig system was described in Chapter 3 and Appendix II (see Chapter 8) but two other external analysers (CO NDIR analyser and FID-GC (see below)) were also used.

Here, MnOₓ/Celite trap was used as described in Chapter 3. In this case, its use was even more important since O₂ in the stream could severely interfere with the reaction (see Chapter 7).
4. Catalysis II: Dry reforming of methane.

4.4. Gases

During the experiments the gases that were used were Ar (neat) as the carrier gas (80±1 cm$^3$ min$^{-1}$), CO$_2$ ((10 % in Ar) 20±1 cm$^3$ min$^{-1}$)) and CH$_4$ ((10% in Ar) 20±1 cm$^3$ min$^{-1}$)) for TP experiments. Pulse work required an Ar flow as above into which CO$_2$ pulses of 0.1±0.001 cm$^3$ (2.24 mmol) and CH$_4$ (10 % in Ar) pulses of 1.0±0.005 cm$^3$ (2.24 mmol) at 523 K and 973 K. Pure H$_2$ was also used as pre-reductant (50±1 cm$^3$ min$^{-1}$).

4.5. Materials

The materials used were the existing catalysts and the final five catalysts selected as a result of N$_2$O decomposition work (see Chapter 3) and their corresponding supports. Shell 405 did not show any activity during the pulse work for this reaction, and hence it was not explored here any further. The supports were: TiO$_2$ (SG) (0.0521 g, 652 µmol), TiO$_2$ (Degussa, P25) (0.0565 g, 707 µmol), Al$_2$O$_3$ pellets (CONDEA) (0.2150 g, 2.11 mmol), the existing catalysts: 0.5 wt % Rh/SiO$_2$ (SG) (0.0521 g, 2.53 µmol. Rh cat.), 0.5 wt % Ru/SiO$_2$ (SG) (0.0521 g, 2.58 µmol. Ru cat.) and 0.5 wt % Ir/SiO$_2$ (SG) (0.0523 g, 1.46 µmol. Ir cat.) and the Rh catalysts that were active in N$_2$O decomposition: 0.5 wt % Rh/TiO$_2$ (SG) (0.0590 g, 2.87 µmol. Rh cat.); and the modified Rh/TiO$_2$ samples: 0.5 wt % Rh/TiO$_2$ (SG IMP) (0.0575, 2.79 µmol. Rh cat.), 0.5 wt % Rh/TiO$_2$ (Degussa, P25, IMP) (0.0656 g, 3.19 µmol. Rh cat.), 5 wt % Rh/Al$_2$O$_3$ pellets (IMP) (0.0526 g, 25.6 µmol. Rh cat.) and 5 wt % Rh/TiO$_2$ (Degussa, P25, IMP) (0.0508 g, 24.7 µmol. Rh cat.).

4.6. Conditions

As described in Chapter 3, the catalyst/support (0.05g, either 0.5 or 5 wt. % loading) was placed on the catalyst bed in the fused silica reactor (volume = 20 cm$^3$) containing silica wool. The sample was pre-reduced with H$_2$ up to 723 K. The carrier gas was Ar (neat) (80±1 cm$^3$ min$^{-1}$) and depending on the nature of the experiment i.e. pulse or TP continuous the appropriate method of analysis was used (see section 4.7.1-2).
Figure 4.1 shows the overall experimental scheme.

The region marked $\alpha$-$\beta$ indicates the period of the low temperature pulsing, typically at 523 K. Initially, a blank run was performed by switching the rig from reaction stream through the reactor to the bypass (see Appendix II). The pulse work for the decomposition of $\text{N}_2\text{O}$ was also done at these temperatures, but the results are shown in Chapter 3. For the bypass, the pulse work was as follows: two $\text{N}_2\text{O}$ pulses, two $\text{CO}_2$ pulses and two $\text{CH}_4$ pulses. This procedure was followed to ensure that the duplicate pulses were repeatable and reproducible. On other occasions the pulses were as follows: two $\text{N}_2\text{O}$ pulses, $\text{CO}_2$ pulse, $\text{CH}_4$ pulse, $\text{CO}_2$ pulse and a $\text{CH}_4$ pulse. This was to ensure that the $\text{CO}_2$ and $\text{CH}_4$ pulses in particular were alternating because the mechanism requires this (see Chapter 7). This latter pulse scheme was important since it provided evidence as to what (if any) particular mechanism was being followed. During this phase, only specific RGA $m/e$ values (see section 4.10.1) were used to detect the products coming off and the reactant consumption. Ar (neat, $80\pm1\text{ cm}^3\text{min}^{-1}$) was used as the carrier gas in all cases.

$\beta$-$\gamma$ indicates the TP region. The reactant gases $\text{CO}_2$ and $\text{CH}_4$ are carried in a continuous mode to the catalyst in Ar carrier gas. The RGA, CO *non-dispersive infrared* (NDIR) analyser and flame ionising detector–gas chromatography (FID-GC) (see section 4.10) were used to monitor the exit gases.
4. Catalysis II : Dry reforming of methane.

\( \gamma-\delta \) indicates the region of pulse work at high temperature, typically 973 K. The pulse work is carried out as described above (region \( \alpha-\beta \) and section 4.6.3).

4.6.1. Pre-treatment

The samples experienced the same pre-treatment conditions as explained in Chapter 3.

4.6.2. TP Continuous

This involved the \( \text{CO}_2 \) (10 % in Ar) (20±1 cm\(^3\) min\(^{-1}\)), \( \text{CH}_4 \) (10 % in Ar) (20±1 cm\(^3\) min\(^{-1}\)) and Ar (neat, 80±1 cm\(^3\) min\(^{-1}\)) stream to be continuously monitored by the RGA (see section 4.10.1 for m/e values used). This was followed by analysis of the supports and catalysts in a TP continuous mode as the temperature was increased from 523 K to 973 K (following Method of Analysis A below). The experiment was terminated but the stream was switched to bypass to check the observations were real.

4.6.3. Pulse methods

In this case, the experiment was performed isothermally first at 523±20 K and then again at 973±50 K at a pressure of 101.3 kPa. It also involved the use of a continuous flow of Ar (neat, 100±1 cm\(^3\) min\(^{-1}\)) as the carrier gas with 1:1 \( \text{CO}_2 \) (neat, 0.1 cm\(^3\), 2.24 mmol) and \( \text{CH}_4 \) (10 % in Ar, 1.0 cm\(^3\), 2.24 mmol) alternating pulses (initially as blanks) to show experimental reproducibility. This was followed by at least two cycles of \( \text{CO}_2 \) and \( \text{CH}_4 \) alternating pulses at each temperature following Method of Analysis B (see section 4.7.2). Therefore, the number of moles of reactive gas per mole of Rh in Rh/TiO\(_2\) in either \( \text{CO}_2 \) or \( \text{CH}_4 \) pulse was \( n_{\text{CO}_2}/n_{\text{Rh}} = n_{\text{CH}_4}/n_{\text{Rh}} = 2.24/2.87 \times 10^{-3} \).
4.7. Data Acquisition

4.7.1. Method of analysis A

**Procedure for continuous catalysis: TP dry reforming of methane**

1) The catalyst was reduced (plus MnO\textsubscript{x} trap) with pre-reductant H\textsubscript{2} at 723 K for about 1 h. The RGA capillary was removed from the reaction stream, otherwise the RGA will be affected and hence data output will not make sense.

2) The Ar and CH\textsubscript{4} bypass was switched on for FID-GC calibration

3) The Ar bypass was switched on for about 10 min and allowed to stabilize.

4) At least three pulses were taken for FID-GC for consistent on-line bypass response.

5) The reaction stream was switched from bypass to reaction stream and left for 20 min flushing, or until the CO\textsubscript{2} levels (for example) were as close as possible to the bypass level.

6) After 20 min, data acquisition via CO/CO\textsubscript{2} analysis (computer controlled via "Pico-log" software) was started, and the FID injections and reaction monitored whilst temperature-programmed up to about 973 K.

7) The reaction stream was switched to bypass and FID-GC injections were checked for reproducibility.

These steps were carefully followed for both blank, support and catalyst runs to obtain information regarding mechanisms, activity, reactant consumption and product formation (see results in *section 4.10.2* and *Chapter 7*).

4.7.2. Method of analysis B

**The procedure for the isothermal alternating pulses of CO\textsubscript{2} (neat) and CH\textsubscript{4} (10 % in Ar)**

1) The catalyst was pre-reduced with H\textsubscript{2} at 723 K for about 1 h . Care had to be taken to remove the RGA capillary from the reaction stream, otherwise the RGA would have been affected.
2) Ar was switched on bypass for 10 min flushing. The RGA capillary was reattached.

3) The reaction stream was switched on and left to stabilise for 10 min.

4) Data acquisition was allowed to start on the RGA.

5) Two cycles of alternating CO$_2$/CH$_4$ pulses were undertaken for a blank reactor and a reaction. This was compared with the bypass.

6) The data was recorded as:

<table>
<thead>
<tr>
<th>t(min)</th>
<th>t(s)</th>
<th>$t_{max}$</th>
<th>$t/t_{max}$</th>
</tr>
</thead>
</table>

special note was taken care of $t_{max}$ (i.e. the time it takes from $t_{inj}$ to the time of maximum RGA response).

It is worth noting that just the RGA was sufficient in this case. These results gave information regarding the reaction mechanisms (see Chapter 7).

4.8. Initial experiments

Initial dry reforming runs were performed in a pulse mode (using Method of Analysis B from section 4.7.2) on three existing acid-catalysed sol-gel samples which were previously prepared (i.e. Rh/SiO$_2$, Ru/SiO$_2$ and Ir/SiO$_2$). This initial experiment was designed to find out which catalytic system to eventually concentrate on and hence develop further. Results are shown in section 4.10.1.

4.9. Instrumental methods

4.9.1. The RGA-MS

As explained in Chapter 3, the analysis was carried out using an "ESS VG Quadrupole, Sensorlab" Residual Gas Analyser (RGA) with a built-in mass spectrometer. The operating procedure was exactly the same except it was looking for the following $m/e$ values: 44 (CO$_2$), 16 (CH$_4$), 28 (CO), 2 (H$_2$), 32 (O$_2$) and 40 (Ar) for continuous TP and pulse work. Prior to this, the RGA calibration was performed by pulse injections on the four gases used for or produced by dry reforming: CO$_2$, CH$_4$, CO and H$_2$ (see Figures 4.2-5 below). During the development stage, dry
reforming was carried out on existing catalysts and related work e.g. propane hydrogenolysis work [1] (see Appendix I in Chapter 9).

Fig. 4.2. - CO$_2$ calibration of RGA

Fig 4.3. – CH$_4$ calibration of RGA
4. Catalysis II: Dry reforming of methane.

Fig. 4.4. – CO calibration of RGA

Fig. 4.5. – H₂ calibration of RGA
4.9.2. Flame Ionising Detector – Gas Chromatography (FID-GC)

This is one of the most widely used analytical techniques for the speciation and quantification of organic compounds. The gas chromatograph consists of a flowing mobile phase, an injection port, a separation column containing the stationary phase, and a flame ionising detector. The organic compounds are separated into their component compounds due to their partitioning behaviour (or the unique affinity for the stationary phase) between the mobile gas phase and the stationary phase in the column. Mobile phases or carrier gases are usually inert gases such as nitrogen, helium or argon. In this particular case, nitrogen was used. The injection port consists of a septum through which a syringe needle is inserted to inject the sample. The injection port is deliberately maintained at a higher temperature than the boiling point of the least volatile component in the sample mixture. Since the partitioning behaviour is dependent on temperature, the separation column is usually contained in a thermostat-controlled oven.

The components appear separately at the effluent end of the column, where they can be detected. The detector gives a signal (in peak form) for each separated component compound, and the intensity of the signal is proportional to the quantity of the compound injected, and hence it is possible to provide a quantitative analysis by calibration. The instrument used was a “Perkin Elmer” FID-GC, model 8500 fitted with a Porapak Q column (80-100 mesh) and was operational at 473 K, which was within the manufacturers maximum temperature limit of 523 K. Figure 4.6 below shows a schematic diagram of the different parts of a typical GC instrument and Figure 4.7 shows a cross-sectional view of a flame ionising detector (FID). The analyte gas is burnt in an inert carrier gas (i.e. N₂ in this case) with H₂/air flame. The H₂ and air pressures were 120 kPa and 130 kPa respectively. The analyte gas containing a hydrocarbon was therefore ionised and these ions migrated to the collector via an electric field. The output was registered on an integrator (Spectra Physics integrator; model SP4290) with a setting of 1000 ±5 mV and the signal was plotted as an integral of the peak area.
The GC was used to monitor the consumption and release of CH\textsubscript{4} (in particular) during the TP continuous dry reforming reaction. Pulses (0.1 ± 0.001 cm\textsuperscript{3}) were taken every minute using a Hamilton gas-tight syringe (model 1800) during the blank run. These were compared during the TP stage of the experiment to see how the reaction was progressing. The retention time (R\textsubscript{t}) for CH\textsubscript{4} was on average 0.29 min which was in excellent agreement with the literature value [2]. The FID-GC was calibrated and showed good reproducibility and linearity (see Figure 4.8 below).

Fig. 4.6. - Schematic diagram of a gas chromatograph.

Fig. 4.7. - Cross section of a FID (Courtesy of Hewlett-Packard Co.) [3].
4. Catalysis II: Dry reforming of methane.

Fig 4.8. - CH$_4$ calibration of FID-GC

The results obtained from it were very reliable as the amount of CH$_4$ detected during the course of a TP continuous dry reforming run were in very good agreement with the RGA results. As an example, a result is shown for % CH$_4$ unreacted as a function of temperature (K) over 5 wt % Rh/Al$_2$O$_3$ pellets. This closely matched the results obtained from the RGA (see Figure 4.19(a)).

Fig. 4.9. - % CH$_4$ unreacted over 5 wt. % Rh/Al$_2$O$_3$ pellets during TP continuous dry reforming as measured on the FID-GC.
A ratio between the % CH$_4$ consumption at 973 K to % CH$_4$ consumption at 523 K was determined, and hence a comparison was drawn between the RGA results and FID-GC results. In the case of the above the ratio ($P_{\text{CH}_4}\text{(RGA)}$ at 973 K / $P_{\text{CH}_4}\text{(RGA)}$ at 523 K) was 0.2±0.05 and the ratio ($P_{\text{CH}_4}\text{(FID-GC)}$ at 973 K / $P_{\text{CH}_4}\text{(FID-GC)}$ at 523 K) also was 0.2±0.05. The independent instruments therefore gave results in close agreement. Similar comparisons were made for the CO ratios between the RGA and CO analyser.

4.9.3. NDIR CO analyser

The CO (MIRA, Analysis Automation Ltd., NDIR analyser 401) analyser measured CO levels in the stream and was PC controlled (pico-log). It was operated with Ar passing through as the carrier gas. CO molecule shows infra red activity (see Chapter 6) and hence it is possible to determine as to what extent the reaction was occurring.

A description of infrared (IR) activity and the CO structure is in Chapter 6. The CO analyser detects absorptions characteristic of the CO stretch at 2143 cm$^{-1}$ [4]. Hence the amount of CO produced during a TP continuous run was monitored.

The CO analyser showed very good reproducibility and linearity in calibration; plots of volume introduced against response were straight lines going through the origin.

![CO calibration of NDIR analyser](image-url)
4. Catalysis II : Dry reforming of methane.

4.10. Results 1

4.10.1. Preliminary results

As explained in section 4.8 above, initial pulse experiments were conducted on existing catalysts to develop the experimental methodology. The results showed that there wasn’t anything particularly interesting during the CO\(_2\) pulse, but there was significant H\(_2\) production for the CH\(_4\) pulse especially in the case of Rh/SiO\(_2\):

![Graph showing H\(_2\) production during CH\(_4\) pulse](image)

**Fig. 4.11** – H\(_2\) production during CH\(_4\) pulse

It is worth noting that in this preliminary phase there was little CO production seen, perhaps due to the need for better experimental design at that time e.g. no CO NDIR analyser was used at that early stage.

The trend in H\(_2\) production was:

\[
\text{Rh/SiO}_2 \gg \gg \text{Ru/SiO}_2 > \text{Ir/SiO}_2 > \text{blank}
\]
Nevertheless, this was a significant result as it provided evidence and justification to pursue the Rh/SiO₂ catalyst further. The Ru/SiO₂ and Ir/SiO₂ in this regard were not as interesting in the present context and hence not used further. As shown in the last chapter, Rh/TiO₂ was shown to be even more promising and so effort was concentrated on this. Ni catalysts were not pursued any further in this regard.

4.10.2. TP-Continuous Results

The results are shown for CO₂/CH₄ consumption and H₂/CO production in each case. The blank reactor is shown first followed by the results for the lone supports and finally those of the catalysts. In terms of CO₂/CH₄ conversion 0.01 atmospheres is 0% conversion tending to 100% conversion towards 0 atmospheres. Conversely, in terms of CO and H₂ production 0 atmospheres is 0% production and 0.02 (since 1:2 stoichiometric ratio) atmospheres is 100% production. Pulse results are considered in section 4.12.

4.10.2.1. Blank reactor

The extent of reaction in the blank reactor was first considered:

Fig. 4.12(a). - TP dry reforming attempted in the blank reactor.
4. Catalysis II: Dry reforming of methane.

Clearly the blank reactor was inactive in converting CO\(_2\) and CH\(_4\) or producing CO and H\(_2\). Thus, Figure 4.12(a) shows TP dry reforming attempted in the blank reactor for CO\(_2\) and CH\(_4\) conversion, where the ratio P\(_{CH4}(RGA)\) at 973 K / P\(_{CH4}(RGA)\) at 523 K was 1.00± 0.01 and P\(_{CH4}(FID-GC)\) at 973 K / P\(_{CH4}(FID-GC)\) at 523 K was 1.00± 0.01. Figure 4.12(b) shows TP dry reforming through blank reactor for CO and H\(_2\) production; where P\(_{CO}(RGA)\) at 973 K / P\(_{CO}(RGA)\) at 523 K was 1.00± 0.01 and P\(_{CO}(NDIR)\) at 973 K / P\(_{CO}(NDIR)\) at 523 K was also 1.00± 0.01.

4.10.2.2. Supports:

The results for the supports alone are now considered. They are TiO\(_2\) (SG), TiO\(_2\) (Degussa, P25) and Al\(_2\)O\(_3\) pellets (2.5 mm diameter).
4. Catalysis II: Dry reforming of methane.

Fig. 4.13(a). - TP dry reforming over TiO$_2$ (SG) alone.

Fig. 4.13(b). - TP dry reforming over TiO$_2$ (SG).
4. Catalysis II: Dry reforming of methane.

Fig. 4.14(a) – TP dry reforming over TiO$_2$ (Degussa, P25).

Fig. 4.14(b) – TP dry reforming over TiO$_2$ (Degussa, P25)
4. Catalysis II: Dry reforming of methane.

Fig. 4.15(a). – TP dry reforming over Al₂O₃ pellets (2.5 mm diameter)

TiO₂ (SG) shows some activity for CO₂ adsorption above 800 K (see Figure 4.13(a)) but no CO and H₂ production (see Figure 4.13(b)). The ratio P_{CH₄}(RGA) at 973 K / P_{CH₄}(RGA) at 523 K was 0.90± 0.01 and P_{CH₄}(FID-GC) at 973 K / P_{CH₄}(FID-GC) at...
523 K was 0.90± 0.01. Similarly Figure 4.13(b) shows no CO production with the ratio \( P_{CO}(RGA) \) at 973 K / \( P_{CO}(RGA) \) at 523 K being 1.00± 0.01 and \( P_{CO}(NDIR) \) at 973 K / \( P_{CO}(NDIR) \) at 523 K was also 1.00± 0.01. TiO\(_2\) (Degussa, P25) shows unusual activity for CH\(_4\) consumption (see Figure 4.14(a)) and slight CO and H\(_2\) production at very high temperatures (see Figure 4.14(b)). The ratio \( P_{CH4}(RGA) \) at 973 K / \( P_{CH4}(RGA) \) at 523 K was 0.55± 0.01 and \( P_{CH4}(FID-GC) \) at 973 K / \( P_{CH4}(FID-GC) \) at 523 K was 0.50± 0.01. For CO production the ratio \( P_{CO}(RGA) \) at 973 K / \( P_{CO}(RGA) \) at 523 K was 1.00± 0.01 and \( P_{CO}(NDIR) \) at 973 K / \( P_{CO}(NDIR) \) at 523 K was also 1.00± 0.01. Al\(_2\)O\(_3\) pellets allows slight CO\(_2\) adsorption as temperature increases (see Figure 4.15(a)) but no CO and H\(_2\) production was observed (see Figure 4.15(b)). The ratio \( P_{CH4}(RGA) \) at 973 K / \( P_{CH4}(RGA) \) at 523 K was 1.00± 0.01 and \( P_{CH4}(FID-GC) \) at 973 K / \( P_{CH4}(FID-GC) \) at 523 K was 1.00± 0.01. For CO production the ratio \( P_{CO}(RGA) \) at 973 K / \( P_{CO}(RGA) \) at 523 K was 1±0.01 and \( P_{CO}(NDIR) \) at 973 K / \( P_{CO}(NDIR) \) at 523 K was also 1.00± 0.01. Table 4.1 shows % CO\(_2\) and % CH\(_4\) conversion together with % H\(_2\) and % CO production at 973 K for selected supports.

<table>
<thead>
<tr>
<th>Support</th>
<th>% CO(_2)</th>
<th>% CH(_4)</th>
<th>% H(_2)</th>
<th>% CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2) (SG)</td>
<td>5± 5</td>
<td>10± 3</td>
<td>3± 3</td>
<td>3± 3</td>
</tr>
<tr>
<td>TiO(_2) (Degussa, P25)</td>
<td>5± 5</td>
<td>40± 5</td>
<td>5± 3</td>
<td>5± 3</td>
</tr>
<tr>
<td>Al(_2)O(_3) pellets</td>
<td>22± 5</td>
<td>5± 5</td>
<td>5± 5</td>
<td>5± 5</td>
</tr>
</tbody>
</table>


4.10.2.3. Catalysts:

Section 4.10.1 showed that existing Rh/SiO\(_2\) was the most active catalyst in dry reforming out of Rh/SiO\(_2\), Ru/SiO\(_2\) and Ir/SiO\(_2\). Hence, investigations on Ru/SiO\(_2\) and Ir/SiO\(_2\) was not pursued further. Early TP continuous N\(_2\)O decomposition runs on 0.5 wt % Rh/SiO\(_2\) (SG) and 0.5 wt % Rh/SiO\(_2\)-TiO\(_2\) (SG) did not show any appreciable activity, but 0.5 wt % Rh/TiO\(_2\) (SG) showed marked activity (see Chapter 3). This was therefore a catalyst of immense interest. TiO\(_2\) appears to aid in the decomposition...
process and this is perhaps due to its strong metal-support interaction (SMSI) [5]. This significant result provided the basis for further development, modification and preparation of modified Rh/TiO$_2$ catalysts (see Chapter 2).

Fig. 4.16(a). – TP dry reforming over 0.5 wt. % Rh/TiO$_2$ (SG).

Fig. 4.16(b). – TP dry reforming over 0.5 wt. % Rh/TiO$_2$ (SG).
4. Catalysis II : Dry reforming of methane.

Fig. 4.17(a). – TP dry reforming over 0.5 wt. % Rh/TiO$_2$ (SG IMP).

Fig. 4.17(b). – TP dry reforming over 0.5 wt. % Rh/TiO$_2$ (SG IMP).
4. Catalysis II: Dry reforming of methane.

Fig. 4.18(a). – TP dry reforming over 0.5 wt. % Rh/TiO₂ (Degussa, P25).

Fig. 4.18(b). – TP dry reforming over 0.5 wt. % Rh/TiO₂ (Degussa, P25).

5 wt % Rh/Al₂O₃ pellets (IMP) and 5 wt % Rh/TiO₂ (Degussa, P25, IMP) were prepared (see Chapters 2 and 3) in order to compare with Shell 405 for the decomposition of nitrous oxide. It is used here however for dry reforming as a comparison to the Rh/TiO₂ catalyst system and also as a comparison to the 0.5 wt % Rh loading on the support.

Fig. 4.19(a). – TP dry reforming over 5 wt % Rh/Al₂O₃ pellets (IMP).

Fig. 4.19(b). – TP dry reforming over 5 wt % Rh/Al₂O₃ pellets (IMP).
4. Catalysis II : Dry reforming of methane.

Fig. 4.20(a). – TP dry reforming over 5 wt. % Rh/TiO₂ pellets (Degussa, P25, IMP).

Fig. 4.20(b). – TP dry reforming over 5 wt. % Rh/TiO₂ pellets (Degussa, P25, IMP).
4. Catalysis II: Dry reforming of methane.

4.10.3. TP continuous observations

For 0.5 wt % Rh/TiO₂ (SG), the catalyst was active from 600 K but started to deactivate after 800 K (see Figures 4.16(a) and 4.16(b)). The α region showed no reaction until about 800 K (region β). There was CH₄ and CO₂ consumption as well as CO and H₂ production. Figure 4.16(a) shows CO₂ and CH₄ consumption where the ratio P(CH₄)(RGA) at 973 K / P(CH₄)(RGA) at 523 K was 0.45± 0.01 and P(CH₄)(FID-GC) at 973K / P(CH₄)(FID-GC) at 523 K was 0.50± 0.01. At 973 K there was 25±5 % CO₂ conversion and 55±5 % CH₄ conversion. 25 % CO₂ conversion occurred at 720±10 K and 25 % CH₄ conversion occurred at 740±10 K. Figure 4.16(b) shows TP dry reforming over ½ wt. % Rh/TiO₂ (SG) for CO and H₂ production. The ratio P(CO)(RGA) at 973 K / P(CO)(RGA) at 523 K was 31.00±0.1 and P(CO)(NDIR) at 973 K / P(CO)(NDIR) at 523 K was 30.00±0.1. At 973 K there was 75± 10 % H₂ production and 60± 7 % CO production. There was 25 % H₂ production at 630±10 K and 25 % CO production at 690±10 K.

For 0.5 wt % Rh/TiO₂ (SG, IMP), the catalyst was active after 600 K but rapidly deactivated after 850 K, probably due to structure collapse and sintering (see Figures 4.17(a) and 4.17(b)). Here also, the α region showed no reaction whereas the β region showed the release of products and consumption of reactants. Figure 4.17(a) shows CO₂ and CH₄ consumption where the ratio P(CH₄)(RGA) at 973 K / P(CH₄)(RGA) at 523 K was 0.55±0.01 and P(CH₄)(FID-GC) at 973 K / P(CH₄)(FID-GC) at 523 K was 0.55±0.01. At 973 K there was only 10±5 % CH₄ conversion and 30±5 % CO₂ conversion due to the effects of sintering at that temperature. There was 25 % CH₄ conversion at 820±10 K and 25 % CO₂ conversion at 740±10 K. Figure 4.17(b) shows CO and H₂ production where the ratio P(CO)(RGA) at 973 K / P(CO)(RGA) at 523 K was 33.0± 0.1 and P(CO)(NDIR) at 973 K / P(CO)(NDIR) at 523 K was 30.0± 0.1. At 973K there was only 10±5 % H₂ production and 5±5 % CO production due to deactivation above 875 K. 25 % H₂ production occurred at 560±10 K and there was 25 % CO production at 610±5 K.
4. Catalysis II: Dry reforming of methane.

In the case of 0.5 wt % Rh/TiO$_2$ (Degussa, P25, IMP), no dry reforming was observed because there was no CO$_2$ consumption and no CO production i.e. CO was retained on the surface (see Figures 4.18(a) and 4.18(b)). The most probable explanation is that CH$_4$ decomposition or partial oxidation reaction was observed (see Chapter 7).

\[ \text{C} + \text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \]

\[ \text{O} + \text{CH}_4 \rightarrow \text{CO} + 2\text{H}_2 (\Delta H_{298K} = -36 \text{kJmol}^{-1}) \]

Nevertheless, the α-β regions were observed. Figure 4.18(a) shows CO$_2$ and CH$_4$ consumption where the ratio $P_{\text{CH}_4}$(RGA) at 973 K / $P_{\text{CH}_4}$(RGA) at 523 K was 0.19±0.01 and $P_{\text{CH}_4}$(FID-GC) at 973K / $P_{\text{CH}_4}$(FID-GC) at 523 K was 0.20±0.01. At 973 K there was 92±5 % CH$_4$ conversion but no CO$_2$ conversion was observed. 25% CH$_4$ conversion occurred at 800±10 K and there was 25 % CO$_2$ conversion at 540±10 K. Figure 4.18(b) shows the corresponding CO and H$_2$ production where the ratio $P_{\text{CO}}$(RGA) at 973 K / $P_{\text{CO}}$(RGA) at 523 K was 1.00±0.01 and $P_{\text{CO}}$(NDIR) at 973K / $P_{\text{CO}}$(NDIR) at 523 K was also 1.00±0.01. At 973 K there was 65±10 % H$_2$ production but no CO production was seen. 25 % H$_2$ production was seen at 820±10 K but there was no corresponding CO production.

5 wt % Rh/Al$_2$O$_3$ (pellets, IMP) was active after 700 K and was stable with increasing temperature. Continuous CO/H$_2$ production and CO$_2$/CH$_4$ consumption was observed with no sign of deactivation throughout the temperature region (see Figures 4.19(a) and 4.19(b)). The α-β regions were again observed as described above. Figure 4.19(a) shows CO$_2$ and CH$_4$ consumption where the ratio $P_{\text{CH}_4}$(RGA) at 973 K / $P_{\text{CH}_4}$(RGA) at 523 K was 0.20±0.01 and $P_{\text{CH}_4}$(FID-GC) at 973 K / $P_{\text{CH}_4}$(FID-GC) at 523 K was also 0.20±0.01. At 973 K there was 60±5 % CH$_4$ conversion and 75±5 % CO$_2$ conversion. 25 % CH$_4$ conversion occurred at 690±10 K and there was 25±% CO$_2$ conversion at 580±10 K. Figure 4.19(b) shows CO and H$_2$ production where the ratio $P_{\text{CO}}$(RGA) at 973 K / $P_{\text{CO}}$(RGA) at 523 K was 22.0±0.1 and $P_{\text{CO}}$(NDIR) at 973 K / $P_{\text{CO}}$(NDIR) at 523 K was 25.0±0.1. At 973 K there was 80±5 % H$_2$ production and 30±5 % CO production. 25 % H$_2$ production occurred at 690±10 K and there was 25% CO production at 800±10 K.

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In the case of 5 wt % Rh/TiO\textsubscript{2} (Degussa, P25, IMP), the catalyst was active after 580K in terms of CO\textsubscript{2}/CH\textsubscript{4} consumption and CO/H\textsubscript{2} production, but it started to deactivate above 900 K (see Figures 4.20(a) and 4.20(b)). Here too the $\alpha$-$\beta$ regions were observed. Figure 4.20(a) shows CO\textsubscript{2} and CH\textsubscript{4} consumption where the ratio $P_{\text{CH}_4}(\text{RGA})$ at 973 K / $P_{\text{CH}_4}(\text{RGA})$ at 523 K was 0.25±0.01 and $P_{\text{CH}_4}(\text{FID-GC})$ at 973K / $P_{\text{CH}_4}(\text{FID-GC})$ at 523 K was also 0.25±0.01. At 973 K there was 90±3 % CO\textsubscript{2} conversion and 75±5 % CH\textsubscript{4} conversion. 25 % CO\textsubscript{2} conversion occurred at 710±10 K and there was 25 % CH\textsubscript{4} conversion at 650±10 K. Figure 4.20(b) shows CO and H\textsubscript{2} production where the ratio $P_{\text{CO}}(\text{RGA})$ at 973 K / $P_{\text{CO}}(\text{RGA})$ at 523 K was 22.0±0.1 and $P_{\text{CO}}(\text{NDIR})$ at 973 K / $P_{\text{CO}}(\text{NDIR})$ at 523 K was 25.0±0.1. At 973 K there was 80±10 % H\textsubscript{2} production and 45±7 % CO production. There was 25 % H\textsubscript{2} production at 620±10K and 25 % CO production at 730±10 K.

Overall, all the catalysts showed no reaction up to a certain temperature before allowing the reaction to occur (i.e. $\alpha$-$\beta$ regions) and products to leave the surface. Apart from 0.5 wt % Rh/TiO\textsubscript{2} (Degussa, P25, IMP), all catalysts showed activity for dry reforming. H\textsubscript{2} production was more extensive than CO production or CO production required higher temperatures than H\textsubscript{2} production (see Figure 4.22). The consumption ratio of CO\textsubscript{2} and CH\textsubscript{4} however was generally 1:1 (see Figure 4.23). Table 4.2 summarises the % CO\textsubscript{2} / % CH\textsubscript{4} conversion and % H\textsubscript{2} / % CO production at 973 K for various catalysts. Similarly Table 4.3 summarises the temperatures (K) at which 25 % CO\textsubscript{2} / 25 % CH\textsubscript{4} is converted and 25 % H\textsubscript{2} / 25 % CO is produced for the same catalysts.

**Table 4.2. - % CO\textsubscript{2}/CH\textsubscript{4} conversion and % H\textsubscript{2}/CO production at 973 K for various catalysts**

<table>
<thead>
<tr>
<th></th>
<th>% CO\textsubscript{2}</th>
<th>% CH\textsubscript{4}</th>
<th>% H\textsubscript{2}</th>
<th>% CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 wt. % Rh/TiO\textsubscript{2} (SG)</td>
<td>25± 5</td>
<td>55± 5</td>
<td>75± 10</td>
<td>60± 7</td>
</tr>
<tr>
<td>0.5 wt. % Rh/TiO\textsubscript{2} (SG, IMP)</td>
<td>30± 5</td>
<td>10± 5</td>
<td>10± 5</td>
<td>5± 5</td>
</tr>
<tr>
<td>0.5 wt. % Rh/TiO\textsubscript{2} (P25)</td>
<td>-----</td>
<td>92± 5</td>
<td>65± 10</td>
<td>-----</td>
</tr>
<tr>
<td>5 wt. % Rh/Al\textsubscript{2}O\textsubscript{3} pellets (IMP)</td>
<td>90± 3</td>
<td>75± 5</td>
<td>80± 10</td>
<td>45± 7</td>
</tr>
<tr>
<td>5 wt. % Rh/TiO\textsubscript{2} (P25)</td>
<td>75± 5</td>
<td>60± 5</td>
<td>80± 5</td>
<td>30± 5</td>
</tr>
</tbody>
</table>

Table 4.2 shows how the catalysts compare at 973 K. Some show low consumption and low production due to sintering and structure collapse. Despite this major problem, most are still showing steady activity. The greater the percentage of CO\textsubscript{2} and CH\textsubscript{4} conversion, and H\textsubscript{2} and CO production, the better the catalyst is. Thus from Table 4.2 the order of activity was:

5 wt. % Rh/Ti\textsubscript{O\textsubscript{2}} (Degussa, P25, IMP) > 5 wt. % Rh/Al\textsubscript{2}O\textsubscript{3} pellets (IMP) > 0.5 wt. % Rh/Ti\textsubscript{O\textsubscript{2}} (SG) > 0.5 wt. % Rh/Ti\textsubscript{O\textsubscript{2}} (Degussa, P25, IMP) > 0.5 wt. % Rh/Ti\textsubscript{O\textsubscript{2}} (SG, IMP).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T(K)(_{CO2})</th>
<th>T(K)(_{CH4})</th>
<th>T(K)(_{H2})</th>
<th>T(K)(_{CO})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 wt. % Rh/Ti\textsubscript{O\textsubscript{2}} (SG)</td>
<td>720±10</td>
<td>740±10</td>
<td>630±10</td>
<td>690±10</td>
</tr>
<tr>
<td>0.5 wt. % Rh/Ti\textsubscript{O\textsubscript{2}} (SG, IMP)</td>
<td>740±10</td>
<td>820±10</td>
<td>560±10</td>
<td>610±10</td>
</tr>
<tr>
<td>0.5 wt. % Rh/Ti\textsubscript{O\textsubscript{2}} (P25)</td>
<td>540±10</td>
<td>800±10</td>
<td>820±10</td>
<td>-----</td>
</tr>
<tr>
<td>5 wt. % Rh/Al\textsubscript{2}O\textsubscript{3} pellets (IMP)</td>
<td>580±10</td>
<td>690±10</td>
<td>690±10</td>
<td>800±10</td>
</tr>
<tr>
<td>5 wt. % Rh/Ti\textsubscript{O\textsubscript{2}} (P25)</td>
<td>710±10</td>
<td>650±10</td>
<td>620±10</td>
<td>730±10</td>
</tr>
</tbody>
</table>

Here the lower the temperature at which 25 % conversion occurs (for CO\textsubscript{2} and CH\textsubscript{4}) and 25 % production occurs (for H\textsubscript{2} and CO), the better the catalyst is. This is because the catalyst will have converted or produced a given percentage with a lower energy input. Hence from Table 4.3 the order of activity was:

5 wt. % Rh/Ti\textsubscript{O\textsubscript{2}} (Degussa, P25, IMP) > 5 wt. % Rh/Al\textsubscript{2}O\textsubscript{3} pellets (IMP) ~ 0.5 wt. % Rh/Ti\textsubscript{O\textsubscript{2}} (SG) ~ 0.5 wt. % Rh/Ti\textsubscript{O\textsubscript{2}} (SG, IMP) > 0.5 wt. % Rh/Ti\textsubscript{O\textsubscript{2}} (Degussa, P25, IMP).

This was a similar trend to % CO\textsubscript{2} and % CH\textsubscript{4} conversion at 973 K (see Table 4.2) in the sense that 5 wt. % Rh/Ti\textsubscript{O\textsubscript{2}} (Degussa, P25, IMP) was the best catalyst followed by 5 wt. % Rh/Al\textsubscript{2}O\textsubscript{3} pellets (IMP).
In order to determine whether the experiments were carried out properly and therefore whether the results were true, *mass balance* calculations and profiles are provided. Simply, the amount of substance reacting must in effect produce the same output. It is accepted that some products or yield may be lost in the process as unwanted side products for example, but none may be produced as extra (since it would contradict first law of thermodynamics). Since the reaction has a 1:2 ratio with respect to the reactants (CO\(_2/\)CH\(_4\)) and products (CO/H\(_2\)):

\[
\text{CO}_2 + \text{CH}_4 \rightarrow 2\text{CO} + 2\text{H}_2
\]

the *mass balance* was given by:

\[
\frac{\text{the change in pressure of CO}_2 \text{ and CH}_4 \text{ consumption over the temperature range}}{\text{twice the change in pressure of CO and H}_2 \text{ production over the temperature range}}
\]

or mathematically represented as:

\[
\frac{(- \Delta P_{CO2}) + (- \Delta P_{CH4})}{2 (+ \Delta P_{CO} + \Delta P_{H2})}
\]

As before the consumption and production are represented by the 'minus' (-) and 'plus' (+) signs respectively. This was plotted against the temperature range concerned, and if mass balance is obeyed then there should be an averaging around the origin since overall, no real net gain or loss is made.

A mass balance profile is shown for 5 wt % Rh/TiO\(_2\) (Degussa, P25, IMP) as an example:
4. Catalysis II: Dry reforming of methane.

Fig. 4.21. - Mass balance for 5 wt % Rh/TiO₂ (Degussa, P25, IMP)

As expected, mass balance exists for these results. Small deviations are noticeable, but this is simply attributed to inherent experimental errors. The results therefore are very useful for interpreting the extent of dry reforming on these catalysts.

Figures 4.22 and 4.23 show $T_{CO}(K)$ versus $T_{H₂}(K)$ for 25 % production and $T_{CO₂}(K)$ versus $T_{CH₄}(K)$ for 25 % conversion respectively. 0.5 wt % Rh/TiO₂ (Degussa, P25, IMP) is not shown because it did not facilitate the dry reforming reaction (i.e. partial oxidation was observed instead). Hence 3 is not shown on the following graphs.

Fig. 4.22. - $T_{CO}(K)$ versus $T_{H₂}(K)$ for 25 % production. The straight line is when $T_{CO}$ exactly equals $T_{H₂}$. Hence $T_{CO}$ production > $T_{H₂}$ production which means H₂ is more likely to occur at lower temperatures. 1 = 0.5 wt. % Rh/TiO₂ (SG); 2 = 0.5 wt. % Rh/TiO₂ (SG, IMP); 4 = 5 wt. % Rh/Al₂O₃ pellets (IMP) and 5 = 5 wt. % Rh/TiO₂ (Degussa, P25, IMP). The associated errors are shown in Table 4.3.
4.10.5. Activation Energies

Activation energies ($E_a$) were worked out for the catalytic results with respect to CO$_2$ and CH$_4$ conversions, and CO and H$_2$ production using the procedure described in Chapter 2. An example is shown for 5 wt. % Rh/TiO$_2$ (Degussa, P25, IMP) in Figures 4.24-4.27 below. $E_a$ and corresponding $\ln A$ for the other catalysts are shown in Table 4.4. Their respective surface areas ($S_{BET}$) are also shown (see Chapter 6).
4. Catalysis II: Dry reforming of methane.

Fig. 4.25. – Pseudo-Arrhenius plot for CH₄ conversion for 5 wt. % Rh/TiO₂ (Degussa, P25, IMP); $E_a = 34.4 \pm 1.0 \text{ kJ mol}^{-1}$ and $\ln A = 9.6 \pm 0.3$.

Fig. 4.26. – Pseudo-Arrhenius plot for CO production for 5 wt. % Rh/TiO₂ (Degussa, P25, IMP); $E_a = 137.0 \pm 4.1 \text{ kJ mol}^{-1}$ and $\ln A = 25.8 \pm 0.8$. 

4. Catalysis II: Dry reforming of methane.

Fig. 4.27. – Pseudo-Arrhenius plot for H₂ production for 5 wt. % Rh/TiO₂ (Degussa, P25, IMP); \( E_a = 48.0 \pm 1.4 \text{ kJmol}^{-1} \) and \( \ln A = 11.2 \pm 0.3 \).

Table 4.4. – comparison of \( E_a \) (kJmol\(^{-1}\)), \( \ln A \) and surface areas (\( S_{\text{BET}} \)) for different catalysts

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_2 ) ( E_a )</td>
<td>83.6±2.5</td>
<td>35.0±1.1</td>
<td>72.6±2.2</td>
<td>12.0±0.4</td>
<td>58.1±1.7</td>
</tr>
<tr>
<td>( \ln A )</td>
<td>17.2±0.5</td>
<td>9.0±0.3</td>
<td>19.4±0.6</td>
<td>5.7±0.2</td>
<td>13.5±0.4</td>
</tr>
<tr>
<td>( \text{CH}_4 ) ( E_a )</td>
<td>28.7±0.9</td>
<td>34.5±1.0</td>
<td>5.4±0.2</td>
<td>12.2±0.4</td>
<td>34.4±1.0</td>
</tr>
<tr>
<td>( \ln A )</td>
<td>8.3±0.3</td>
<td>8.5±0.3</td>
<td>5.3±0.2</td>
<td>6.1±0.2</td>
<td>9.6±0.3</td>
</tr>
<tr>
<td>( \text{CO} ) ( E_a )</td>
<td>88.7±2.7</td>
<td>41.7±1.3</td>
<td>---</td>
<td>108.0±3.2</td>
<td>137.0±4.1</td>
</tr>
<tr>
<td>( \ln A )</td>
<td>18.6±0.6</td>
<td>11.3±0.3</td>
<td>---</td>
<td>20.3±0.6</td>
<td>25.8±0.8</td>
</tr>
<tr>
<td>( \text{H}_2 ) ( E_a )</td>
<td>46.9±1.4</td>
<td>15.1±0.5</td>
<td>9.46±0.3</td>
<td>14.3±0.4</td>
<td>48.0±1.4</td>
</tr>
<tr>
<td>( \ln A )</td>
<td>12.1±0.4</td>
<td>6.6±0.2</td>
<td>5.5±0.2</td>
<td>6.3±0.2</td>
<td>11.2±0.3</td>
</tr>
<tr>
<td>( S_{\text{BET}} ) (m(^2)/g)</td>
<td>80±3</td>
<td>563±5</td>
<td>46±3</td>
<td>206±5</td>
<td>25±3</td>
</tr>
</tbody>
</table>

where 1 = 0.5 wt. % Rh/TiO₂ (SG); 2 = 0.5 wt. % Rh/TiO₂ (SG, IMP); 3 = 0.5 wt. % Rh/TiO₂ (Degussa, P25, IMP); 4 = 5 wt. % Rh/Al₂O₃ pellets (IMP) and 5 = 5 wt. % Rh/TiO₂ (Degussa, P25, IMP).

These \( E_a \)s were in excellent agreement with the typical literature values [7] shown in Table 4.5 below. In many cases, lower \( E_a \)s were obtained indicating better catalysts or diffusion control.
4. Catalysis II: Dry reforming of methane.

<table>
<thead>
<tr>
<th>Catalyst system</th>
<th>CO₂</th>
<th>CH₄</th>
<th>CO</th>
<th>H₂</th>
</tr>
</thead>
</table>

In $E_a$ terms therefore the order of activity seemed to be:

5 wt. % Rh/Al₂O₃ pellets (IMP) > 0.5 wt. % Rh/TiO₂ (Degussa, P25, IMP) ~ 0.5 wt. % Rh/TiO₂ (SG, IMP) > 0.5 wt. % Rh/TiO₂ (SG) > 5 wt. % Rh/TiO₂ (Degussa, P25, IMP).

This trend was different from those with respect to % CO₂/CH₄ conversions and % H₂/CO productions at 973 K (see Table 4.2) and T(25 % CO₂/CH₄ conversion) and T(25 % H₂/CO production) (see Table 4.3) where 5 wt. % Rh/TiO₂ (Degussa, P25, IMP) was the best catalyst. Here this is the worst catalyst in the sequence and 5 wt. % Rh/Al₂O₃ pellets (IMP) was the best catalyst.

4.10.6. Compensation plots

For related catalysts, the compensation effect is often experienced whereby $\ln A$ increases as the $E_a$ increases across a series, and hence ‘compensation effect’ (see Chapter 2).

$E_a$ is plotted against $\ln A$ for CO₂ and CH₄ consumption (see Figures 4.28 and 4.29) and CO and H₂ production (see Figures 4.30 and 4.31):
4. Catalysis II: Dry reforming of methane.

Fig. 4.28. – Compensation plot for CO\textsubscript{2} conversion at 973 K.

Fig. 4.29. – Compensation plot for CH\textsubscript{4} conversion at 973 K.
There is thus reasonable correlation between the $E_a$ and $\ln A$ terms for all species concerned, hence *compensation effect* [12] exists between these catalysts. There was also a general relationship between surface area ($S_{\text{BET}}$) and $E_a$ (see *Figure 4.32*) i.e. the higher the surface area the lower the $E_a$ is likely:
Thus the overall TP activity order (taking into account % CO₂/CH₄ conversions and % H₂/CO productions at 973 K (see Table 4.2), T(25 % CO₂/CH₄ conversion) and T(25 % H₂/CO production) (see Table 4.3) and Eₐ's (see Table 4.4) was:

5 wt. % Rh/Al₂O₃ pellets (IMP) > 5 wt. % Rh/TiO₂ (Degussa, P25, IMP) > 0.5 wt. % Rh/TiO₂ (SG) ~ 0.5 wt. % Rh/TiO₂ (SG, IMP) > 0.5 wt. % Rh/TiO₂ (Degussa, P25, IMP).

The activity order above was different from the order seen for TP N₂O decomposition where 0.5 wt. % Rh/TiO₂ (Degussa, P25, IMP) was the best catalyst (see Chapter 3). Here it was the worst. 5 wt. % Rh/Al₂O₃ pellets (IMP) was the best catalyst for TP dry reforming but was moderately active for TP N₂O decomposition. It was also different from the activity order seen in dry reforming pulse work in which case 5 wt % Rh/TiO₂ (Degussa, P25, IMP) was the best catalyst (see section 4.11).
4. Catalysis II: Dry reforming of methane.

4.11. Pulse results at Low Temperature (523 K) and High Temperature (973 K)

Dry reforming pulse results are now considered. The blank reactor and support results are followed by the catalyst results (see section 4.12.2).

4.11.1. Pulse results for blank reactor

Fig. 4.33 - (a) Duplicate CO₂ bypass pulses and (b) duplicate CH₄ bypass pulses for blank reactor.

Figures 4.33(a) and 4.33(b) show that for a blank reactor, there is excellent reproducibility for duplicate CO₂ pulses and duplicate CH₄ pulses respectively. The pulse results were therefore very reliable.

Fig. 4.34. – (a) CO₂ pulse for blank reactor at 523 K and (b) CO₂ pulse for blank reactor at 973K.
Fig. 4.35. – (a) CH₄ pulse for blank reactor at 523 K and (b) CH₄ pulse for blank reactor at 973 K.

Despite some pulse dilution going through the blank reactor, Figures 4.34(a)-(b) and 4.35(a)-(b) show that at either 523 K or 973 K, there was no CO₂ and CH₄ decomposition in the blank reactor.

4.11.2. Pulse results for supports

The duplicate CO₂ and CH₄ bypass pulses were the same as the blank reactor (see Figure 4.33(a)-(b)). The pulse results for the supports are now considered:

Fig. 4.36. – (a) CO₂ pulse for TiO₂ (SG) support at 523 K and (b) CO₂ pulse for TiO₂ (SG) support at 973 K

Figure 4.36(a)-(b) shows that there was no CO₂ decomposition or adsorption in the CO₂ pulse for TiO₂ (SG) support.
4. Catalysis II: Dry reforming of methane.

Figure 4.37(a)-(b) shows very little CH₄ decomposition in the CH₄ pulse but there is evidence of some 10± 5 % CO pulse production and about 5± 3 % H₂ pulse production (see Figure 4.37(b)).

Figure 4.38(a)-(b) shows 20± 5 % CO₂ adsorption and decomposition on the support surface in the CO₂ pulse. CO products have been retained on the surface and therefore are not seen in Figure 4.38(b).
4. Catalysis II: Dry reforming of methane.

Fig. 4.39. – (a) CH$_4$ pulse for TiO$_2$ (Degussa, P25) support at 523 K and (b) CH$_4$ pulse for TiO$_2$ (Degussa, P25) support at 973 K

*Figure 4.39(a)-(b) shows 20±5% CH$_4$ decomposition on the support surface in the CH$_4$ pulse. There was also evidence of 20±5% CO and H$_2$ production at 973 K (see Figure 4.39(b)).*

Fig. 4.40. – (a) CO$_2$ pulse for Al$_2$O$_3$ pellets at 523 K and (b) CO$_2$ pulse for Al$_2$O$_3$ pellets at 973 K

*Figure 4.40(a)-(b) shows that there was no CO$_2$ decomposition at either 523 K or 973K in the CO$_2$ pulse for Al$_2$O$_3$ pellets.*
4. Catalysis II : Dry reforming of methane.

![Graphs showing CH₄ and CO₂ pulses](image)

**Fig. 4.41.** (a) CH₄ pulse for Al₂O₃ pellets at 523 K and (b) CH₄ pulse for Al₂O₃ pellets at 973 K

Similarly **Figure 4.41(a)-(b)** shows that there was no CH₄ decomposition at either 523K or 973 K in the CH₄ pulse for Al₂O₃ pellets.

**Table 4.6** shows % pulse CO₂ decomposition in the CO₂ pulse and % pulse CH₄ decomposition in the CH₄ pulse for the blank reactor and various supports.

<table>
<thead>
<tr>
<th></th>
<th>% CO₂</th>
<th>% CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank reactor</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TiO₂ (SG)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TiO₂ (Degussa, P25)</td>
<td>20± 5</td>
<td>20± 5</td>
</tr>
<tr>
<td>Al₂O₃ pellets</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

It is clear therefore that no reaction occurs in the blank reactor or on either TiO₂ (SG) or Al₂O₃ pellets as supports. Only TiO₂ (Degussa, P25) allows very moderate decomposition in either case (i.e. 20± 5 %).
4. Catalysis II: Dry reforming of methane.

4.11.3. Pulse results for catalysts

The pulse results for the various catalysts are now considered.

Fig. 4.42. — (a) Duplicate CO$_2$ bypass pulses and (b) duplicate CH$_4$ bypass pulses for 0.5 wt. % Rh/TiO$_2$ (SG).

Figures 4.42(a) and 4.42(b) show duplicate CO$_2$ bypass pulses and duplicate CH$_4$ bypass pulses for 0.5 wt. % Rh/TiO$_2$ (SG) as an example. The pulses show excellent reproducibility and are in close agreement with those seen for the blank reactor (see Figure 4.33 (a)-(b)).

Fig. 4.43. — (a) CO$_2$ pulse for 0.5 wt. % Rh/TiO$_2$ (SG) at 523 K and (b) CO$_2$ pulse for 0.5 wt. % Rh/TiO$_2$ (SG) at 973 K.

Figure 4.43(a) shows no CO$_2$ decomposition in the CO$_2$ pulse at 523 K over 0.5 wt % Rh/TiO$_2$ (SG) catalyst. Figure 4.43(b) however showed 10±5 % CO$_2$ decomposition in the CO$_2$ pulse over the same catalyst at 973 K.
4. Catalysis II: Dry reforming of methane.

**Fig. 4.44.** - (a) CH\(_4\) pulse for 0.5 wt. % Rh/TiO\(_2\) (SG) at 523 K and (b) CH\(_4\) pulse for 0.5 wt. % Rh/TiO\(_2\) (SG) at 973 K

*Figure 4.44(a)* showed very little reaction in the CH\(_4\) pulse at 523 K for 0.5 wt % Rh/TiO\(_2\) (SG), but there was considerable activity at 973 K in the CH\(_4\) pulse for the same catalyst (see *Figure 4.44(b)*). There was 75±10 % CH\(_4\) pulse decomposition, 20±5 % CO production and 90±10 % H\(_2\) production in the CH\(_4\) pulse. Interestingly 15±5 % CO\(_2\) desorption was also noted at 973 K. The CO\(_2\) and CH\(_4\) pulse observations for this catalyst were consistent with the TP continuous results (see *Figures 4.16(a)-(b)*). At 973 K the catalyst was beginning to deactivate but was still very active.

CO\(_2\) pulses at 523 K and 973 K for 0.5 wt % Rh/TiO\(_2\) (SG, IMP) are shown in *Figure 4.45(a)-(b)*. The duplicate CO\(_2\) and CH\(_4\) bypass pulses for this catalyst were the same as 0.5 wt Rh/TiO\(_2\) (SG) (see *Figure 4.42(a)-(b)*).

**Fig. 4.45.** - (a) CO\(_2\) pulse for 0.5 wt. % Rh/TiO\(_2\) (SG, IMP) at 523 K and (b) CO\(_2\) pulse for 0.5 wt. % Rh/TiO\(_2\) (SG, IMP) at 973 K

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Figure 4.45(a) shows that there was no CO₂ decomposition in the CO₂ pulse at 523 K over 0.5 wt % Rh/TiO₂ (SG, IMP). Despite severe deactivation occurring at 973 K for TP continuous dry reforming for the same catalyst (see Figure 4.17(a)-(b)), Figure 4.45(b) above shows 25± 5 % CO₂ decomposition and 15± 5 % CO production in the CO₂ pulse at 973 K for the same catalyst.

The CO₂ pulses at 523 K and 973 K for 0.5 wt. % Rh/TiO₂ (Degussa, P25, IMP) are shown in Figure 4.47(a)-(b). Duplicate CO₂ and CH₄ bypass pulses for this catalyst were the same as 0.5 wt. Rh/TiO₂ (SG) (see Figure 4.42(a)-(b)).
4. Catalysis II: Dry reforming of methane.

Fig. 4.47. — (a) CO\textsubscript{2} pulse for 0.5 wt. % Rh/TiO\textsubscript{2} (Degussa, P25, IMP) at 523 K and (b) CO\textsubscript{2} pulse for 0.5 wt. % Rh/TiO\textsubscript{2} (Degussa, P25, IMP) at 973 K.

*Figure 4.47(a)* shows that there was no CO\textsubscript{2} decomposition in the CO\textsubscript{2} pulse at 523 K over 0.5 wt. % Rh/TiO\textsubscript{2} (Degussa, P25, IMP) and *Figure 4.47(b)* shows 25± 5 % CO\textsubscript{2} pulse decomposition in the CO\textsubscript{2} pulse at 973 K for the same catalyst. 20± 5 % CO production in the CO\textsubscript{2} pulse at 973 K was also noted. This observation was unexpected because CH\textsubscript{4} decomposition and/or *partial oxidation* may have occurred (with O\textsubscript{2} impurity) during continuous TP work (see *Figure 4.18(a)*).

Fig. 4.48. — (a) CH\textsubscript{4} pulse for 0.5 wt. % Rh/TiO\textsubscript{2} (Degussa, P25, IMP) at 523 K and (b) CH\textsubscript{4} pulse for 0.5 wt. % Rh/TiO\textsubscript{2} (Degussa, P25, IMP) at 973 K.

*Figure 4.48(a)* shows there was no CH\textsubscript{4} decomposition in the CH\textsubscript{4} pulse at 523 K over 0.5 wt. % Rh/TiO\textsubscript{2} (Degussa, P25, IMP) and *Figure 4.48(b)* shows that there was 100±5 % CH\textsubscript{4} decomposition in the CH\textsubscript{4} pulse at 973 K over the same catalyst. There was also 200±10 % H\textsubscript{2} production and 100±5 % CO production. The 2 : 1 stoichiometric ratio in H\textsubscript{2} : CO production is attributed to partial oxidation:
4. Catalysis II: Dry reforming of methane.

\[ \text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \text{ with } \Delta H^0_{(298 \text{ K})} = -36 \text{ kJmol}^{-1} \text{ (see Chapter 1).} \]

40±5 % CO\textsubscript{2} desorption was also noted at 973 K in the CH\textsubscript{4} pulse over the same catalyst. CH\textsubscript{4} pulse data for the same catalyst was consistent with continuous TP analysis (see Figure 4.18(a)-(b)) which indicated that partial oxidation was occurring instead of dry reforming of CH\textsubscript{4}.

The CO\textsubscript{2} pulses at 523 K and 973 K for 5 wt. % Rh/Al\textsubscript{2}O\textsubscript{3} pellets (IMP) are shown in Figure 4.49(a)-(b). Duplicate CO\textsubscript{2} and CH\textsubscript{4} bypass pulses for this catalyst were the same as 0.5 wt. Rh/Ti\textsubscript{O}\textsubscript{2} (SG) (see Figure 4.42(a)-(b)).

![Fig. 4.49. - (a) CO\textsubscript{2} pulse for 5 wt. % Rh/Al\textsubscript{2}O\textsubscript{3} pellets (IMP) at 523 K and (b) CO\textsubscript{2} pulse for 5 wt. % Rh/Al\textsubscript{2}O\textsubscript{3} pellets (IMP) at 973 K](image)

Figure 4.49(a) showed that there was no CO\textsubscript{2} decomposition in the CO\textsubscript{2} pulse at 523K over 5 wt % Rh/Al\textsubscript{2}O\textsubscript{3} pellets (IMP) and Figure 4.49(b) showed 15±5 % CO\textsubscript{2} decomposition in the CO\textsubscript{2} pulse at 973 K over the same catalyst. There was however no evidence of CO production at 973 K in the CO\textsubscript{2} pulse. TP continuous work (see Figure 4.19(a)-(b)) seemed to indicate that 75±5 % CO\textsubscript{2} decomposition had occurred at 973 K, but this was not reflected in the CO\textsubscript{2} pulse results above.
4. Catalysis II: Dry reforming of methane.

Figure 4.50(a)-(b) showed 65±5% CH$_4$ decomposition in the CH$_4$ pulse at 973 K over 5 wt % Rh/Al$_2$O$_3$ pellets (IMP) with 80±5% CO production and 85±5% H$_2$ production. There was also 60±5% CO$_2$ desorption in the CH$_4$ pulse at 973 K over the same catalyst. There was however no reaction in the CH$_4$ pulse at 523 K (see Figure 4.50(a)). These observations were in good agreement with the TP continuous analysis for the same catalyst (see Figure 4.19(a)-(b)).

The CO$_2$ pulses at 523K and 973 K for 5 wt. % Rh/TiO$_2$ (Degussa, P25, IMP) are shown in Figure 4.51(a)-(b). Duplicate CO$_2$ and CH$_4$ bypass pulses for this catalyst were the same as 0.5 wt. Rh/TiO$_2$ (SG) (see Figure 4.42(a)-(b)).
Figure 4.51(a) shows no CO$_2$ decomposition in the CO$_2$ pulse at 523 K over 5 wt. % Rh/TiO$_2$ (Degussa, P25, IMP) and Figure 4.51(b) shows 17±5 % CO$_2$ decomposition in the CO$_2$ pulse at 973 K over the same catalyst but no CO production was observed. It is thought that the CO remains adsorbed on the catalyst surface (see Chapter 7). These observations were fairly modest compared to the continuous TP results (see Figure 4.20(a)) where up to 90±3 % CO$_2$ decomposition occurred.

![Figure 4.51a](image1)

Figure 4.52(a) shows that no reaction was occurring in the CH$_4$ pulse at 523 K over 5 wt. % Rh/TiO$_2$ (Degussa, P25, IMP) and Figure 4.52(b) shows 100±5 % CH$_4$ decomposition in the CH$_4$ pulse at 973 K over the same catalyst. 100±5 % H$_2$ and 55 ±5 % CO was also produced with 37±5 % CO$_2$ being desorbed from the catalyst surface at 973 K. These observations were in general agreement with those observed for the continuous TP work for the same catalyst (see Figure 4.20(a)-(b)).

![Figure 4.52](image2)

Table 4.7 shows a summary of pulse data in terms of % CO$_2$ pulse decomposition and % CO pulse production in the CO$_2$ pulse; and % CH$_4$ pulse decomposition, % CO and H$_2$ pulse production, and % CO$_2$ pulse desorption in the CH$_4$ pulse at 973 K for various catalysts. % CO$_2$/CH$_4$ pulse decomposition, % CO/H$_2$ pulse production and CO$_2$ pulse desorption were worked out in terms of peak heights and areas in relation to those obtained for the respective bypass data.
4. Catalysis II: Dry reforming of methane.

Table 4.7. - Summary of pulse data in the CO₂ and CH₄ pulse at 973 K for various catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO₂ pulse</th>
<th>CH₄ pulse</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% CO₂</td>
<td>% CO</td>
</tr>
<tr>
<td>1</td>
<td>10±5</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>25±5</td>
<td>15±5</td>
</tr>
<tr>
<td>3</td>
<td>25±5</td>
<td>20±5</td>
</tr>
<tr>
<td>4</td>
<td>15±5</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>17±5</td>
<td>0</td>
</tr>
</tbody>
</table>

% CH₄ and % H₂ are not shown for CO₂ pulse simply because they are not involved in CO₂ decomposition. 1 = 0.5 wt. % Rh/TiO₂ (SG); 2 = 0.5 wt. % Rh/TiO₂ (SG, IMP); 3 = 0.5 wt. % Rh/TiO₂ (Degussa, P25, IMP); 4 = 5 wt. % Rh/Al₂O₃ pellets (IMP) and 5 = 5 wt. % Rh/TiO₂ (Degussa, P25, IMP).

Since CH₄ decomposition and/or partial oxidation was observed for 0.5 wt. % Rh/TiO₂ (Degussa, P25, IMP) (see Figures 4.18(a)-(b), 4.47(a)-(b) and 4.48(a)-(b)) instead of dry reforming of CH₄, this catalyst was disregarded. From the remainder Table 4.7 indicates that the order of activity for catalysts in dry reforming was:

5 wt. % Rh/TiO₂ (Degussa, P25, IMP) > 0.5 wt. % Rh/TiO₂ (SG) > 5 wt. % Rh/Al₂O₃ pellets (IMP) > 0.5 wt. % Rh/TiO₂ (SG, IMP).

This order is very similar to that obtained for N₂O pulse work (see Chapter 3) but different from continuous TP results of N₂O decomposition and dry reforming. The similarity with N₂O pulse work was in the sense that the best catalyst in either case was 5 wt. % Rh/TiO₂ (Degussa, P25, IMP) and the worst was 0.5 wt. % Rh/TiO₂ (SG, IMP).

4.11.4. Summary of pulse observations

The bypass pulse data for the blank reactor shows good reproducibility (see Figure 4.33(a)-(b)) while pulses for the blank reactor at 523 K and 973 K (see Figures 4.34-35) suggested some pulse dilution but no reaction.

TiO₂ (SG) support showed no reaction for either pulse at 523 K and 973 K (see Figures 4.36-37). Again TiO₂ (Degussa, P25) also showed no reaction at 523 K (see Figures 4.38-39), but at 973 K 20±5 % CO was observed during the CH₄ pulse (see Figures...
In the case of $\text{Al}_2\text{O}_3$ pellets no reaction was observed at either 523 K or 973 K (see Figures 4.40–41).

0.5 wt % Rh/TiO$_2$ (SG) showed no activity at 523 K (see Figure 4.43(a) and 4.44(a)) but 10±5 % CO$_2$ adsorption was observed during the CO$_2$ pulse (see Figure 4.43(b)). There was evidence of 90±10 % H$_2$ and 20±5 % CO pulse production as well as 15±5 % CO$_2$ desorption during the CH$_4$ pulse (see Figure 4.44(b)) at 973 K. For 0.5 wt % Rh/TiO$_2$ (SG, IMP), no reaction was observed at 523 K (see Figure 4.45(a) and 4.46(a)). Again at 973 K there was 25±5 % CO$_2$ adsorption during CO$_2$ pulse (see Figure 4.45(b)) but unusually no CO or H$_2$ products in the CH$_4$ pulse (see Figure 4.46(b)). This could be because deactivation had already occurred by this stage according to TP results (see Figure 4.17(b)).

0.5 wt % Rh/TiO$_2$ (Degussa, P25, IMP) also witnessed no pulse reaction at 523 K (see Figure 4.47(a)) in the CO$_2$ pulse but at 973 K there seemed to be 20±5 % CO production (see Figure 4.47(b)) and 200±10% H$_2$ and 100±5 % CO production together with 40±5 % CO$_2$ desorption during CH$_4$ pulse (see Figure 4.48(b)). These observations were attributed to the fact that CH$_4$ decomposition and/or partial oxidation was occurring instead of dry reforming (see section 4.12.3).

5 wt % Rh/Al$_2$O$_3$ pellets (IMP) showed no reaction at 523 K (see Figures 4.49(a) and 4.50(a)). At 973 K there wasn’t anything interesting observed in the CO$_2$ pulse (see Figure 4.49) but during the CH$_4$ pulse there was evidence of 85±5 % H$_2$ and 80±5 % CO production with 60±5 % CO$_2$ desorption (see Figure 4.50(b)). Finally, for the 5 wt % Rh/TiO$_2$ (Degussa, P25, IMP), there was no reaction observed at 523 K (see Figures 4.51(a) and 4.52(a)) but at 973 K there was 17±5 % CO$_2$ adsorption during the CO$_2$ pulse (see Figure 4.51(b)) and 100±5 % H$_2$ and 55±5 % CO production during the CH$_4$ pulse (see Figure 4.52(b)). There was also evidence of 37±5 % CO$_2$ desorption.

None of the catalysts showed activity at 523 K and with the exception of 0.5 wt % Rh/TiO$_2$ (SG, IMP), all showed activity at 973 K with very little CO$_2$ adsorption during CO$_2$ pulse, and consistent production of CO and H$_2$ with some CO$_2$ desorption during
the CH₄ pulse. A significant amount of H₂ was produced, more than CO indicating greater selectivity towards H₂ (like the TP results). No significant activity was seen for 0.5 wt % Rh/TiO₂ (SG, IMP) due to deactivation at 973 K as a result of sintering. These observations agree with the mechanisms described in the literature (see Chapter 7). It is worth noting that some CO is always seen in the fragmentation pattern of CO₂ when CO₂ is pulsed (see Chapter 3).

4.12. Conclusions

- During TP work, α-β regions were noticed. In the α region, there was no reaction observed and during the β region the reaction was observed since there was a rapid release of products and consumption of reactants.
- During the CO₂ pulse, there was little surface O present.
- During the CH₄ pulse there was CO and H₂ production with greater selectivity for H₂ than CO. There was also some CO₂ desorption. These aspects agree with the reported mechanism (see Chapter 7). The CO₂/CH₄ consumption ratio was generally 1:1.
- With the exception of 0.5 wt. % Rh/TiO₂ (Degussa, P25, IMP), all catalysts have produced CO and H₂ during the CH₄ pulse.
- The activity order from continuous TP dry reforming was: 5 wt. % Rh/Al₂O₃ pellets (IMP) > 5 wt. % Rh/TiO₂ (Degussa, P25, IMP) > 0.5 wt. % Rh/TiO₂ (SG) ~ 0.5 wt. % Rh/TiO₂ (SG, IMP) > 0.5 wt. % Rh/TiO₂ (Degussa, P25, IMP).
- The activity order from CO₂/CH₄ pulse work was: 5 wt. % Rh/TiO₂ (Degussa, P25, IMP) > 0.5 wt. % Rh/TiO₂ (SG) > 5 wt. % Rh/Al₂O₃ pellets (IMP) > 0.5 wt. % Rh/TiO₂ (SG, IMP). This was similar to the activity order for N₂O decomposition pulse work.

4.13. References

4. Catalysis II: Dry reforming of methane.


CHAPTER V

Catalysis III: Heterogeneous Photocatalysis

In recent times photocatalysis has gained more and more attention from scientists all over the world [1-5].

5.1. Introduction

Many reactions take place between molecules that are normally in their ground electronic states, i.e. of lowest energy and therefore most stable state. They are described as thermal reactions because thermal motions of molecules and radicals are used to overcome the activation energy barrier. Chapters 3 and 4 explored reactions of that nature. Reactions can also be initiated by electromagnetic radiation. Electrons with suitable energy can move from the ground state energy level of a molecule to a higher level; usually from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Molecular orbitals are formed by the combination of the constituent atomic orbitals (see Chapter 1). In metals energy levels are so close together that bands of energy levels exist. Band gaps are principally due to the periodic electrical potential associated with crystallinity, but can also occur in semiconductors like Si and insulators like Se [6-7].

The valence band (B_v) and the conduction band (B_c) are defined by their respective molecular orbitals. The B_v is lower in energy since it contains the valence electrons in bonding orbitals and essentially bonds all the atoms in the solid together. The B_c is higher in energy and therefore its orbitals are usually unoccupied. In conductors like Cu for example, both bands are so close together that there is in fact overlapping to the extent that there is often no distinction between the two, i.e. one continuous band. In this case no band gap (the energy difference between the B_v and the B_c) exists and therefore most metals allow continuous flow of electrons i.e. they are very good electrical conductors. Insulators however have very large band gaps with B_v normally filled and B_c usually vacant. The large band gap means that it is very difficult to promote electrons from the B_v to the B_c. In semiconductors (like TiO_2) the band gap is small enough to allow electrons to transfer between the two (see Figure 5.1). Energy levels are quantized so that excitation involves a fixed quantity meaning that
photons of only suitable energy will allow the transition to occur. The majority of studies for heterogeneous photocatalysis have been undertaken using visible or near-UV radiation \((E_h < 5 \text{ eV})\) \[8\].

During a transition an electron from the ground state \((S_0)\) can go to an excited state \((S_1)\) or undergo a "spin-forbidden" transition to a triplet state \((T_1)\) \[9\]. Excited states lose energy rapidly and the various paths are illustrated in the Jablonski diagram in Figure 5.2. Here the objective, however, was to determine whether photocatalytic decomposition of \(\text{N}_2\text{O}\) and dry reforming of methane will occur on \(\frac{1}{2}\) wt % Rh/TiO\(_2\) (SG) (see section 5.9).
Photocatalysis is when a catalytic process occurs “during which one or more reaction steps occur by means of electron-hole pairs photogenerated on the surface of semiconductor materials illuminated by light of suitable energy” [10]. An electron-hole pair \((e^- - h^+)\) is when an electron is promoted from the \(B_v\) to the \(B_C\), in turn creating a positive hole in the \(B_v\). As before, the process is heterogeneous when the reactants and the photocatalyst are in a different phase from each other. The use of photocatalysts like \(\text{ZrO}_2\)-hv for example have been shown to be effective in the photoreduction of \(\text{CO}_2\) [11]. There are other such examples reported widely in the literature (see section 5.2) [12-13].
Semiconductors like TiO₂ (anatase and rutile) are often used as photocatalysts because of their low toxicity, low cost, photostability and small band gap (3.03 eV at 300 K for rutile and 3.2 eV for anatase at 300 K). The main disadvantage is however that TiO₂ only absorbs UV at λ < 400 nm [14]. This means that a “significant fraction of the solar radiation is not used in TiO₂ photocatalytic reactions”.

Photocatalysis is technically misleading, since light cannot be a catalyst, in the sense that it cannot be recovered unchanged [15].

Photoproduced pairs can be consumed in different ways:

- they can recombine with liberation of thermal energy and/or luminescence,
- they can react with an electron acceptor (for reduction) or a donor (for oxidation).

Kinetics are dependent upon ‘global reaction resistances’ and the concentration of e⁺-h⁺ pairs. Once in the steady state, it is dependent on chemical, electronic and morphological properties of the semiconductor. This aspect was not explored here.

Methods of preparations and dopants can influence the photoactivity of TiO₂. For example metal ions

- can increase the absorption in the visible region, but the band-gap of TiO₂ is unaffected,
- are equivalent to introducing defects (i.e. Ti³⁺) in the lattice,
- may vary the photoactivity when the transition metal ion (e.g. Rh⁺) is in the lattice or on the surface; but the dependence is not straight forward,
- can be beneficial, detrimental or not influence the photoactivity, and these can depend on the preparative methods used. For example,

  i) Co-precipitation (see Chapter 2) leads to more uniform distribution of species on the surface.
  ii) Wet impregnation means a less uniform distribution on the support surface (e.g. Rh/Al₂O₃ materials, see Chapters 2 and 6).
  iii) High temperature can cause diffusion of the metal into the lattice [16-19].
5. Catalysis III: Heterogeneous photocatalysis.

Metal species generally allow formation of a permanent space charge region, improving electron-hole pairs separation. Loading of more than 2 wt % is detrimental because segregation of metal species occurs at high temperatures and these can cover the surface of TiO_2 particles [20]. Bifunctional photocatalysts (i.e. powdered semiconductors with a metal deposited on the particle surface) have been used elsewhere for CO_2 photoreduction [21-23]. Examples of metals that have been used as dopants on TiO_2 include Ag, Pd and Pt as well as group VIII transition metals. This is said to improve electron-hole pairs separation and therefore catalytic efficiency, i.e. increased rate [24].

5.2. Examples of photocatalytic reactions

Many organic oxidations, reductions and rearrangements show photochemical transformations at a semiconductor interface [25-26]. Whilst the subject of photocatalysis is very widely studied, the use of TiO_2 in this context is less well explored. Examples of the use of TiO_2 photocatalysts include photodehydrogenation of C_2H_2 and C_2H_4, but only if TiOH surface groups are present after irradiation. The TiOH behaves as a source of hydrogen [27]. Other examples include the photochemical oxidation of hydrocarbons [28-29], the photo-Kobe reaction (decarboxylation of acetic acid) [30] with Pt on anatase; and the photocatalysed oxidation of alcohols by heteropolytungstates [31]. UV irradiated on platinized TiO_2 have also led to oxidation of aqueous cyanide [32] and to the water-gas shift reaction (CO + H_2O → H_2 + CO_2) [33]. Mechanistic aspects of the photo-oxidation of water to O_2 have even been discussed [34]. More recently, TiO_2 in combination with zeolites has shown photocatalytic reactivity for the decomposition of NO into N_2, O_2 and N_2O [35].

Photocatalysed electrolysis of H_2O can be achieved:

TiO_2 electrode: TiO_2 + hv → 2e^- + 2p^+ \quad (p^+ =\text{positive hole})

\[ 2p^+ + H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 \]

Pt electrode: \[ 2H^+ + 2e^- \rightarrow H_2 \]
as can alkylphenol degradation in water

\[
\begin{align*}
\text{TiO}_2 + \text{hv} &\rightarrow e^- + p^+ \quad (p^+ = \text{positive hole}) \\
\text{OH}^*_{(\text{Ti IV})} + p^+ &\rightarrow \text{OH}^*_{(\text{Ti III})} \quad (X = X \text{ adsorbed on surface}) \\
\text{H}_2\text{O}_{(\text{Ti IV})} + p^+ &\rightarrow \text{OH}^*_{(\text{Ti III})} + \text{H}^+ \\
\text{OH}^* + \text{phenols} &\rightarrow \text{oxidised products}
\end{align*}
\]

There is a similar mechanism for CH\(_3\)CN degradation.

Another use of TiO\(_2\) is in the production of H\(_2\)O\(_2\):

\[
\begin{align*}
\text{TiO}_2(s) + \text{hv} (>\text{E}_g) &\rightarrow h^+ - e^- \\
h^+ - e^- &\rightarrow h^+_{(\text{BV})} + e^-_{(\text{BC})} \quad \text{(space charge)} \\
h^+ + \text{OH}^- &\rightarrow \text{OH}_2 \quad \text{(radical)} \\
e^- + \text{O}_2 (\text{ads}) &\rightarrow \text{O}_2^\cdot (\text{ads}) \\
\text{OH}_2 (\text{radical}) + \text{OH}_2 (\text{radical}) &\rightarrow \text{H}_2\text{O}_2 (\text{ads})
\end{align*}
\]

where \(E_g\) = band gap energy, B\(_V\) = valence band and B\(_C\) = conduction band.

Other photoreactions include N\(_2\) photoreduction to NH\(_3\) [36-39], CO\(_2\) photoreduction to organic compounds [40-47] and water photosplitting: H\(_2\)O (hv) \(\rightarrow\) H\(_2\) + \(\frac{1}{2}\) O\(_2\) [48-50].

5.3. Photocatalytic Rig used here

The same rig system was used as described in *Chapter 3* and *Appendix II* [51] with the exception that the reactor was enclosed and accommodated in a darkened box to prevent external light affecting the experiment; and also to protect persons from harmful UV rays. The same furnace was used as described in *Chapters 3* and *4*, and the same reactor was also used as described in *Chapters 3* and *4*, but the reactor lid was modified slightly to allow UV radiation to pass through the reactor and onto the catalyst sample. Various photocatalytic sources have been known (e.g. a W filament that produces hv at 400-800 nm passing through the sample (gas, liquid, solid-liquid, solid-gas)). In this particular case however, a UV source was used to supply the
suitable energy. The source was a 30 W deuterium lamp with a wavelength of 383 nm. This was judged to be suitable for providing enough energy to generate the electron hole pair for the titania band gap:

Using

\[ \Delta E = h\nu = hc/\lambda \]

where \( \Delta E \) = change in energy (band gap energy in this case), \( h \) = Planck’s constant \((6.63 \times 10^{-34} \text{Js})\), \( c \) = velocity of light \((2.998 \times 10^8 \text{ms}^{-1})\) and \( \lambda \) = wavelength \((383 \text{ nm})\) [52].

\[ \Delta E = \frac{(6.63 \times 10^{-34} \times 2.998 \times 10^8)}{3.83 \times 10^{-7}} = 5.12 \times 10^{-19} \text{J}. \]

The units are Js x ms\(^{-1}\)/m and after cancelling J remains. Using the conversion factor 1J = 1.602x10\(^{-19}\) eV:

\[ \Delta E = \frac{5.12 \times 10^{-19} \text{J}}{1.602 \times 10^{-19} \text{eV}} = 3.24 \text{eV}. \]

This energy is greater than the band gap energies for rutile and anatase \((3.03 \text{ eV} \text{ and } 3.2 \text{ eV} \text{ respectively})\) [53]. A mixture of both these phases was present in the sample (see XRD results in Chapter 6).

5.4. Gases

Neat Ar was used as the carrier gas \((80 \text{ cm}^3\text{min}^{-1} \pm 1 \text{ cm}^3\text{min}^{-1})\) and into this was injected CO\(_2\) pulses \((0.1 \text{ cm}^3 \pm 0.001 \text{ cm}^3\), 2.24 mmol\) or CH\(_4\) pulses \((10 \% \text{ in Ar}, 1.0 \text{ cm}^3 \pm 0.005 \text{ cm}^3\), 2.24 mmol\) and N\(_2\)O (neat) pulses \((0.1 \text{ cm}^3 \pm 0.001 \text{ cm}^3\), 2.24 mmol\) at 473 K. H\(_2\) (neat) was used as pre-reductant and this flowed at 50 cm\(^3\)min\(^{-1}\) \((\pm 1 \text{ cm}^3\text{min}^{-1})\). The method for the data acquisition was the same as for the pulse work using conventional heat treatments (like the furnace) except that the reduction with H\(_2\) only was required up to 473 K. All other conditions were the same. The catalyst experienced the same pre-treatment conditions as described in Chapter 3.
5. Materials

0.5 wt % Rh/TiO\(_2\) (SG) (0.0590 g, 2.87 \(\mu\)mol. Rh cat.) was used because it produced good results for both the decomposition of N\(_2\)O and dry reforming of CH\(_4\). ½ wt % for metal loading was judged to be appropriate since a large percentage is shown to cause a loss in activity [20]. It was also one of the original sol-gel catalysts and was taken one step further in this context.

5.6. Pulse methods

The UV energy was supplied by a deuterium power source (model no. 288450) as the source of energy instead of the heat provided for by the furnace. This was used because the energy supplied is ideally within the UV region. Deuterium is a stable isotope of hydrogen with a natural abundance of one part in seven thousand of hydrogen [54-55].

Ideally, the temperature can be chosen to limit the amount of energy being transferred to the catalyst in order to ensure that no reaction occurs, and therefore any reaction that is experienced will only be as a direct result of the effects of the UV energy source with the reactant gases on the catalyst surface. In order to ensure this, the experiment was carried out in a darkened room and the apparatus was enclosed in a specially-designed black box (due to health and safety reasons). Apart from this, the N\(_2\)O/CH\(_4\)/CO\(_2\) pulse tests can be carried out as described in Chapters 3 and 4.

The experiment was thus carried out isothermally at 473 K (±20 K). As before, Ar was used as the carrier gas (100± 1 cm\(^3\) min\(^{-1}\)) with 2 x N\(_2\)O (neat, 0.1 cm\(^3\), 2.24 mmol) pulses followed by alternating CO\(_2\) (neat, 0.1 cm\(^3\), 2.24 mmol) and CH\(_4\) (10 % in Ar, 1 cm\(^3\), 2.24 mmol) pulses initially through a blank reactor to show experimental reproducibility. This was done in the absence of UV irradiation followed by its presence. The same procedure was followed for the catalyst and the whole process was monitored by the use of RGA. The results were compared to see whether the UV photocatalysed the decomposition of N\(_2\)O and the dry reforming reaction.
5.7. Data acquisition and method of analysis

1) The catalyst was reduced with pre-reductant H\textsubscript{2} at 473 (± 10) K for 1 h. Care had to be taken to remove the RGA capillary from the reaction stream, otherwise the RGA will be affected and hence data output will not make sense.

2) Ar was switched on bypass for 10 min flushing. The RGA capillary was reattached.

3) The reaction stream was switched on and left to stabilise for 10 min.

4) Data acquisition was allowed to start on the RGA.

5) 2 pulses of N\textsubscript{2}O and 2 cycles of alternating CO\textsubscript{2}/CH\textsubscript{4} pulses were taken for a blank run and reaction. This was compared with the bypass.

6) The data was recorded as

\[ t(m) \quad t(s) \quad t_{max} \quad t/t_{max} \]

special note was taken of \( t_{max} \) i.e. the time it takes from \( t_{inj} \) to maximum point on curve.

7) The data was saved.

The RGA was only required in this case. As before, the results gave information regarding the mechanisms of the respective processes.

5.8. Instrumental method – the RGA-MS

The RGA was used in the same way as described in Chapter 3 and was set to look for the following \( m/e \) values: 40(Ar), 31(N\textsubscript{2}O), 44(CO\textsubscript{2}), 16(CH\textsubscript{4}), 32(O\textsubscript{2}), 28(CO) and 2(H\textsubscript{2}). Here the secondary \( m/e \) (mass spectrometry (MS) peak) for N\textsubscript{2}O had to be used since the primary MS peak shared the same \( m/e \) value with CO\textsubscript{2}.

5.9. Results

Results for N\textsubscript{2}O decomposition and dry reforming in the (a) absence and (b) presence of UV radiation are shown:
5. Catalysis III: Heterogeneous photocatalysis.

5.9.1. \(\text{N}_2\text{O} \) decomposition

![Figure 5.1 - \(\text{N}_2\text{O} \) pulse over \(\frac{1}{2}\) wt % \(\text{Rh/TiO}_2 \) (SG) in the (a) absence and (b) presence of UV irradiation at 473 K](image)

There is evidence in Figure 5.1 to suggest that in the presence of UV irradiation there was \(\text{N}_2\text{O} \) consumption and \(\text{O}_2 \) production (see Figure 5.1(b)). The proposed mechanism for photocatalysed \(\text{N}_2\text{O} \) decomposition is:

- \(\text{N}_2\text{O} \rightarrow \text{N}_2 + \frac{1}{2}\text{O}_2 \) (in presence of hv and \(\text{TiO}_2 \))
- Mechanism: \(\text{TiO}_2: \text{TiO}_2 + \text{hv} \rightarrow 2e^- + 2p^+ \quad (p^+ = \text{positive hole})\)
  \(\text{N}_2\text{O} + 2e^- \rightarrow \text{N}_2\text{O}^2- \rightarrow \text{N}_2 + \text{O}^2-\)
  \(\text{Rh}: \text{Rh}^0 + 2p^+ \rightarrow \text{Rh}^{2+}\)
  \(\text{Rh}^{2+} + \text{O}^2- \rightarrow \text{RhO}\)
  \(\text{RhO} \rightarrow \text{Rh}^0 + \frac{1}{2}\text{O}_2\)

5.9.2. Dry reforming

\(\text{CO}_2 \) pulse results showed nothing interesting (as in the normal high temperature route), but the \(\text{CH}_4 \) pulse did show interesting \(\text{H}_2 \) production, supported by the mechanism described previously (see Chapters 4 and 7).
Here there is evidence of a significant level of H$_2$ production from the CH$_4$ pulse on the Rh/TiO$_2$ surface that is being UV irradiated. However no CO production was observed. Furthermore, despite the fact that the photoreduction [11] and photofixation [56] of CO$_2$ is well known, the corresponding photocatalytic mechanism for dry reforming of methane is not so well known. The mechanism discussed in Chapter 7 is principally for the thermal reactions that are described in Chapter 4.

Reactivity parameters like Quantum Yield ($\phi$) were not explored here since the experiments were of a qualitative nature and designed in order to determine whether these reactions were possible with this initial design. The results prove that this is possible. Nevertheless, Quantum yield ($\phi$) [57] is normally used to express the efficiency of a photocatalytic process. It is the number of reactant molecules converted to product for each photon absorbed:

$$\phi = \frac{\text{No. molecules converted}}{\text{No. photons absorbed}}$$

For chain reactions $\phi$ can be $10^4$, but purely photochemical reactions need at least 1 quanta of light per molecule. This aspect was not investigated here.
5.10. Conclusions

The results presented provide an insight into possible applications of photocatalysis on present catalyst surfaces. A significant start has been made in this area and indicates the possibility of improvement in the future. The experiment can be improved by:

- better line alignment for the photon source and reactor so that the UV radiation has maximum impact on the catalytic surface,
- allowing the distance between the reactor containing the catalyst and the source to be reduced as much as possible to allow maximum photon intensities reaching the surface.

Despite the fact that heterogeneous photocatalysis is well documented in the literature, it is a relatively new area that has yet to find major practical application. The only real commercial application has been the photovoltaic cell (solar cell) [58]. It is hoped therefore that this research has shown potential for an interesting application, i.e. reduction of greenhouse gases.

5.11. References

5. Catalysis III: Heterogeneous photocatalysis.

5. Catalysis III: Heterogeneous photocatalysis.


CHAPTER VI

Characterisation of catalysts

6.1. Introduction

Present catalysts have been characterised using a range of analytical techniques. This was because one particular technique gives a very limited understanding of the nature of the catalyst; therefore a range of complementary and contrasting techniques were used. The chapter describes the various instrumental and characterisation techniques that were used together with the results produced.

Table 6.1. shows the various regions of the electromagnetic spectrum and the energies associated with these. Each region has a particular influence with respect to molecular processes. Radio frequencies (10 m < λ < 1 cm involve energy of 0.001 – 10 Jmol⁻¹) cause a change of spin of a nucleus or electron i.e. nuclear magnetic resonance (NMR) and electron spin resonance (ESR) respectively. Microwave radiation (1 cm < λ < 100 μm and energy is the order of 0.1 kJmol⁻¹) is associated with rotational spectroscopy. The infrared region (100 μm < λ < 1 μm and energy of about 10 kJmol⁻¹) is associated with vibrational spectroscopy. The visible and ultra-violet (UV) regions (1 μm < λ < 10 nm and energy of 100 – 1,000 kJmol⁻¹) involve the energy levels of valence electrons whilst X-rays (10 nm < λ < 100 pm and energy in the order of 10⁴ kJmol⁻¹) affect energy changes involving the inner electrons of an atom or molecule i.e. change of electron distribution (see Figure 6.1). Finally γ-ray region is at 100 pm < λ < 1 pm with an energy typically between 10⁶ – 10⁸ kJmol⁻¹ [1]. Here the infrared and X-ray regions in particular were explored. This was because infrared provided information about any surface species and whether the surface was active (using CO as a probe molecule); and XPS gave information about oxidation states before and after a reaction and relative atomic composition.

Other techniques like X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDAX) gave information about the texture and atomic composition of catalysts. Pore character and surface area were given by adsorption isotherms derived from the BET equation (see section 6.9).

Table 6.1. – Energy of electromagnetic radiation [1]

<table>
<thead>
<tr>
<th>Description</th>
<th>Wavelength Range</th>
<th>Wave Number, cm⁻¹</th>
<th>Frequency, Hz</th>
<th>Energy kJ mol⁻¹</th>
<th>Energy eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radio frequency</td>
<td>3 × 10⁻⁸ m</td>
<td>3.33 × 10⁻⁶</td>
<td>10⁵</td>
<td>3.98 × 10⁻⁷</td>
<td>4.12 × 10⁻⁶</td>
</tr>
<tr>
<td></td>
<td>0.30 m</td>
<td>0.0333</td>
<td>10⁹</td>
<td>3.98 × 10⁻⁴</td>
<td>4.12 × 10⁻⁶</td>
</tr>
<tr>
<td>Microwave</td>
<td>0.0006 m (600 µm)</td>
<td>16.6</td>
<td>4.98 × 10¹¹</td>
<td>0.191</td>
<td>2.07 × 10⁻¹³</td>
</tr>
<tr>
<td>Far infrared</td>
<td>30 µm</td>
<td>333</td>
<td>10⁻¹³</td>
<td>3.98</td>
<td>0.0412</td>
</tr>
<tr>
<td>Near infrared</td>
<td>0.8 µm (800 nm)</td>
<td>1.25 × 10⁴</td>
<td>3.75 × 10¹⁴</td>
<td>149.8</td>
<td>1.55</td>
</tr>
<tr>
<td>Visible</td>
<td>400 nm</td>
<td>2.5 × 10⁴</td>
<td>7.5 × 10⁴</td>
<td>299.2</td>
<td>3.10</td>
</tr>
<tr>
<td>Ultraviolet</td>
<td>150 nm</td>
<td>6.06 × 10⁴</td>
<td>19.98 × 10⁴</td>
<td>795</td>
<td>8.25</td>
</tr>
<tr>
<td>Vacuum ultraviolet</td>
<td>5 nm</td>
<td>2 × 10⁶</td>
<td>6 × 10⁶</td>
<td>2.39 × 10⁶</td>
<td>247.8</td>
</tr>
<tr>
<td>X-rays and γ-rays</td>
<td>10⁻⁴ nm</td>
<td>10¹¹</td>
<td>3 × 10²¹</td>
<td>1.19 × 10⁷</td>
<td>1.24 × 10⁷</td>
</tr>
</tbody>
</table>

It is well known that energy is quantised (see Chapter 5) but at any given time a molecule is not only in a given electronic state but also in a given vibrational and rotational state. The difference between two adjacent vibrational levels is much smaller than those between two adjacent electronic levels, and smaller still between two adjacent rotational levels. Figure 6.1 below shows potential energy versus internuclear distance energy curves for a diatomic molecule (e.g. CO). It is derived from the anharmonic oscillator model because it takes into account bond extensions and compressions. It also accounts for nuclear repulsions as the internuclear distance tends to 0 and bond breaking (cleavage) as the internuclear distance tends to infinity (∞). This is deviated from the harmonic oscillator model i.e. a perfect parabola with equation: Energy (E) = ½k(r-r_eq)² resulting from a bond behaving like a spring between two atoms and obeying Hooke’s law, f = -k(r - r_eq) where f = the restoring force, k = force constant, r = internuclear distance and r_eq = equilibrium distance or bond length [2].


It is worth noting that the SiO₂ and SiO₂-TiO₂ systems were not characterised because of their low catalytic activity (see Chapters 3 and 4). TiO₂ on the other hand was of much more interest and was subject to more detailed analysis.

6.2. Fourier Transform infra-red (FT-IR) [4-5]

The contribution of FTIR to catalyst characterisation is well documented [6-11]. As mentioned above IR spectroscopy is associated principally with vibrational transitions and these are shown diagrammatically in Figure 6.1 and includes wavelengths (\( \lambda \)) between 2.5 \( \mu \)m and 15 \( \mu \)m, and wavenumbers between 4000 – 650 cm\(^{-1} \) (where cm\(^{-1} \) = 10,000/\( \mu \)m). Since energy is quantised, only those frequencies of infrared radiation that match the natural vibrational frequencies of the molecule in question are absorbed. There is however an important selection rule to determine whether a molecule would in principle be IR active, and this is that the electric dipole moment of the molecule must change during the vibration. The molecule does not need to have a permanent dipole moment, only a change (e.g. the asymmetric stretching and bending modes of CO₂ [12]). Some vibrations do not affect the molecule’s dipole moment (e.g. the stretching motion of a homonuclear diatomic molecule (like N₂)) and consequently these are said to be infrared inactive.

The instrument used here was a PE 2000 Fourier Transform-Infrared (FT-IR) spectrophotometer with Nicolet 510P software. Infrared measurements cannot usually be made in aqueous solution because water absorbs intensely in this region and can mask genuine signals in the solute. Measurements were therefore made of catalysts in contact with the gas phase, with the sample being mixed in a suitable inorganic salt (i.e. KBr) and pressed into a transparent disc. This was mounted in a holder which was supported in the beam of the infrared instrument. The results were plotted as wavenumbers (cm\(^{-1}\)) against absorbance. The absorbance, A (or optical density) of the species is given by

\[
A = -\log(I/I_o)
\]

(equation 6.1)

where I = intensity of the transmitted light and I\(_o\) = intensity of the incident light. This expression is derived from the Beer-Lambert law [13]. FTIR results are shown for 0.5 wt % Rh/TiO\(_2\) (SG) and TiO\(_2\) as the support after calcining at 373 K and 773 K. Results were also compared before and after using 0.5 wt % Rh/TiO\(_2\) (SG) for dry reforming reaction at 973 K. 0.5 wt % Rh/TiO\(_2\) (SG) was used because it was the most active (hence most interesting) material after the initial scanning work for N\(_2\)O decomposition (see Chapter 3). IR has also been used in-situ in many studies to investigate the nature of CO molecule adsorbed on metal surfaces. This aspect was explored in section 6.10 [14].

![FT-IR spectrum for TiO\(_2\) (SG) after calcinations at (a) 373 K and (b) 773 K.](image)

Fig. 6.2 - FT-IR spectrum for TiO\(_2\) (SG) after calcinations at (a) 373 K and (b) 773 K.

*Figure 6.2(b)* shows that after calcination at 773 K the surface groups (perhaps containing CH$_3$ and CH$_2$ bends) at 1628 and 1379 cm$^{-1}$ (see *Figure 6.2(a)*) have partially desorbed from the surface. A broad peak at 1628 cm$^{-1}$ also means that H$_2$O had adsorbed on the surface at low temperatures and gradually desorbed from the surface at the higher temperature (i.e. 773 K) [15, 19]. 1628 cm$^{-1}$ may also be due to OH deformation absorptions [16]. The peak at 1379 cm$^{-1}$ is thought to be due to *out of plane* C-H bending modes [17]. Stretching vibrations for OH species were also seen at the 4000-3000 cm$^{-1}$ region at 373 K. These groups are known to complete the coordination spheres of surface ions [18]. KBr data is not shown but gave an absorbance of 0 for all wavenumbers (cm$^{-1}$).

![Fig. 6.3 - FT-IR spectrum for 0.5 wt. % Rh/TiO$_2$ (SG) after calcinations at (a) 373 K and (b) 773 K.](image)

*Figure 6.3(b)* shows that organic species have been removed by calcination at 773 K. *Figure 6.3(a)* shows 1628 cm$^{-1}$ as residual H$_2$O after calcining at 373 K [15, 19] and 1700 cm$^{-1}$ was due to C=C stretching vibrations [20]. It is interesting to note that 1628 cm$^{-1}$ appeared for both TiO$_2$ (SG) and 0.5 wt % Rh/TiO$_2$ (SG) after calcining at 373 K (see *Figures 6.2(a) and 6.3(a)*). However the peak was much sharper in the case of 0.5 wt. % Rh/TiO$_2$ (SG). Furthermore C=C stretching vibrations (1700 cm$^{-1}$) was not observed on TiO$_2$ (SG) at 373 K but only seen for 0.5 wt. % Rh/TiO$_2$ (SG) (see *Figure 6.3(a)*).

Fig. 6.4 - FT-IR spectrum for used 0.5 wt. % Rh/TiO₂ (SG) catalyst after the dry reforming reaction at 973 K.

*Figure 6.4* shows a clean surface with no organic species present for 0.5 wt % Rh/TiO₂ (SG) catalyst that has been used in dry reforming reaction at 973 K. Organic and carbonaceous species that do not possess a change in electric dipole moment will obviously not be seen in IR, but may be seen using Raman spectroscopy (see *Section 6.3.1*). Observations from *Figures 6.2 - 6.4* were consistent with those seen in the literature for Rh and TiO₂-based catalysts [69].

6.3.1. Raman spectroscopy

This technique was discovered by the Indian physicist C.V. Raman (1888-1970) in 1928 [21]. Raman spectroscopy is a non-destructive technique that is useful for characterising materials through their vibrational spectrum. The sample is illuminated with monochromatic light (produced by a laser) and two types of light are scattered by the sample: Rayleigh and Raman. Rayleigh is scattered with exactly the same energy and wavelength as the incident light i.e. elastically scattered and constitutes most of the scatter. Raman scatter however is much less intense than Rayleigh scatter (i.e. inelastic scatter where energy is lost, and can also emerge at longer or shorter wavelengths than the incident beam). Incident photons (with frequency \(v_o\)) cause transitions in the sample and the photons gain or lose energy as a result. For a vibrational transition of frequency \(v_1\), Raman lines of frequency \(v_o \pm v_1\) appear in the scattered beam, and perpendicular to the incident beam. \(v_o + v_1\) is known as the *anti-
Stokes line and $v_0 - v_1$ is the Stokes line. Anti-Stokes scattering can only arise if the molecule is already in an excited state. Since the proportion of molecules in the excited vibrational state is much less than those in the ground state, anti-Stokes transitions are much less intense than the corresponding Stokes transition. Anti-Stokes lines are higher in energy than $v_0$ because energy is released from the excited state, and Stokes line are lower in energy than $v_0$ because some of the energy from $v_0$ has been used to promote the molecule to a vibrationally excited state. A vibrational Raman line only occurs however if the polarizability of the molecule changes during the vibration. The polarizability of the molecule is a measure of the extent to which an applied electric field (such as a photon of electromagnetic radiation) can induce an electric dipole in the molecule.

A Renishaw System 2000 using a 782 nm diode laser as the excitation source was used. At maximum power (about 13 mW) the laser irradiates an area of 0.5 $\mu$m$^2$ of the sample. However, using neutral density filters, this was attenuated to 1 % of full power to minimise damage to the sample. The system was set up to provide a spectral resolution of 4 cm$^{-1}$, and the spectra were run over either 3500 - 200 or 1800 - 200 cm$^{-1}$. 10 - 128 seconds of integration were generally sufficient to provide reasonable quality data. Raman has been known to be useful for detecting carbonaceous deposits [29-32], and hence was used here to see whether carbonaceous species can be seen on the surface after the catalysts have been used.

Analysis was carried out on the 0.5 wt % Rh/TiO$_2$ (SG) sample after Stage V (see Chapter 4) on unused material and the sample after use in catalysis of dry reforming at 973 K. The unused sample had been calcined at 773 K. Analysis was also carried out on the used and unused TiO$_2$ (SG) for comparison. The main purpose of this was to see whether carbonaceous species had accumulated on the surface during the dry reforming reaction, and also to see whether the TiO$_2$ phase ratios were affected with increasing temperature (i.e. whether anatase changed to rutile). Library spectra of rutile and anatase are shown in Figure 6.5 (run by H. Herman of University of Surrey on a Perkin Elmer System 2000 FT-Raman).
Fig. 6.5. - Raman spectra of TiO$_2$ rutile (solid line) and anatase (dotted line).

Fig. 6.6 - Raman spectrum of unused TiO$_2$ (SG) that had been pre-calcined at 773 K. This shows three anatase peaks seen in Figure 6.5.

Fig. 6.7. - Expanded Raman region showing no carbonaceous species on the surface of unused TiO\textsubscript{2} (SG) pre-calcined at 773 K. These species would be seen at \(\sim 1600\) cm\(^{-1}\) for graphitic C and 1450-1350 cm\(^{-1}\) for amorphous C (see Figure 6.9).

**Used TiO\textsubscript{2} (SG)**

Fig. 6.8. - Raman spectrum for used TiO\textsubscript{2} (SG) used in dry reforming reaction at 973 K showing that the anatase phase is still dominating but there is now also a shoulder peak (448 cm\(^{-1}\)) for rutile.

Fig. 6.9. – Expanded Raman region showing carbonaceous species (graphitic and amorphous C) on TiO$_2$ (SG) used in the dry reforming reaction at 973 K.

Fig. 6.10. – Raman spectrum of unused 0.5 wt. % Rh/TiO$_2$ (SG) (32s) revealing anatase support peaks. This is similar to unused TiO$_2$ (SG) in Figure 6.6.

**Fig. 6.13** – Expanded Raman region showing no carbonaceous species on unused 0.5 wt % Rh/TiO$_2$ (SG). This is similar to *Figure 6.7* for unused TiO$_2$ (SG).

**Fig. 6.12** – Raman spectrum of 0.5 wt. % Rh/TiO$_2$ (SG) used in dry reforming reaction at 973 K showing that its anatase phase has converted to the rutile structure to a greater extent than TiO$_2$ (SG) (see *Figure 6.8*).
Fig. 6.13. – Expanded Raman region showing presence of amorphous and graphitic C on 0.5 wt. % Rh/TiO$_2$ (SG) used in dry reforming reaction at 973 K. Interestingly these were not as clear as for TiC$^\ast$ (SG) that was used in the same reaction (see Figure 6.9).

The Raman spectra for TiO$_2$ (SG) and 0.5 wt % Rh/TiO$_2$ (SG) used in the dry reforming of CH$_4$ reaction at 973 K showed the presence of two forms of surface carbon: amorphous and graphitic carbon (see Figures 6.6 - 6.13). Amorphous carbon is without long range crystalline order. The term is restricted to the description of carbonaceous materials with localised $\pi$-electrons [22]. In addition, even though short range order exists there are deviations of the interatomic distances and bond angles with respect to the graphite and diamond lattice. Graphitic carbon is a description of the allotropic form with layers of three dimensional hexagonal crystalline long-range order, irrespective of the presence of structural defects. Graphitic and amorphous carbon assignments in Raman have been justified [30-33]. Graphitic carbon had a broad band at about 1600 cm$^{-1}$ and amorphous carbon was a broad band at about 1380 cm$^{-1}$. Surprisingly neither unused TiO$_2$ (SG) or Rh/TiO$_2$ (SG) gave any suggestion of alkoxide-derived carbonaceous impurities. However both samples exhibited the presence of amorphous and graphitic surface carbon after catalysing the dry reforming reaction at 973 K. It is interesting to note that TiO$_2$ (SG) alone allows the build up of
carbonaceous species (see Figure 6.9 and Chapter 4) more than Rh/TiO₂ (SG). This was also revealed by the lower CH₄ concentration from 523K to 973 K (see Figure 4.13(a) in Chapter 4) while no CO and H₂ were produced (see Figure 4.13(b)). Temperature programmed oxidation (TPO) would have shown carbonaceous species oxidising from the surface. This technique was not explored here. Carbonaceous species were more pronounced in the TiO₂ (SG) case because no products evolved during the reaction, whereas in the case of 0.5 wt. % Rh/TiO₂ (SG) there was significantly less C impurities because CO and H₂ as products were being formed (see Chapter 4). Further work on mass balances is required.

Regions where anatase and rutile was predominant were explored [23-29]. In addition anatase was shown to convert fully to rutile in the Rh/TiO₂ (SG) case and only partially in the TiO₂ (SG) case. XRD results supported the fact that anatase converts to the rutile structure at high temperatures (see sections 6.5 and 6.6). It therefore seems that Rh has catalysed the transformation.

6.3.2. Raman microscopy

The microscopy images were taken in the visible region using a conventional CCD camera:

![Raman microscopy of unused TiO₂ (SG)](image-url)

Fig. 6.15 — Raman microscopy of TiO$_2$ (SG) used in dry reforming reaction at 973 K.

Fig. 6.16 — Raman microscopy of unused 0.5 wt % Rh/TiO$_2$ (SG).

Raman microscopy is useful in analytical science [69]. It provides an interesting insight into the nature of the catalyst surface. In the used cases, both TiO$_2$ (SG) and 0.5 wt % Rh/TiO$_2$ (SG) exhibited sintering effects as particles coagulated together and led to the reduction of their respective surface areas (see section 6.8).

Raman spectroscopy has shown qualitatively that carbonaceous species (as graphitic and amorphous carbon) were present on the surface of both TiO$_2$ (SG) and 0.5 wt % Rh/TiO$_2$ (SG) used in dry reforming of CH$_4$ reaction at 973 K. Anatase was shown to convert to rutile at high temperatures. Anatase peaks were also seen at 639, 518 and 397 cm$^{-1}$ and rutile peaks were seen at 610 and 447 cm$^{-1}$. These were in agreement with the literature values [23-29].
6.4. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is also sometimes known as Electron Spectroscopy for Chemical Analysis (ESCA). XPS has its origins based on the photoelectric effect (discovered by Hertz in 1887) [34] although the technique itself was developed during the 1940s in Uppsala, Sweden. It is a useful technique for giving characteristic information in terms of identifying an element as a result of its binding energy (B.E.) and changes of relative concentration of surface atoms. The change in B.E. gives information about the change in oxidation states and hence whether a reaction has actually taken place. The B.E is determined from its relationship with the kinetic energy (K.E) of the ejected photoelectron and the excitation source, Al Kα (hv = 1486.6 eV). The relationship is:

\[
K.E. = h\nu - B.E - \phi_s
\]

where \( h\nu \) is the incident energy source and \( \phi_s \) is the spectrometer work function i.e. an instrumental correction factor.

The samples were therefore bombarded with monoenergetic photons of Al Kα which ejected electrons from core and valence shells in which the B.E was less than the primary photon energy. The K.E of the ejected electrons were measured and hence the B.E. was determined. The element from which the electron was ejected was identified by comparing the measured B.E. with tables of X-ray absorption data [35]. Secondly, the relative concentration of surface atoms were revealed by the intensity of the specific signals from these atoms. It was difficult to be absolutely quantitative because of the complex range of factors affecting the signal intensity, such as photoelectron cross-section, escape depth, sample orientation with respect to the collector slit, surface roughness, surface geometry, distribution of species within the sampling depth, phase homogeneity and contamination.
The analysis was carried out on the 0.5 wt. % Rh/TiO₂ (SG) catalyst using a Thermo VG Scientific Sigma Probe. Data analysis was carried out with its Avantage data system. The area of analysis was approximately 0.8 mm². The powders requiring analysis were pressed onto double sided tape on an Al disc about 10 mm in diameter. These were then held on the sample stage with spring clips. Survey spectra were collected using a pass energy of 150 eV and the high resolution spectra with a pass energy of 50 eV. The relative quantification was achieved from the high resolution spectra.

Fig. 6.18 - C₁₅ of 0.5 wt. % Rh/TiO₂ (SG) after (a) reduction at 673 K and (b) dry reforming.

Fig. 6.19 - O₁₅ of 0.5 wt % Rh/TiO₂ (SG) after (a) reduction at 673 K and (b) dry reforming.

Fig. 6.20 - Rh\textsubscript{3d}(3/2) of 0.5 wt. % Rh/TiO\textsubscript{2} (SG) after (a) reduction at 673 K and (b) dry reforming.

Fig. 6.21 - Ti\textsubscript{2p}(3/2) of 0.5 wt. % Rh/TiO\textsubscript{2} (SG) after (a) reduction at 673 K and (b) dry reforming.

Table 6.2 - XPS results for ½ wt % Rh/TiO\textsubscript{2} (SG), after correcting for C\textsubscript{1s} (284.6 eV)

<table>
<thead>
<tr>
<th>C\textsubscript{1s}</th>
<th>Rh\textsubscript{3d}</th>
<th>Ti\textsubscript{2p}</th>
<th>O\textsubscript{1s}</th>
<th>Inference</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.E. (eV)</td>
<td>284.6</td>
<td>306.8</td>
<td>458.2</td>
<td>-</td>
</tr>
<tr>
<td>rel. at. %</td>
<td>18.6</td>
<td>0.07</td>
<td>22.06</td>
<td>Rh\textsuperscript{0}, Ti\textsuperscript{4+} in pre-reduced catalyst</td>
</tr>
<tr>
<td>B.E. (eV)</td>
<td>284.6</td>
<td>309.6</td>
<td>458.6</td>
<td>-</td>
</tr>
<tr>
<td>rel. at. %</td>
<td>32.76</td>
<td>0.05</td>
<td>17.17</td>
<td>Rh\textsuperscript{3+} (Rh\textsubscript{2}O\textsubscript{3}), Ti\textsuperscript{4+} in used catalyst</td>
</tr>
</tbody>
</table>

Following reductive pre-treatment, Rh\textsuperscript{0} was shown to be present (see Table 6.2). Following dry reforming it was found to be oxidised to Rh\textsuperscript{3+}. This was thought to exist as Rh\textsubscript{2}O\textsubscript{3} on the support surface (see Chapter 7). It was also found that 0.02 relative atomic weight % (28.6±1.0 % in absolute terms) was lost during the reaction.

As anticipated there was gain in C indicating the presence of carbonaceous species on the surface (see Chapter 4, Chapter 7 and Raman results above) although it was at lower binding energy than expected. There was no change in the Ti oxidation state on reaction.

6.5. X-ray diffraction (XRD)

XRD has been used since the early part of the last century and is one of the most important and useful techniques in solid state chemistry. It is used for the fingerprint characterisation of crystalline materials and determination of their crystal structures. It can therefore show whether the material is crystalline i.e. a sample with a structure that has extensive regular order of repeating units (unit cell) and showing full symmetry of the crystal throughout, such as NaCl, or the degree of amorphocity (i.e. non-crystalline).

The technique was first discovered by von Laue in 1912 [36] and was developed for crystal analysis by W.H. and W.L. Bragg in 1913 [37]. It was realised that atoms in a crystal lattice act as diffraction gratings because the planes of atoms have spacings of a few Angstrom units, which are similar to the wavelengths of X-rays. Single crystals and powders can be used for analysis. Powders were used here because it’s the most widely used method. Figure 6.24 shows the starting point of the derivation of Bragg’s law.

![Fig. 6.22. – Starting point of the derivation of Bragg’s Law (where 1 and 2 are incident rays at angle θ, 1’ and 2’ are the reflected rays at angle θ, while A and B are rows of atoms separated by the d-spacing shown).](image)

Hence:

\[ xy = yz = d \sin \theta \]
\[ xyz = 2d \sin \theta \]

but

\[ xyz = n \lambda \]

where \( n \) is an integer number of wavelengths for constructive interference to give a diffraction peak, and is usually equal to 1.

\[ n \lambda = 2d \sin \theta \] (Bragg’s Law) (Equation 6.2)

For the angles at which \( xyz \neq n \lambda \), there will be destructive interference and the reflected rays will be cancelled out.

6.5.1. Lattice Planes and Miller indices

Lattice planes simply provide a reference grid by which atoms in a crystal plane are usually referred. They sometimes coincide with layers of atoms but this is not necessarily the case. Lattice planes can bisect a 3-dimensional \( xyz \) crystal structure through any number of fractional points \( abc \) to give any number of \( hkl \) planes. The \( hkl \) values are known as Miller indices and their derivation is shown in Figure 6.25. The plane in question cuts each of the \( x \), \( y \) and \( z \) axes at points \( a/2 \), \( b/2 \) and \( c/2 \) respectively. The fractional intersections are \( \frac{1}{2} \), \( \frac{1}{2} \) and \( \frac{1}{2} \); and their reciprocal values are \( (222) \). These integers are the \( hkl \) Miller indices of the plane and all other planes that are parallel to it and separated by the same d-spacing.

![Figure 6.23. (222) plane](image)


For orthogonal crystals where \( \alpha = \beta = \gamma = 90^\circ \), the d-spacing for any set of planes is related to the Miller indices by:

\[
\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}
\]

*(Equation 6.3)*

The equation simplifies for tetragonal crystals (i.e. \( a = b \)) and simplifies further for cubic crystals (\( a = b = c \)):

\[
\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}
\]

*(Equation 6.4)*

Now, by substituting the d-term from the Bragg equation *(equation 6.2)* into the d-spacing equation *(equation 6.3)*, and taking into account that TiC\(_2\) is tetragonal, the following expression is obtained:

\[
\frac{4\sin^2\theta}{\lambda^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}
\]

*(Equation 6.5)*

For a TiO\(_2\) (110) rutile plane, where \( 2\theta = 41.2^\circ \) and \( \lambda \) is the X-ray wavelength (1.5418 Å), the \( l^2/c^2 \) term is irrelevant since \( l = 0 \), but \( a = b = 3.10 \text{ Å} \) and d-spacing = 2.19 Å.

6.5.2. Conditions and instrument details

The diffractometer used here was a *Seifert XRD3003TT diffractometer*. Its focussing geometry is shown in *Figure 6.26*. Overnight runs were performed in an attempt to reduce the signal/noise ratio. The conditions were: monochromatic X-ray source, Cu K\( \alpha \) with \( \lambda = 1.5418 \text{ Å} \); voltage of 40 kV and a current of 30 mA; X-ray detector at 115 kV; 5 - 90° 2\( \theta \) scan range; 3.17 mm primary slit width; and a dwell time of 1 to 5 s at an angle of 0.02° 2\( \theta \) (step interval). The results were compared with files from the *Joint Committee of Powder Diffraction Standards* (JCPDS, 1998) as a library reference against unknown samples.

The main problems associated with this technique that affect the intensity of diffractograms [38] are i) polarisation effects i.e. intensity is reduced as a function of angle, ii) fluorescence, iii) multiplicities i.e. the number of reflections that may contribute to an observed powder line iv) absorption factor (i.e. X-rays may be absorbed rather than reflected) and v) scattering rather than reflection occurring.

Despite these inherent potential problems, the results obtained were reliable since standard samples like Cu and Al gave reproducible results. Nevertheless, care had to be taken to grind the samples to an extent in order to minimise the preferred orientation effects, but without compromising the intrinsic physical properties of the catalyst (see Chapter 2).
6.5.3. Rh Results

Fig. 6.25. – XRD of blank sample holder.

Fig. 6.26. – XRD profiles of SiO$_2$ and SiO$_2$-TiO$_2$ (SG). Their amorphous nature remains even after the addition of the Ni and Rh precursors (see Chapter 2 and Figures 6.27 and 6.28).

---


Fig 6.27. - XRD profiles of 0.5 wt % Ni/SiO₂ (SG) and 0.5 wt % Ni/SiO₂-TiO₂ (SG).

Fig. 6.28. – XRD profiles of 0.5 wt% Rh/SiO₂ (SG) and 0.5 wt % Rh/SiO₂-TiO₂ (SG).

Figures 6.25 – 6.28 show a broad peak at 20 = 13.8° that is associated with the sample holder and Figures 6.26 – 6.28 confirm the amorphous nature of each of the materials.
TiO$_2$ is known to principally exist in two crystallographic forms: rutile and anatase (see *Chapters 2 and 5*). Anatase is known to convert to the rutile structure at high temperatures (i.e. above 773 K). TiO$_2$ (SG) was therefore calcined (heated in a furnace in the presence of oxygen) at various temperatures. Rutile has a characteristic peak at $2\theta = 41.2^\circ$ (111) and anatase has one at $2\theta = 48^\circ$ (200) and d-spacing of 207 pm. *Figure 6.30* shows various XRD profiles of how anatase converts to rutile as the temperature increases. *Figure 6.29(a)* shows an XRD profile for pre-calcined TiO$_2$ (SG) at 973 K where $2\theta = 41.2^\circ$ and *Figure 6.29(b)* shows an XRD profile of an anatase peak for untreated TiO$_2$ (SG) at $2\theta = 48.0^\circ$. It was clear that either one or the other predominates at any given temperature.

Fig. 6.29(a) – XRD profile of a rutile peak for pre-calcined TiO$_2$ (SG) at 973 K where $2\theta = 41.2^\circ$.

Fig. 6.29(b) – XRD profile of an anatase peak seen for untreated TiO$_2$ (SG) at $2\theta = 48.0^\circ$. 
However for TiO₂ (Degussa, P25) the ratios of rutile : anatase were found to be almost 1 : 3 (i.e. rutile = 11.72 (28.87 %) and anatase = 28.86 (71.13 %)). These were in agreement with the literature values of 25 % rutile and 75 % anatase for TiO₂ (Degussa, P25) [39].

Fig. 6.30. - Effect of calcination T on TiO₂ (SG) (held for 3 h at each T) - anatase converted to the rutile structure as temperature was increased. The rutile peaks were when 2θ = 27.5° (110), 36.1° (101), 39.3° (200), 41.2° (111), 44.1° (210), 54.4° (211), 56.7° (220), 62.8° (002), 64.1° (310), 69.1° (301), 69.8° (112), 72.5° (311), 76.6° (202), 79.9° (212), 82.4° (321), 84.3° (400) and anatase peaks were at 2θ = 25.6° (101), 38.1° (004), 48.0° (200), 54.2° (105), 55.3° (211), 62.9° (204), 69.0° (116), 70.5° (220), 75.4° (215) and 82.9° (224).

Figure 6.30 shows that the principal anatase peak was at 2θ = 48.0° and the principal rutile peak was at 2θ = 41.2°, and these are shown by the lines labelled A and R respectively. Rutile peaks were also at 2θ = 27.5° (labelled as R) and an anatase peak is shown at 2θ = 25.6° (labelled as A). As expected, anatase in TiO₂ (SG) converts to rutile with increasing calcination temperature (see Figure 6.30). At low temperatures the anatase structure dominates and by 973 K rutile is already dominating (see Chapter 2). Furthermore, with an increase in temperature the amorphous TiO₂ grains become increasingly crystalline (see section 6.6). These features were also noticeable

during the catalysis work and in the presence of Rh (see Figures 6.33 and 6.34). The $E_a$ in principle may be determined with more data points.

Fig. 6.31. – XRD profile for 0.5 wt % Rh/TiO$_2$ (SG, IMP) and modified 0.5 wt % Rh/TiO$_2$ (SG, IMP). Anatase (101) at $\theta = 25.0^\circ$ changes to rutile (110) at $\theta = 27.5^\circ$ after catalysis. Rh$_2$O$_3$ peaks are not shown because they were small but seen at $\theta = 39.5^\circ$ (112), 46.3$^\circ$ (531), 62.8$^\circ$ (208) and 69.2$^\circ$ (660). At 773 K anatase dominates but at 1173 K, rutile dominates (see Figure 6.30).

Fig. 6.32. – XRD profile for 0.5 wt % Rh/TiO$_2$ (Degussa, P25, IMP). TiO$_2$ (Degussa, P25) has both anatase and rutile so their characteristic peaks are visible at $\theta = 48^\circ$ and $\theta = 41^\circ$ respectively. Anatase (A) : rutile (R) ratio is 3:1 before catalysis (as expected) and 1:1 after catalysis because anatase converts to rutile. Anatase peaks were seen before catalysis and rutile after (see Figure 6.30) and Rh$_2$O$_3$ peaks were seen as above (see Figure 6.31).

Fig. 6.33. - XRD profile for 5wt % Rh/TiO\textsubscript{2} (Degussa, P25, IMP). As before anatase, 25.0\(^\circ\) (101) and rutile, 27.5\(^\circ\) (110) was seen. Anatase (A) : rutile (R) is 3:1 before catalysis and anatase is greatly reduced after catalysis. As before Rh\textsubscript{2}O\textsubscript{3} peaks were also seen at 2\(\theta\) = 39.5\(^\circ\) (122), 46.3\(^\circ\) (531), 62.8\(^\circ\) (208) and 67.2\(^\circ\) (660) and these were in agreement with JCPDS files.

Fig. 6.34. - XRD profile for Al\textsubscript{2}O\textsubscript{3} pellets. Al\textsubscript{2}O\textsubscript{3} peaks were seen at 2\(\theta\) = 39.5\(^\circ\) (111), 45.9\(^\circ\) (200) and 66.9\(^\circ\) (220). A shoulder peak for Rh\textsubscript{2}O\textsubscript{3} was seen at 2\(\theta\) = 46.3\(^\circ\) (531) and 67.2\(^\circ\) (660) for 5 wt % Rh/Al\textsubscript{2}O\textsubscript{3} pellets (IMP).

Fig. 6.35. – XRD profile for V-Rh/Al₂O₃ pellets (see Chapter 2). The structure appears to remain the same before and after the decomposition. An Al₂O₃ peak was seen at 2θ = 66.9° (220).

Figures 6.31 – 6.33 showed anatase (A) (101) and rutile (R) (110) peaks for 0.5 wt % Rh/TiO₂ (SG), 0.5 wt % Rh/TiO₂ (SG, IMP), 0.5 wt % Rh/TiO₂ (Degussa, P25, IMP) and 5 wt % Rh/TiO₂ Degussa, P25, IMP). 0.5 wt % Rh/TiO₂ (SG, IMP) was amorphous but 0.5 wt % Rh/TiO₂ (SG) used in dry reforming at 973 K converted anatase (101) in TiO₂ (SG) to rutile (110) (see Figure 6.31). In the case of 0.5 wt % Rh/TiO₂ (Degussa, P25, IMP) and 5 wt % Rh/TiO₂ (Degussa, P25, IMP) it was shown that anatase (101) : rutile (110) ratio was 3:1 before catalysis (i.e. dry reforming) and 1:1 after dry reforming at 973 K. This was because anatase (101) was converting to rutile (110) at high temperatures (see Figures 6.32-6.33). Figure 6.34 showed that in addition to Al₂O₃ peaks, Rh₂O₃ peaks were also noted for 5 wt % Rh/Al₂O₃ pellets (IMP). The Rh₂O₃ peaks appeared as shoulder peaks to the main Al₂O₃ peaks at 2θ = 46.3° (531) and 67.2° (660). Figure 6.35 showed that there was no structural difference before and after N₂O decomposition for V-Rh/Al₂O₃ pellets (see Chapter 2). All the assigned peaks in all the XRD profiles agreed with the JCPDS files (see section 6.5.2).

6.6. X-ray diffraction line broadening (XRD LB)

XRD LB is an extension to XRD that allows for the determination of crystallite sizes \( t \) using the Debye-Scherrer equation \([40-41]\):

\[
t = \frac{K\lambda}{B \cos \theta_{\text{Bragg}}}
\]

\( (\text{equation 6.1}) \)

where \( t \) = crystallite thickness in Angstroms (Å), \( K \) = shape factor (0.893), \( \lambda \) = x-ray wavelength (1.540 Å), \( \theta \) = Bragg angle, \( B \) = line broadening measured from the full-width half-maximum (FWHM) in radians.

The experimental line broadening was corrected for the instrumental broadening using Al (as described below) by obtaining the \( B \) value from the Warren formula:

\[
B^2 = B_M^2 - B_S^2
\]

\( (\text{equation 6.2}) \)

where \( B_M \) = measured FWHM and \( B_S \) = standard FWHM.

Line broadening occurs below 0.1 μm either due to the shape of the crystallites or lattice distortions. So when \( t \) increases the line broadening is reduced. Originally, Al powder (Aldrich, 99.99 %) was considered as the standard reference material for the correction of instrumental line broadening, with a known particle size of 50 μm and \( t = 44.7 \) nm. Cu powder (Aldrich, 99 %) was found to give narrower peaks compared to Al powder with \( t = 100 \) nm. However TiO₂ (SG) calcined at 1273 K proved to be the most useful standard because it had the least broadening effect with \( t = 147.7 \) nm. Figure 6.38 shows the \( \theta - B_S \) relationship for a particular Bragg angle.

Figure 6.38 shows the \( \theta - B_S \) relationship for a particular Bragg angle.

Fig. 6.36. – XRD profile for an Al standard (2$\theta$ = 39.5° (111), 45.9° (200) and 66.9° (220)).

Fig. 6.37. – XRD profile for a Cu powder (2$\theta$ = 43.3° (111), 50.4° (200) and 74.1° (220)).

Fig. 6.38. - $\theta$-Bs relationship for standard TiO$_2$ (SG) pre-calcined at 1273 K.

The crystallite size ($t$) for standard TiO$_2$ (SG) (pre-calcined at 1273 K) was found to be 147.7 nm (see Table 6.3) and this was calculated by using the Debye-Scherrer equation (equation 6.1). The appropriate values were substituted into equation 6.1 for each Bragg angle and the average of the subsequent crystallite sizes were taken resulting in an average crystallite size of 147.7 nm.

If line broadening is due to crystallite size only, then $B_s$ is obtained simply by rearranging the Debye-Scherrer equation:

$$B_s = K_1 \lambda / t \cos \theta$$  \hspace{1cm} (equation 6.3)

If other line broadening effects like strain are present, then strain line broadening is given by

$$B_2 = k_2 \tan \theta$$  \hspace{1cm} (equation 6.4)

where $k_2$ is a constant that is proportional to the strain of the sample. If both effects are taken into consideration and added:

\[ B = B_1 + B_2 = K_1 \lambda / t \cos \theta + k_2 \tan \theta \]

\[ \Rightarrow \]

\[ B \cos \theta = K_1 \lambda / t + k_2 \sin \theta \]  \( \text{(equation 6.5)} \)

and if \( B \cos \theta \) is plotted against \( \sin \theta \), then a straight line will result with gradient \( k_2 \) and intercept \( K_1 \lambda / t \). Hence \( t \) (in Å) is obtained and if there are no strain effects then \( k_2 = 0 \) and \( k_2 > 0 \) when the effect is present. The data unfortunately gave too much scatter and so this approach was not used, and consequently it was assumed that there was negligible strain effects.

Hence, by using the Debye-Scherer equation and the correction for instrumental line broadening the \( t \) values obtained were:

Table 6.3 - Crystallite size for TiO\(_2\) (SG) after calcinations at various temperatures

<table>
<thead>
<tr>
<th>TiO(_2), SG (calcined, K)</th>
<th>( t ) (nm)</th>
<th>structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>373</td>
<td>5.30±0.1</td>
<td>amorphous</td>
</tr>
<tr>
<td>773</td>
<td>24.5±0.1</td>
<td>anatase</td>
</tr>
<tr>
<td>973</td>
<td>39.6±0.1</td>
<td>rutile</td>
</tr>
<tr>
<td>1173</td>
<td>88.7±0.1</td>
<td>rutile</td>
</tr>
<tr>
<td>1273</td>
<td>147.7±0.1</td>
<td>rutile</td>
</tr>
</tbody>
</table>

Table 6.3 shows that as temperature increases the crystallite sizes increase and hence reduce the extent of line broadening, and the structure also changes from amorphous anatase to crystalline rutile. Table 6.4 shows that the crystallite sizes obtained for TiO\(_2\) were in very good agreement with the literature value range of 10 - 20 nm [42]. Rh and Rh\(_2\)O\(_3\) could not be differentiated and therefore shown together as Rh/Rh\(_2\)O\(_3\) (for the purpose of labelling only). Rh particles appeared to be surprisingly large (27.3±0.1 nm) which was as large as TiO\(_2\) particles. This was unusual and may have been caused by the effects of sintering at 973 K.

Table 6.4. - Crystallite size (nm) for TiO$_2$ samples

<table>
<thead>
<tr>
<th>Material</th>
<th>anatase</th>
<th>rutile</th>
<th>Rh/Rh$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 wt % Rh/TiO$_2$ (Degussa, P25, IMP)</td>
<td>29.2±0.1</td>
<td>33.2±0.1</td>
<td>25.0±0.1</td>
</tr>
<tr>
<td>½ wt % Rh/TiO$_2$ (Degussa, P25, IMP)</td>
<td>21.3±0.1</td>
<td>29.0±0.1</td>
<td>27.3±0.1</td>
</tr>
<tr>
<td>TiO$_2$ (Degussa, P25)</td>
<td>29.6±0.1</td>
<td>26.3±0.1</td>
<td>-</td>
</tr>
<tr>
<td>½ wt % Rh/TiO$_2$ (SG)</td>
<td>15.9±0.1</td>
<td>22.3±0.1</td>
<td>23.8±0.1</td>
</tr>
<tr>
<td>½ wt % Rh/TiO$_2$ (SG, IMP)</td>
<td>9.6±0.1</td>
<td>-</td>
<td>13.7±0.1</td>
</tr>
<tr>
<td>TiO$_2$ (SG), calcined 773 K</td>
<td>24.5±0.1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.5. - Crystallite size (nm)

<table>
<thead>
<tr>
<th>Material</th>
<th>Al</th>
<th>Al$_2$O$_3$</th>
<th>Rh/Rh$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 wt % Rh/Al$_2$O$_3$ (pellets, IMP)</td>
<td>-</td>
<td>10.0±0.1</td>
<td>7.3±0.1</td>
</tr>
<tr>
<td>Al$_2$O$_3$ pellets</td>
<td>-</td>
<td>7.8±0.1</td>
<td>-</td>
</tr>
<tr>
<td>Al powder</td>
<td>44.7±0.1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

6.7. Scanning Electron Microscopy (SEM and EDAX)

SEM is a useful technique for giving detailed information about surface morphology, topology and material composition. Figure 6.39 shows schematically how the technique works.

**Fig. 6.39.** - Schematic diagram of SEM set-up and principles of related techniques [43].


The incident beam is usually produced by high energy electrons at the cathode of a W filament (thermoionic emission). These electrons are accelerated via a potential energy of 20 keV, \( \lambda = 0.8 \) pm and focussed on the sample through a series of condenser lenses. The SEM images were scanned by an *Hitachi 3200 N* instrument with a variable pressure (VP) microscope attached. Samples were mounted on specimen stubs and non-conducting materials were Au-coated prior to examination. Images, known as micrographs were monitored at 100 and 500 times the magnification. *Energy dispersive analysis of X-ray* (EDAX) spectra and *electron dot maps* were taken where appropriate. EDAX considers the characteristic X-rays produced from ionised electrons of inner core-shells and electron dot maps gives a profile (from 100 count scans) that indicates likelihood of surface elements. The greater the relative counts the higher the ratio of the element on the surface in comparison to other elements. These techniques are semi-quantitative (in terms of providing relative atomic ratios) but are useful when coupled with SEM.

Secondary electrons are specimen electrons that obtain energy by inelastic collisions with beam electrons. They are defined as electrons emitted from the specimen with energy less than 50 eV. Secondary electrons are predominantly produced by the interactions between energetic beam electrons and weakly bonded conduction-band electrons in metals or the valence electrons of insulators and semiconductors. There is a great difference between the amount of energy contained by beam electrons compared to the specimen electrons and because of this, only a small amount of kinetic energy can be transferred to the secondary electrons.

6.7.1. Elastic Scattering of Primary Electrons

Elastic scattering results in little (<1 eV) or no change in energy of the scattered electron, although there is a change in momentum. Since momentum, \( p = mv \) (m = mass and \( v = \) velocity), and m doesn't change, the direction of the velocity vector must change. The angle of scattering can range from 0-180°, with a typical value being about 5°. Elastic scattering occurs between the negative electron and the positive nucleus. This is essentially Rutherford scattering. Sometimes the angle is
such that the electron comes back out of the sample. These are back scattered electrons.

6.7.2. Inelastic Scattering

During inelastic scattering, energy is transferred to the electrons surrounding the atoms and the kinetic energy of the energetic electron involved decreases. A single inelastic event can transfer various amounts of energy from the beam electron ranging from a fraction to many keV. The main processes include phonon excitation, plasmon excitation, secondary electron excitation, continuous X-ray generation, and ionization of inner shells. In all processes of inelastic scattering, energy is lost, though different processes lose energy at varying rates.

6.7.3. Results

Acid-etched (HNO₃ treatment, 3 M) Al₂O₃ ceramic foams (CF; see Chapter 2) became more disordered and showed disfigured arrays on their surfaces as if structural collapse had occurred. Untreated material looked more ordered and symmetrical. There was EDAX proof that Al₂O₃ was on the surface (see Figure 6.42). The first figure in each case shows a scale of 500 µm width which is then magnified to 100 µm.

Fig. 6.40. – SEM images of untreated Al₂O₃ CF at (a) x100 and (b) x500 magnification.

Fig. 6.41. – SEM images of treated $\text{Al}_2\text{O}_3$ CF at (a) x100 and (b) x500 magnification.

Fig. 6.42. – EDAX of $\text{Al}_2\text{O}_3$ CF, showing that only Al and O (as expected) is on the surface.

Fig. 6.43. – SEM images of 0.5 wt. % Rh/TiO$_2$ (SG-100 %)/Al$_2$O$_3$ (CF); – a significant level of flaking is seen on the surface.

Fig. 6.44. – SEM images of unused 0.5 wt. % Rh/TiO$_2$ (SG-80 %)/Al$_2$O$_3$ (CF) where some channels look blocked.

Fig. 6.45. – SEM images of 0.5 wt. % Rh/TiO$_2$ (SG-80 %)/Al$_2$O$_3$ (CF) used in N$_2$O decomposition at 973 K. The channels seem to have cleared.

Fig. 6.46. – SEM images of unused 0.5 wt. % Rh/TiO$_2$ (SG-30 %)/Al$_2$O$_3$ (CF). The channels seem clearer than 0.5 wt. % Rh/TiO$_2$ (SG-80 %)/Al$_2$O$_3$ (CF) used in N$_2$O decomposition at 973 K (see Figure 6.45).

Fig. 6.47. - SEM image and elemental maps for $\frac{1}{2}$ wt % Rh/TiO$_2$ (SG) unused. Full width = 100 $\mu$m

Fig. 6.48. – EDAX of unused 0.5 wt. % Rh/TiO$_2$ (SG) showing TiO$_2$ and Rh on the surface

In the case of used ceramic foam samples, the SEM pictures and EDAX profile were very similar indicating that much of the original Rh was retained on the surface.

Fig. 6.49. - SEM image and elemental maps for 5 wt % Rh/Al$_2$O$_3$ (pellets IMP). Full width = 100 µm
Fig. 6.50. - EDAX of unused 5 wt % Rh/Al₂O₃ (pellets IMP) showing Rh and Al₂O₃ on the surface.

Fig. 6.51. - SEM image and elemental maps for white 5 wt % Rh/Al₂O₃ (pellets IMP) after the 3rd use by SSTL for N₂O decomposition (see Chapter 3). Full width = 100 μm.

6.8. Texture - BET

In order to determine a catalyst's total surface area (see Chapter 2), the BET technique was used. This idea was developed by S. Brunauer, P.H. Emmett and E. Teller in 1938 [44]. Typically, N\textsubscript{2} physisorption [45] is conducted on the surface at 77 K and this results in a profile known as an adsorption isotherm. Overall five types of profiles exist depending on the types of pores (see Figures 6.55 and 6.56). Most heterogeneous catalysts are porous solids and the nature of the pores i.e. size, shape and volume, depends on the preparation methods used (see Chapter 2). Pores can be cylindrical and of uniform size, ink-bottle shaped (where the pore mouth is smaller than the pore body), funnel shaped (the contrary) or slit shaped. They can also be through (open at both ends), blind (open only at one end) or closed (no openings and therefore inaccessible from the outside). Often the catalyst is made up of many different types of pores that are all interconnected throughout the whole sample, forming a porous network that enables the catalyst to have very large surface areas (typically 10 – 1000 m\textsuperscript{2}/g compared to 0.01 – 10 m\textsuperscript{2}/g for the external area).
The pores are classified (depending on pore size) as *microporous* \((x < 2 \text{ nm})\), *mesoporous* \((2 < x < 50 \text{ nm})\) and *macroporous* \((x > 50 \text{ nm})\) where \(x\) is the characteristic pore size in a direction that is perpendicular to the motion of the molecules during the filling of the pores [46-52]. Most catalysts contain pores of various sizes, so *pore size distribution* (PSD) was considered (i.e. pore volume against pore size).

The BET method mathematically takes the form:

\[
p/V(p_0-p) = (1/V_mC) + [(C-1)p/p_0]/V_mC
\]

If the data is represented by this equation, a linear relationship is found when \(p/V(p_0-p)\) is plotted against \(p/p_0\), and the values of \(V_m\) and \(C\) are obtained from the slope and the intercept of the line respectively. The value of \(C\) is usually expressed as:

\[
C = \exp.[(H_L-H_1)RT]
\]

where \(H_1\) is the *enthalpy of adsorption of the first layer* and \(H_L\) is the *enthalpy of formation of further layers*. \(R\) is simply the *ideal gas constant* and \(T\) is of course the *temperature* (in K). Once the value for \(V_m\) is known, the *total surface area* \(S_{\text{total}} = \text{m}^2 \text{g}^{-1}\) can be calculated from:

\[
S = \left(\frac{V_m}{22414}\right) \times (L.A.10^{18})
\]

where \(A\) is the cross-sectional area of \(N_2\) \((0.162 \text{ nm}^2)\) and \(L\) is the Avogadro’s constant \((6.023 \times 10^{23})\). It gave information with regards to a materials surface area \(S_{\text{BET}}\) and *pore size distribution* (PSD). As mentioned above there are five types of BET isotherms [53-54].
Fig. 6.53. – IUPAC classification of the five types of BET isotherms [53]

For many years Type I isotherm used to be thought of as showing the limiting value ($n_s$) corresponding to a monolayer coverage ($\theta = 1$) in accordance with the Langmuir theory (see Chapter 2) [55]. It is now thought to be representative of adsorption on a typical microporous solid, where the limiting value is controlled by the pore volume [52]. The isotherm is reversible and concave to the relative pressure ($p/p_0$) axis and the adsorption, $n$, reaches the limiting value as $p/p_0 \rightarrow 1$.

Type II isotherms are reversible and characteristic of non-porous or macroporous solids or unrestricted monolayer-multilayer adsorption. The uptake at point $B$ provides a measure of the monolayer capacity.

Isotherms of Types III and V are not common and their theoretical basis is not well understood. Their adsorbent-adsorbate interaction is weak, and at high $p/p_o$ there is limited pore filling for Type V.

Type IV isotherms however are of immense interest and many industrial catalysts are of this type. Isotherms of this type are mostly associated with mesoporous solids and are likely to display a hysteresis loop i.e. the adsorption and desorption curves follow different paths due to the secondary process of capillary condensation. This means that a molecule evaporating from a highly curved surface is more likely to recondense than one evaporating from a plane surface.

Fig. 6.54. – Type IV isotherms showing the possible hysteresis loops formed from either cylindrical pores (type A), slit shaped (type B) or "ink-bottle" shaped pores (type E) [53].

The instrument used was a “micromeritics” ASAP 2000 model, using ASAP 2010 software. It was equipped with burettes that allowed sample analysis. Prior to analysis the empty burettes were outgassed (10 h) and weighed. The sample (10 – 30 mg) was then placed into the clean and outgassed burette and re-weighed. The burette (containing the sample) was outgassed and weighed once again before being transferred to the analysis port (6 – 8 h). The burette was re-weighed after the analysis and the data was saved. The sample was then discarded and the burette was cleaned, dried and outgassed in preparation for the next analysis. The profiles are shown as volume of N\textsubscript{2} adsorbed (cm\textsuperscript{3}/g) against relative pressure (p/p\textsubscript{o}) for surface areas and pore volume (cm\textsuperscript{3}/g) against pore diameter (nm) for pore size distribution (PSD).

A Si-Al standard with a surface area of 217± 6 m\textsuperscript{2}/g was provided by Micromeritics for calibration of the ASAP 2000. This standard ensured that the instrument was working effectively within its limits. The standard was run three times and the average S\textsubscript{BET} of 217 m\textsuperscript{2}/g was in excellent agreement with expected values. TiO\textsubscript{2} (Degussa, P25) catalysts were difficult to classify. It is thought that they may be Type II isotherms but Point B is not easily identifiable (very low p/p\textsubscript{o}) and there is N\textsubscript{2} uptake at considerably high p/p\textsubscript{o}. This was probably because they exist as ultra-fine powders (see Figures 6.63, 6.66, 6.70, 6.75 and 6.77).

6.8.1. Si-Al standard

Fig. 6.55. - First $\text{N}_2$ adsorption data at 77 K for a silica-alumina standard ($220\pm 1 \text{ m}^3/\text{g}$, Type IV(A) isotherm with cylindrical pores) and the derived pore-size distribution.

Fig. 6.56. - Second $\text{N}_2$ adsorption data at 77 K for a silica-alumina standard ($224\pm 1 \text{ m}^3/\text{g}$) and the derived pore size distribution.

Fig. 6.57. - Third $\text{N}_2$ adsorption data at 77 K for a silica-alumina standard ($208\pm 1 \text{ m}^3/\text{g}$) and the derived pore size distribution.
An analysis was also carried out using an empty BET burette in order to make sure that the instrument was working properly. As expected the surface area was found to be 0 m$^2$/g.

6.8.2. Results for TiO$_2$ based samples

![Graph](image1)

**Fig. 6.58.** – N$_2$ adsorption data for TiO$_2$ (SG) (pre-heated to only 298 K) at 77 K (603± 1 m$^2$/g, Type IV(E) isotherm (ink bottle)) and derived pore size distribution.

![Graph](image2)

**Fig. 6.59.** – N$_2$ adsorption data at 77 K for TiO$_2$ (SG), pre-calcined at 373 K (563± 1 m$^2$/g, Type IV(E) isotherm (ink bottle)) and derived pore size distribution.

Fig. 6.60. – N\textsubscript{2} adsorption data at 77 K for TiO\textsubscript{2} (SG), pre-calcined at 523 K (344± 1 m\textsuperscript{2}/g, Type IV(E) isotherm (ink bottle)) and derived pore size distribution.

Fig. 6.61. – N\textsubscript{2} adsorption data at 77 K for TiO\textsubscript{2} (SG), pre-calcined at 773 K (72.2± 1 m\textsuperscript{2}/g, Type IV(E) isotherm (ink bottle)) and derived pore size distribution.

Fig. 6.62. – N\textsubscript{2} adsorption data at 77 K for TiO\textsubscript{2} (SG), pre-calcined at 973 K (0.19± 0.1 m\textsuperscript{2}/g) and derived pore size distribution.

Samples that were calcined at 1173 and 1273 K showed very low surface areas due to structure collapse and sintering of TiO\textsubscript{2} particles.
6.8.3. Results for supports before catalysis

As described in Chapters 3 and 4, TiO₂ (SG) was used as the support after being calcined at 773 K because the catalysis work involved pre-treatment at 723 K. Therefore the BET profile for TiO₂ (SG) was the same as in Figure 6.61 above. The surface area of TiO₂ (Degussa, P25, see Figure 6.63) was in agreement with the commercially quoted value of 48 m²/g [56].

![Figure 6.63](image1.png)

**Fig. 6.63.** - N₂ adsorption data at 77 K for TiO₂ (Degussa P25) before catalysis (52± 1 m²/g, Type II isotherm) and derived pore size distribution.

![Figure 6.64](image2.png)

**Fig. 6.64.** - N₂ adsorption data at 77 K for Al₂O₃ pellets before catalysis (213± 1 m²/g, Type IV(A) isotherm (cylindrical)) and derived pore size distribution.

6.8.4. Results for supports after catalysis

Fig. 6.65. – N₂ adsorption data at 77 K for TiO₂ (SG) after catalysis (10±1 m²/g; structure collapse has led to reduced surface area) and derived pore size distribution.

Fig. 6.66. – N₂ adsorption data at 77 K for TiO₂ (Degussa, P25) after catalysis (61±1 m²/g, type II isotherm) and derived pore size distribution.

Fig. 6.67. – N₂ adsorption data at 77 K for Al₂O₃ pellets after catalysis (214±1 m²/g, type IV(A) isotherm (cylindrical)) and derived pore size distribution.
6.8.5. Results for catalysts before reaction

Fig. 6.68. - N\textsubscript{2} adsorption data at 77 K for 0.5 wt % Rh/TiO\textsubscript{2} (SG) after 773 K before catalysis (80±1 m\textsuperscript{2}/g, Type IV(A) isotherm (cylindrical)) and derived pore size distribution.

Fig. 6.69. - N\textsubscript{2} adsorption data at 77 K for 0.5 wt % Rh/TiO\textsubscript{2} (SG, IMP) before catalysis (563±1 m\textsuperscript{2}/g, Type IV(E) isotherm (ink bottle)) and derived pore size distribution.

Fig. 6.70. - N\textsubscript{2} adsorption data at 77 K for 5 wt % Rh/TiO\textsubscript{2} (Degussa, P25) before catalysis (37±1 m\textsuperscript{2}/g, Type II isotherm) and derived pore size distribution.

Fig. 6.71 - N$_2$ adsorption data at 77 K for 5 wt. % Rh/Al$_2$O$_3$ pellets (IMP) before catalysis (210± 1 m$^2$/g, Type IV(A) isotherm (cylindrical)) and derived pore size distribution.

Fig. 6.72. – N$_2$ adsorption data at 77 K for Vadim-Rh/Al$_2$O$_3$ (165± 1 m$^2$/g, Type IV(B) isotherm (slit shaped)) and derived pore size distribution.

6.8.6. Results for used catalysts

Fig. 6.73. – N$_2$ adsorption data at 77 K for 0.5 wt. % Rh/TiO$_2$ (SG) used in dry reforming at 973 K (4.7±1 m$^2$/g, Type III isotherm) and derived pore size distribution.

Fig. 6.74. – N$_2$ adsorption data at 77 K for 0.5 wt. % Rh/TiO$_2$ (SG, IMP) used in dry reforming at 973 K (96±1 m$^2$/g, Type IV(E) isotherm (ink bottle)) and derived pore size distribution.

Fig. 6.75. – N$_2$ adsorption data at 77 K for 0.5 wt. % Rh/TiO$_2$ (Degussa, P25) used in dry reforming at 973 K (33±1 m$^2$/g, Type II isotherm) and derived pore size distribution.

Fig. 6.76. – N$_2$ adsorption data at 77 K for 5 wt. % Rh/Al$_2$O$_3$ pellets (IMP) used in dry reforming at 973 K (230.8±1 m$^2$/g, Type IV(A) isotherm (cylindrical)) and derived pore size distribution.

Fig. 6.77. – N₂ adsorption data at 77 K for 5 wt. % Rh/TiO₂ (Degussa, P25) used in dry reforming at 973 K (23.4± 1 m³/g, Type II isotherm) and derived pore size distribution.

Table 6.6 provides a summary of textural data:

Table 6.6. – Textural data

<table>
<thead>
<tr>
<th>Material</th>
<th>S_{BET} (m² g⁻¹)</th>
<th>mean pore diameter (nm)</th>
<th>total pore volume (cm³ g⁻¹)</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>St. 1</td>
<td>220± 1</td>
<td>15± 1</td>
<td>0.62± 0.01</td>
<td>132± 1</td>
</tr>
<tr>
<td>St. 2</td>
<td>224± 1</td>
<td>13± 1</td>
<td>0.62± 0.01</td>
<td>135± 1</td>
</tr>
<tr>
<td>St. 3</td>
<td>208± 1</td>
<td>15± 1</td>
<td>0.63± 0.01</td>
<td>141± 1</td>
</tr>
<tr>
<td>TiO₂(SG)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298 K</td>
<td>603± 1</td>
<td>3.7± 1</td>
<td>0.33± 0.01</td>
<td>40.3± 1</td>
</tr>
<tr>
<td>373 K</td>
<td>563± 1</td>
<td>2.2± 1</td>
<td>0.43± 0.01</td>
<td>40.6± 1</td>
</tr>
<tr>
<td>523 K</td>
<td>344± 1</td>
<td>15± 1</td>
<td>0.22± 0.01</td>
<td>45.1± 1</td>
</tr>
<tr>
<td>773 K</td>
<td>72.2± 1</td>
<td>3.7± 1</td>
<td>0.32± 0.01</td>
<td>40.3± 1</td>
</tr>
<tr>
<td>973 K</td>
<td>0.19± 0.1</td>
<td>7.8± 1</td>
<td>&lt;0.01± 0.01</td>
<td>-</td>
</tr>
<tr>
<td>1173 K</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1273 K</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Supports</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂(SG)</td>
<td>72.2± 1</td>
<td>3.7± 1</td>
<td>0.32± 0.01</td>
<td>40.3± 1</td>
</tr>
<tr>
<td></td>
<td>(10± 1)</td>
<td>(3.2± 1)</td>
<td>(0.0012)</td>
<td>(-57.6± 1)</td>
</tr>
<tr>
<td>TiO₂(P25)</td>
<td>52± 1</td>
<td>2.8± 1</td>
<td>0.42± 0.01</td>
<td>103± 1</td>
</tr>
<tr>
<td></td>
<td>(61± 1)</td>
<td>(2.6± 1)</td>
<td>(0.37± 0.01)</td>
<td>(219± 1)</td>
</tr>
<tr>
<td>Al₂O₃(pellets)</td>
<td>213± 1</td>
<td>11± 1</td>
<td>0.50± 0.01</td>
<td>101± 1</td>
</tr>
<tr>
<td></td>
<td>(214± 1)</td>
<td>(12± 1)</td>
<td>(0.54± 0.01)</td>
<td>(153± 1)</td>
</tr>
<tr>
<td>Catalyst</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>80± 1</td>
<td>7.2± 1</td>
<td>0.21± 0.01</td>
<td>92± 1</td>
</tr>
<tr>
<td></td>
<td>(4.7± 1)</td>
<td>(8± 1)</td>
<td>(0.1± 0.01)</td>
<td>(-26.2± 1)</td>
</tr>
<tr>
<td>2</td>
<td>563± 1</td>
<td>18± 1</td>
<td>0.36± 0.01</td>
<td>38.2± 1</td>
</tr>
<tr>
<td></td>
<td>(96± 1)</td>
<td>(3.9± 1)</td>
<td>(0.2± 0.01)</td>
<td>(88.9± 1)</td>
</tr>
<tr>
<td>3</td>
<td>46± 1</td>
<td>2.8± 1</td>
<td>0.47± 0.01</td>
<td>64.7± 1</td>
</tr>
<tr>
<td></td>
<td>(33± 1)</td>
<td>(3± 1)</td>
<td>(0.35± 0.01)</td>
<td>(213± 1)</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Material</th>
<th>(S_{\text{BET}}) (m(^2)g(^{-1}))</th>
<th>mean pore diameter (nm)</th>
<th>total pore volume (cm(^3)g(^{-1}))</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>210±1</td>
<td>13±1</td>
<td>0.50±0.01</td>
<td>109±1</td>
</tr>
<tr>
<td>(231±1)</td>
<td></td>
<td>(17.5±1)</td>
<td>(0.68±0.01)</td>
<td>(312±1)</td>
</tr>
<tr>
<td>5</td>
<td>37±1</td>
<td>12±1</td>
<td>0.12±0.01</td>
<td>92.4±1</td>
</tr>
<tr>
<td>(23.4±1)</td>
<td></td>
<td>(13±1)</td>
<td>(0.26±0.01)</td>
<td>(-120±1)</td>
</tr>
<tr>
<td>6</td>
<td>103±1</td>
<td>16.5±1</td>
<td>0.12±0.01</td>
<td>92.4±1</td>
</tr>
<tr>
<td>(48.4±1)</td>
<td></td>
<td>(18±1)</td>
<td>(0.12±0.01)</td>
<td>(133.4±1)</td>
</tr>
<tr>
<td>7</td>
<td>165±1</td>
<td>8.0±1</td>
<td>0.45±0.01</td>
<td>119.4±1</td>
</tr>
</tbody>
</table>

where \(S_{\text{BET}}\) is the total surface area, St. 1, St. 2 and St. 3 = silica-alumina standard provided by Micromeritics for ASAP 2000 instrument; 1 = 0.5 wt. % Rh/TiO\(_2\) (SG), 2 = 0.5 wt. % Rh/TiO\(_2\) (SG, IMP), 3 = 0.5 wt. % Rh/TiO\(_2\) (Degussa, P25, IMP), 4 = 5 wt. % Rh/Al\(_2\)O\(_3\) pellets (IMP), 5 = 5 wt. % Rh/TiO\(_2\) (Degussa, P25, IMP), 6 = commercial Shell 405 (36 wt. % Ir/Al\(_2\)O\(_3\) pellets) and 7 = V-Rh/Al\(_2\)O\(_3\). Values quoted are before catalysis and brackets show results after catalysis. The \(C\) value is a constant that indicates adsorbate-adsorbent interaction.

Figures 6.55 – 6.57 show that for Si-Al standard the surface area (\(S_{\text{BET}}\)) was in excellent agreement with the expected value of 217± 6 m\(^2\)g\(^{-1}\). The total pore volume (TPV) was constant at about 0.62± 0.01 cm\(^3\)g\(^{-1}\) and mean pore diameter was about 15 nm (see Table 6.6). Therefore the Micromeritics ASAP 2000 was working properly.

For TiO\(_2\) (SG) support the \(S_{\text{BET}}\) was found to be decreasing as calcination temperature increased (see Figures 6.58 – 6.62). Similarly the TPV also decreased as temperature increased (see Table 6.6). TiO\(_2\) (SG) and TiO\(_2\) (Degussa, P25) also witnessed a similar trend in the sense that \(S_{\text{BET}}\) and TPV decreased after catalysis (i.e. \(S_{\text{BET}}\) and TPV were higher prior to catalysis). There was an exception for Al\(_2\)O\(_3\) pellets which had both \(S_{\text{BET}}\) and TPV increase slightly after catalysis (see Table 6.6).

A similar trend was followed by all the catalysts (i.e. \(S_{\text{BET}}\) and TPV decreased after catalysis) except in the case of 5 wt % Rh/Al\(_2\)O\(_3\) pellets (IMP) where \(S_{\text{BET}}\) and TPV increased after catalysis (see Table 6.6). It was also noted that in the case of 5 wt % Rh/TiO\(_2\) (Degussa, P25, IMP), \(S_{\text{BET}}\) decreased but TPV increased after catalysis.

6.9. Ir results

6.9.1. XRD and XRD LB

Fig. 6.78. – XRD profile for 36 wt % Ir/Al₂O₃ (Shell 405). Before N₂O decomposition the structure was mostly amorphous with broad peaks for Ir when 2θ = 40.1° (200) and two broad Al peaks at 2θ = 45.9° (200) and 66.9° (220). After N₂O decomposition the structure was crystalline and IrO₂ was seen at 2θ = 28.1° (110, 34.7° (101), 40.1° (200), 45.0° (211), 54.0° (211), 58.5° (473), 66.1° (112), 69.3° (30.) and 73.2° (202).

Figure 6.78 shows the amorphous nature of Shell 405 before N₂O decomposition and its crystalline nature after the decomposition.

Table 6.7. – Crystallite sizes (nm) of commercial Shell 405 (36 wt. % Ir/Al₂O₃ pellets)

<table>
<thead>
<tr>
<th></th>
<th>Al₂O₃</th>
<th>Ir</th>
<th>IrO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before N₂O decomposition</td>
<td>8.2±0.1</td>
<td>1.7±0.1</td>
<td>-</td>
</tr>
<tr>
<td>After N₂O decomposition</td>
<td>-</td>
<td>74.0±0.1</td>
<td>31.8±0.1</td>
</tr>
</tbody>
</table>

Table 6.7 shows that the crystallite size of Ir in Shell 405 increases dramatically after N₂O decomposition perhaps due to the effects of sintering (see SEM/EDAX results in section 6.9.3).

6.9.2. BET

Fig. 6.79. - N₂ adsorption data at 77 K for Shell 405 before catalysis (103±1 m²/g, Type IV(B) isotherm (slit shaped)) and derived pore size distribution.

Fig. 6.80. - N₂ adsorption data at 77 K for Shell 405 (36 wt. % Ir/Al₂O₃) used in N₂O decomposition at 973 K (48.4±1 m²/g, distorted Type IV(B) isotherm (slit shaped)) and derived pore size distribution.

Figures 6.79 – 6.80 showed that S_{BET} decreased from 103±1 to 48.4±1 m²/g⁻¹ for Shell 405 during N₂O decomposition. The total pore volume however remained the same and the mean pore diameter slightly increased from 16.5±1 to 18±1 nm.

6.9.3. SEM/EDAX

Fig. 6.81. - SEM data and elemental maps for unused Shell 405. Full width = 100 µm

Fig. 6.82. - EDAX of unused Shell 405 showing Al₂O₃ and Iₗ on the surface.

Fig. 6.83. - SEM data and elemental maps for spent Shell 405. Full width = 100 μm

Fig. 6.84. – EDAX of used Shell 405 showing Al₂O₃ on the surface and displaced Ir.

SEM and EDAX profiles of Shell 405 clearly show that Ir has been displaced from the surface and that sintering had occurred (see Figure 6.83). This has resulted in the reduction of surface area and subsequent inactivity. It was found that 50±5 % Ir was lost from the Al₂O₃ support surface during N₂O decomposition (see EDAX results in Figures 6.82 and 6.84).

6.10. Surface activity by CO as a probe molecule

*In-situ*-IR spectroscopy has been successfully used for many years to study adsorbed species on catalyst surfaces. CO as probe molecules are the most extensively studied. Its interaction with transition metal (TM) surfaces like Rh can be understood by the Blyholder model [57-58]. Only the frontier orbitals of CO are involved with a dₓ metal orbital in the two step process: the 3σ highest occupied molecular orbital (HOMO) and the anti-bonding 2π* lowest unoccupied molecular orbital (LUMO) are involved sequentially. A charge transfer from the 3σ orbital to the unoccupied metal orbitals is followed by back-donation from dₓ metal orbitals to the 2π* LUMO of CO. This mechanism is therefore referred to as the σ donation - π back-donation, where the completely filled 3σ orbital becomes partially empty, and the empty 2π* orbitals become partially filled.

*Figure 6.85* shows the molecular orbital (MO) diagram for CO. The 3σ HOMO and 2π* LUMO are labelled and these interact with the metal d orbitals (see Chapter 2). The CO molecular orbital is generated from the linear combination of atomic orbitals (LCAO) due to similar symmetry and energy of the respective 1s, 2s and 2p atomic orbitals of the constituent elements C and O [59].

Various IR techniques can be used for this purpose. Examples include the use of a transmission cell, diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) and reflection-absorption (RAIRS). Here the transmission cell mode (see Figure 6.86) was used and it was carefully mounted on the FTIR spectrophotometer described at *section 6.2*. The IR beam passes through thin wafer-samples (KBr) at 423 and 773 K in the presence of CO (6 % in N₂) atmosphere. As before the fraction of transmitted IR radiation is converted to absorbance and plotted against wavenumbers.

(cm$^{-1}$). A blank sample was run with nothing passing through the IR cell. CO as a background was also recorded. The analysis was carried out on TiO$_2$ (SG) and 0.5 wt % Rh/TiO$_2$ (SG) after being exposed to a CO atmosphere for 30 minutes. The CO atmosphere was switched to N$_2$ prior to analysis.

Fig. 6.85. – MO diagram for CO showing the 3σ HOMO and 2π LUMO frontier orbitals [59].

It is known that CO forms terminal (linear) and bridged bonds with Rh [60-63]. Bridged CO normally appears between the region 2000-1930 cm$^{-1}$ and 2120 – 2090 cm$^{-1}$ for terminal CO. Unfortunately no absorbance was seen in these regions but an absorbance peak was seen at 1622 cm$^{-1}$ for TiO$_2$ (SG) at 423 K (see Figure 6.89(a)) and at 1627 cm$^{-1}$ for 0.5 wt. % Rh/TiO$_2$ (SG) at 423 K (see Figure 6.90(a)). In both cases, the peaks in question were not observed at the higher temperature of 773 K (see Figures 6.89(b) and 6.90(b)). It is generally known that IR absorption occurring in the broad region 2100-1600 cm$^{-1}$ is associated with the CO stretching mode. It is thought that CO was loosely bound on the surface at 423 K and broke away from the surface as the temperature was increased to 773 K. Gaseous CO stretch is seen at 2143 cm$^{-1}$ and this was seen during analysis for CO as background (see Figure 6.88).

Fig. 6.86. - a schematic diagram showing a transmission cell for in situ-FTIR, where 1 = CaF$_2$ windows, 2 = sample, 3 = furnace, 4 = CaF$_2$ plate, 5 = gas convection shield, 6 = thermocouple, 7 = heating wire and 8 = connection to the gas lines [64-66].

Fig. 6.87. - *In-situ* FTIR spectrum with nothing passing through the transmission cell.

Fig. 6.88. - *In-situ* FT-IR spectrum for CO atmosphere as background. 2143 cm\(^{-1}\) is gaseous CO and 2360 cm\(^{-1}\) was due to residual CO\(_2\) as a result of some CO oxidation.

Fig. 6.89. - *In-situ* FT-IR spectrum during CO/N\(_2\) for TiO\(_2\) (SG) at (a) 423 K and (b) 773 K.

Fig. 6.90. - *In-situ* FT-IR spectra during CO/N\(_2\) for 0.5 wt. % Rh/TiO\(_2\) (SG) at (a) 423 K and (b) 773 K.

The broad peaks at 1622 cm\(^{-1}\) for TiO\(_2\) (SG) at 423 K (see Figure 6.89(a)) and 1627 cm\(^{-1}\) for 0.5 wt % Rh/TiO\(_2\) (SG) at 423 K (see Figure 6.90(a)) are thought to be associated with loosely bound CO on the support surface [67]. These observations mean that TiO\(_2\) (SG) and 0.5 wt % Rh/TiO\(_2\) (SG) adsorb CO at 423 K but this desorbs from the surface at 773 K (see Figures 6.89(b) and 6.90(b)).

6.11. References


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CHAPTER VII

Discussion.

7.1. Summary

In the early stages of this work it was shown that Ni/SiO$_2$-TiO$_2$ (SG) and Rh/SiO$_2$-TiO$_2$ (SG) were ineffective in N$_2$O decomposition (see Chapter 3). This is because SiO$_2$-TiO$_2$ was too stable as a support (i.e. there was no metal-support interaction) [1]. From earlier work (not described here), it was known that SiO$_2$ could increase the total surface area ($S_{BET}$) of TiO$_2$ (see Chapter 2) but it also limited vacancy concentrations at the surface of the mixed oxide. These could have opposing effects on the activity of TiO$_2$. Therefore TiO$_2$ alone and TiO$_2$-supported catalysts did show some activity towards N$_2$O decomposition. TiO$_2$ had the ability to be an effective support for catalysts and also be an effective photocatalyst. This is largely due to its intrinsic property of being a semi-conductor (i.e. its band gap is only about 3 eV or 288 kJmol$^{-1}$) and due to its potential for a strong metal support interaction (SMSI) [1] which facilitates the reaction. It was then shown that 0.5 wt % Rh/TiO$_2$ (SG) was an effective catalyst for N$_2$O decomposition and dry reforming. These explanations relate to the observations made in Chapters 3 and 4.

7.2. Chapter reviews.

Chapter 1 provided the foundation and basis of the research undertaken. It concluded that global warming is inevitable but the present generation needs to be aware of two important issues:

- realising the need to reduce GHG emissions, and
- the need to use alternative energy resources in the light of limited energy resources like fossil fuel.

Chapter 2 described sol-gel (SG) and impregnation techniques for sample preparation. SG routes readily led to sintering effects at high temperatures (typically above 973 K). Traditional impregnation techniques (e.g. 5 wt. % Rh/Al$_2$O$_3$ (pellets, IMP)) provided thermal stability in terms of sustained activity and resistance to sintering effects, even
at high temperatures. It was noted that the amount of Rh loading affected catalytic performance. For SG catalysts 0.5 wt % Rh loading on TiO₂ was most suitable in dry reforming and N₂O decomposition (see Chapter 2, 3 and 4).

Chapter 3 described N₂O decomposition experiments and results with the aim to reducing its impact of global warming and promoting its use as a monopropellant fuel for satellite microthrusters. In the former case it was found that 0.5 wt. % Rh/TiO₂ (SG) was most suitable for N₂O decomposition and dry reforming of CH₄. Considering weight for weight metal loading 5 wt% Rh/Al₂O₃ (pellets, IMP) was better than commercial Shell 405 in the latter case. It therefore seems that despite Rh being more expensive than Ir, it could prove to be more economical and profitable to use Rh in the long term because Rh was shown to be retained on the surface and caused the same effect up to three times whereas in the Ir case, it all volatilised after the first use (see SEM/EDAX results in Chapter 6). TP continuous work clearly showed that the presence of a suitable catalyst increased the likelihood of the reaction to occur at relatively lower temperatures. It was exciting and promising that a novel catalyst (5 wt % Rh/Al₂O₃ (pellets, IMP)) had been prepared that challenged the present commercial Shell 405 catalyst in terms of performance and lifetime (see Chapters 3 and 6). At present however Shell 405 is better at N₂O decomposition but it does contain 36 wt % Ir on the surface. Isothermal pulse experiments at 523 K and 973 K showed mechanistically that N₂O decomposition was occurring in agreement with the literature (see section 7.3). Furthermore CF catalysts have been shown to have potential use as supports for Rh/TiO₂ catalysts.

Chapter 4 described and provided the results for dry reforming of CH₄. As expected TP continuous work revealed that the reaction occurred significantly more on the supported Rh catalysts than the respective supports alone. Furthermore, deactivation at higher temperatures above 973 K was notable. This was thought to be due to sintering effects, structure collapse for TiO₂ (SG) and poisoning from C on the surface (see Chapter 4 and Raman results in Chapter 6). The results in Chapter 4 indicate two important regions: α and β. The α region showed no reaction had occurred on the surface, but dry reforming was observed during the β region. There was accumulation of C at higher temperatures (i.e. above 973 K, see Raman Spectroscopy results in
7. Discussion.

Chapter 6); which caused deactivation of the surface. It was also noted that the effect of H$_2$O did not seem to facilitate the CO$_2$ in producing CO and surface O as originally suggested by Bodrov et al [2]. In addition compensation effects were seen for related catalysts in both N$_2$O decomposition and CO$_2$-CH$_4$ (see Chapters 3 and 4 respectively). This means that there was an arbitrary relationship between the used catalysts and their respective $E_a$ and In A term. Generally as $E_a$ increased, the ln A compensated by also increasing.

Chapter 5 provided an insight into aspects of heterogeneous photocatalysis. The UV pulse work via a deuterium power supply clearly indicated that it is possible to decompose N$_2$O and facilitate the dry reforming reaction at modest temperatures (523 K). It is interesting to note that the mechanism for either reaction followed that of the normal high temperature route. This area of work was concluded to have promising future prospects.

Chapter 6 provided the characterisation results of present catalysts and supported the results that were observed in Chapters 3 and 4. XRD showed that TiO$_2$ as anatase converted to the rutile structure during catalysis and became increasingly crystalline. High temperatures however led to sintering and deactivation effects (see Chapters 3 and 4). SEM and EDAX clearly showed sintering effects and loss of surface Rh and Ir (in particular for Shell 405). Raman results confirmed the presence of graphitic and amorphous C on the surface and also supported the fact that anatase converts to rutile at high temperatures, and especially during catalysis. BET results showed loss of surface area after catalysis for both reactions, often due to structure collapse (e.g. see Figure 6.67). FTIR showed that the effect of calcination cleaned the surface from organic species and this gave an indication of using ideal calcination temperatures (see Chapter 2); this was thought to be 773 K. XPS showed that Rh was oxidised during the reaction and surface species like C were increased whilst TiO$_2$ was decreased in relative terms. This indicated that the reaction had successfully occurred. Finally insitu-FTIR showed some activity for CO as a probe molecule at low temperatures (i.e. 373 K), but increasingly little activity at high temperatures (due to reasons above).
It is clear therefore that over supported group VIII metals (Rh in particular) both dry reforming and \( \text{N}_2\text{O} \) decomposition occur and have the potential to lead to high value oxygenated or unsaturated chemical products. This is important, even if it is not yet certain to lead to new modes of realistic abatement [3] of anthropogenic \( \text{CO}_2 \).

7.3. Mechanism for dry reforming

\( \text{CO}_2 \) reforming with \( \text{CH}_4 \) produces syngas (\( \text{CO} : \text{H}_2 \) ratio of 1:1) via primary steps that are thought [4] to be

\[
\begin{align*}
\text{CO}_2 + 2_\cdot & \leftrightarrow \text{CO} + \text{O} \\
\text{CH}_4 + 2_\cdot & \rightarrow \text{CH}_3 + \text{H} \\
\text{CH}_3 + \text{O} & \rightarrow \text{CO} + 3/2\text{H}_2 + 2_\cdot
\end{align*}
\]

Several mechanisms have been outlined in the literature and they usually undergo a *Langmuir-Hinshelwood* mechanism for bimolecular surface reactions (see Chapter 2) [5]. Keulen *et al* [6] suggest that both \( \text{CH}_4 \) and \( \text{CO}_2 \) dissociate independently of one another. The dissociation of carbon dioxide acts primarily as an oxygen supplier (i.e. generates an \( \text{O} \) pool on the surface), while the dissociation products of methane extract the oxygen from the catalyst. However when oxygen presence is abundant, methane pulsing leads to the production of carbon dioxide.

The total reaction scheme is proposed to be:

![Fig. 7.1. - mechanism for dry reforming.](image-url)
Thus methane decomposes on the surface to form H and C. The H may desorb as H₂ or be oxidised to H₂O. CO₂ also dissociates on the catalytic surface to produce an oxygen species and CO. The C formed reacts with the O to produce CO, which can either be oxidised to CO₂ or remain as CO. The outcome is dependent upon the concentration of O. If there is a shortage of O, CO₂ will dissociate to CO and CO will not oxidise. However, an abundance of O will cause the CO to oxidise and CO₂ will not dissociate. Furthermore, it was noted that the sooner the CO₂ is pulsed after the CH₄ one, the higher is the CO₂ conversion. However, the sooner the CH₄ is pulsed after CO₂, the lower is the selectivity for the conversion of CH₄ to CO.

Au et al [7] on the other hand consider a CH₄ pyrolysis mechanism:

\[
\begin{align*}
O_2(g) + & \rightarrow 2O \\
CH_4(g) + & \rightarrow CH_3 + (4-x)H \rightarrow C + 4H \\
C + O & \rightarrow CO \rightarrow CO(g) \\
H + H & \rightarrow H_2 \rightarrow H_2(g)
\end{align*}
\]

Adsorption energies increase as x tends to 0, which means the last step (CH \rightarrow C + H) has the highest activation energy \(E_a\) (1.30 eV or 125 kJmol⁻¹). It is also suggested that oxygen located ‘on-top’ metal sites (as opposed to ‘hollow’ sites) promote CH₄ dehydrogenation or dissociation by increasing the adsorption energy of H.

Kroll et al [8] suggest the following mechanism:

\[
CH_4 + \rightleftharpoons C + 2H_2(g)
\]

This is a reversible fast step where _ represents surface sites. The following fast step is as a result of two elementary steps:

\[
\begin{align*}
CO_2 + & \leftrightarrow CO + O \quad \text{highly reversible, fast} \\
C + O & \rightarrow CO + _ + _ \quad \text{rds (rate determining step)} \\
CO_2 + C & \leftrightarrow 2CO + _ \quad \text{fast}
\end{align*}
\]
Furthermore, it was noted that water interacts reversibly with the surface via an adsorption/desorption equilibrium, which is similar to that of carbon dioxide:

\[ H_2O + _\leftrightarrow O + H_2 \]

Bodrov and Apel’baum [9] suggest the same mechanism in terms of:

\[ CO_2 + _\rightarrow O + CO \]

\[ CH_4 + _\rightarrow CH_3 \rightarrow CH_2 \rightarrow CH \rightarrow C \]

\[ CH_5 + O \rightarrow CO + x/2 H_2 + 2_ \]

\[ H_2O + _\rightarrow O + H_2 \]

\[ CO + 2_ \rightarrow C + O \]

CO\(_2\) dissociates to adsorbed O and gaseous CO while CH\(_4\) dissociates in a stepwise fashion to produce H\(_2\) and CH\(_5\) adspecies. The latter can then further react with O to form CO. Like CO\(_2\), water would also be in equilibrium with the surface.

However Erdohelyi et al [10] and Mark and Maier [11] argue that, at least with regards to noble metals, CO\(_2\) can actually react directly from the gas phase (Eley Rideal mechanism) with the CH\(_5\) and C adspecies generated from CH\(_4\) decomposition:

\[ CH_4 + _= C + 2H_2 \]

\[ C + CO_2 = 2CO + _ \]

Stagg et al [12] note that the “major obstacle preventing commercialisation of this process is that, due to the endothermic nature” (\(\Delta H\)\(_{298,\text{dry\ reforming\ of\ methane}}\) = + 247kJmol\(^{-1}\)) “of the process, high temperatures are required to reach high conversions”. The mechanism proposed is in agreement with other commentators:

\[ CH_4,\text{decomposition} \rightarrow 2H_2 + C_{\text{carbonaceous deposits}} \]

\[ CO_2,\text{dissociation} \rightarrow CO + O \]

\[ O + C \rightarrow CO \]
Bitter et al [13] highlight the mechanism proposed by Mark et al [11] and Erdohelyi et al [10]. The mechanism proposed by Bodrov et al [9] is also mentioned. With regards to the step:

$$\text{CO}_2 \rightarrow \text{CO} + \text{O}$$

Qin et al [14] suggest that the CO$_2$ dissociates on the metal to form M-CO and M-O. This is supported by Bodrov et al [9] when considering the CO$_2$/CH$_4$ reforming over a Ni foil. Bradford et al [15] in contrast, however suggest the following sequence of events:

$$\text{CO}_2 + \text{H} \rightarrow \text{CO} + \text{OH} \quad \text{fast}$$
$$\text{OH} + \text{CH}_x \rightarrow \text{CH}_x\text{O} + \text{H} \quad \text{fast}$$
$$\text{CH}_x\text{O}_{\text{decompose}} \rightarrow \text{CO} + \text{H}_2 \quad \text{slow, RDS}$$

In a separate contribution, Bradford et al [16] note that lattice oxygen may participate in the activation of both CH$_4$ and CO$_2$ at elevated temperatures, which is in agreement with Au et al [7], who point out that an 'on-top' site is more activating than a 'hollow' one.

Ashcroft et al [17] suggest that the equations of steam reforming ($\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2\text{O}, \Delta H = 226\text{kJmol}^{-1}$) and the reverse water-gas shift reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}, \Delta H = 35\text{kJmol}^{-1}$) (see Chapter 1) as models are also important and useful in terms of explaining the mechanism of dry reforming of methane.

In parallel, Bitter et al [18] pointed out that the major cause of catalytic deactivation is largely a result of the blocking of active sites by carbon deposited from CH$_4$ (i.e. not sintering). In addition, the rates of carbon formation and deactivation of the catalysts depend on the stability of the carbonates formed from CO$_2$ (which will subsequently react with the C adspecies formed from CH$_4$). It is suggested that in order to have stable catalysts, one needs to fine tune or balance the particle size of the metal and the acid-base properties (i.e. strong enough to stabilise carbonate formation, and low enough concentration of acid sites to avoid pronounced CH$_4$ decomposition).
7. Discussion.

Ruckenstein et al [19] show how the reaction between CH$_4$ and surface lattice oxygen occurs on a Rh catalyst. The result is the formation of CO$_2$ and H$_2$O while the Rh$_2$O$_3$ is reduced to Rh$^0$:

$$3\text{CH}_4(g) + 8\text{Rh}^{3+} + 12[O^2_] \rightarrow 3\text{CO}_2(g) + 6\text{H}_2\text{O}(g) + 8\text{Rh}^0 + 12_.$$

The Rh$^0$ is then re-oxidised by the gaseous oxygen, which restores the catalyst to its original state:

$$4\text{Rh}^0 + 3\text{O}_2 + _ \rightarrow 4\text{Rh}^{3+} + 6[O^2_]$$

where _ denotes an anion vacancy.

Here pulse work showed that CO and H$_2$ were produced during CH$_4$ pulses (as well as displaced CO$_2$), but only displaced CH$_4$ during CO$_2$ pulsing. FTIR results (see *Chapter 6*) showed that the surface was clean from organic species before catalysis but there was accumulation of carbonaceous species after catalysis (see Raman and SEM results in *Chapter 6*). This is in good agreement with the mechanisms highlighted in the literature. The pulse results in *Chapter 4* indicate the following proposed mechanism:

$$\text{CO}_2 + 2_ \rightarrow \text{CO} + \text{O}$$
$$\text{CH}_4(g) + 2_ \rightarrow \text{CH}_3 + (4-x)\text{H} \rightarrow \text{C} + 4\text{H}$$
$$\text{C} + \text{O} \rightarrow \text{CO} + 2_$$
$$4\text{H} \rightarrow 2\text{H}_2 + _$$

The CO$_2$ dissociation to CO and O adsorption is in agreement with Wang et al [4]. This is followed by the stepwise dissociation of CH$_4$ and surface interaction between C and O leads to CO products. Adsorbed 4H then desorbs as 2H$_2$ (see Figures 4.64(b) and 4.67(b) as examples in *Chapter 4*). Since CO from CO$_2$ dissociation does not desorb the reaction appeared to be H$_2$ selective (see *Chapter 4*). O$_2$ impurity did not affect the reaction due to the presence of MnO$_x$/Celite (see *Chapter 2*). Further work is needed to discover where accumulated CO is held.
7. Discussion.

It was shown here (Chapter 4) that TP continuous catalysis of CH$_4$+CO$_2$ dry reforming over sol-gel mesoporous Rh/TiO$_2$ (SG) catalysts (see BET results in Chapter 6) involved accumulation of surface CH$_x$ species and that this was accompanied by an increase in dry reforming activity and an increase in the H$_2$:CO product ratio. This is potentially important as it indicates that selectivity tends more towards H$_2$ than CO. At high temperatures however (i.e. > 900 K) C caused a decrease in activity.

The activity of the catalysts can be measured and compared in terms of the apparent turnover frequency (TOF). Although this is not the actual TOF, all the results were treated the same way and so the apparent TOF gives a relative correlation of the catalysts' activities.

TOF is defined as:

\[
\text{TOF} = \frac{\text{no. of molecules converted per second per gram catalyst}}{\text{no. of active site per gram catalyst}}
\]

In terms of CO$_2$ and CH$_4$ conversion it takes the form:

\[
\frac{[\text{flow rate of CO}_2 \text{ or CH}_4 (\text{cm}^3/\text{s})/V_M]}{[\text{wt. of sample x } \% \text{Rh/100) / RAM of Rh}] \times L}
\]

where L is Avogadro constant, $V_M$ is the molar volume and RAM is relative atomic mass. A similar expression is derived for the TOF of CO and H$_2$ production. Table 7.1 shows activation energies (kJmol$^{-1}$) and TOFs (s$^{-1}$) for the dry reforming reactants and products. The molar volumes ($V_M$) of 22 414 cm$^3$mol$^{-1}$ were taken to be at 273 K and 101 kPa. In future TOFs need to be calculated with Rh surface areas deduced from X-ray diffraction line broadening.

---

7. Discussion.

Table 7.1 - Comparison of $E_a$ (kJ mol$^{-1}$) and TOFs (s$^{-1}$) at 973 K for different catalysts

<table>
<thead>
<tr>
<th></th>
<th>CO$_2$</th>
<th></th>
<th>CH$_4$</th>
<th></th>
<th>CO</th>
<th></th>
<th>H$_2$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$</td>
<td>TOF</td>
<td></td>
<td>$E_a$</td>
<td>TOF</td>
<td></td>
<td>$E_a$</td>
<td>TOF</td>
</tr>
<tr>
<td>1</td>
<td>72.6</td>
<td>-----</td>
<td>5.4</td>
<td>-----</td>
<td></td>
<td>9.46</td>
<td>2.33</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>83.6</td>
<td>2.22</td>
<td>28.7</td>
<td>1.48</td>
<td></td>
<td>88.7</td>
<td>2.59</td>
<td>46.9</td>
</tr>
<tr>
<td>3</td>
<td>12.0</td>
<td>0.03</td>
<td>12.2</td>
<td>0.05</td>
<td></td>
<td>108.0</td>
<td>0.02</td>
<td>143.0</td>
</tr>
<tr>
<td>4</td>
<td>58.1</td>
<td>0.005</td>
<td>34.4</td>
<td>0.005</td>
<td></td>
<td>137.0</td>
<td>0.03</td>
<td>48.0</td>
</tr>
<tr>
<td>5</td>
<td>35.0</td>
<td>0.19</td>
<td>34.5</td>
<td>0.13</td>
<td></td>
<td>417.0</td>
<td>3.42</td>
<td>15.1</td>
</tr>
</tbody>
</table>

where $1 = 0.5$ wt. % Rh/TiO$_2$ (Degussa, P25, IMP), $2 = 0.5$ wt. % Rh/TiO$_2$ (SG), $3 = 5$ wt. % Rh/Al$_2$O$_3$ pellets (IMP), $4 = 5$ wt. % Rh/TiO$_2$ (Degussa, P25, IMP) and $5 = 0.5$ wt. % Rh/TiO$_2$ (SG, IMP). $E_a$ values were taken from page 174 (see Chapter 4). The errors associated with $E_a$ were ±3% and 0.01 s$^{-1}$ for TOF.

TOF is expressed in terms of the apparent number of CO$_2$ molecules or CH$_4$ molecules converted at 973 K per second per Rh$_{total}$ atom; and the apparent number of CO molecules or H$_2$ molecules produced at 973 K per second per Rh$_{total}$ atom.

The range of TOF values for each of the species were in good general agreement with the literature [22-24] although in most cases they were slightly low in comparison. For CO$_2$ 5 wt % Rh/Al$_2$O$_3$ pellets (IMP) (no. 3) gave an apparent TOF of 0.03 s$^{-1}$ compared to the literature value of 0.11 s$^{-1}$ [25], but there was excellent agreement with CH$_4$ where TOF = 0.05 s$^{-1}$ compared to the literature value of 0.06 s$^{-1}$ [25]. CO and H$_2$ TOFs were lower than the literature values of 0.17 s$^{-1}$ and 0.07 s$^{-1}$ respectively [10]. For Rh/TiO$_2$ catalysts, CO$_2$ and CH$_4$ TOFs were small compared to typical literature values of 15 s$^{-1}$ and 25 s$^{-1}$ respectively [26]. However the TOFs for CO and H$_2$ production were in better agreement with the literature values of 0.21 s$^{-1}$ and 0.11 s$^{-1}$ respectively [10]. In the case of 0.5 wt % Rh/TiO$_2$ (SG) (no. 2), the TOFs were actually higher than these values (i.e. 2.59 s$^{-1}$ and 2.96 s$^{-1}$ respectively). For 0.5 wt % Rh/TiO$_2$ (SG, IMP) (no. 5), the CO and H$_2$ TOFs were considerably high at 3.42 s$^{-1}$ for both even though CO$_2$ and CH$_4$ TOFs were not very good. In addition the catalyst deactivated easily at high temperatures due to sintering and structure collapse (see Chapter 4). 0.5 wt % Rh/TiO$_2$ (SG) was therefore the best catalyst for this reaction despite having a moderate CO$_2$ and CH$_4$ conversion (60 % and 80 % respectively). The activation energies were also in very good agreement with the literature (see Chapter 4) and the relative higher H$_2$ TOFs compared to that of CO further confirmed the selectivity for H$_2$. In addition there was no correlation between $E_a$ and TOF.
During the pulse work there was typically 2.87 µmol of Rh in the reactor with 2.24 mmol of alternating CO$_2$ and CH$_4$ pulses. This meant that in mole terms the reactant pulses were very much greater than those of Rh and therefore reduction or oxidation of Rh$_x$ was not directly observed (i.e. minicatalysis). Most of the supported RhO$_x$ catalysts showed activity above 650 K whereas TiO$_2$ (as the support) was only active above 800 K. The activity in this case can be explained in terms of reduction and oxidation of Rh$_2$O$_3$, TiO$_2$ and Al$_2$O$_3$. Hence this involves Rh-O, Ti-O and Al-O bond strengths. Rh$_2$O$_3$ is more active because the Rh-O is easier to break. Its bond strength is only 405 kJmol$^{-1}$ [27] compared to 672.4 kJmol$^{-1}$ for Ti-O and 511.0 kJmol$^{-1}$ for Al-O [28-29].

Rh has the electronic configuration [Kr]4d$^8$5s$^1$ which means that upon reduction the Rh$^0$ metal (see XPS results in Chapter 6) is in the d$^8$ configuration, but after catalysis it is oxidised to Rh$_2$O$_3$ (see XRD results in Chapter 6; i.e. Rh is in the +3 oxidation state which is more stable than the +4 oxidation state of RhO$_2$) with a d$^6$ configuration: one electron is lost from the 5s orbital and two from the 4d orbitals. The d$^6$ configuration either exhibits low spin in a strong ligand field (t$_2g^6$) with all electrons paired up or high spin in a weak ligand field (t$_2g^4$e$_g^2$) and 4 unpaired electrons. The d$^6$ configuration means that Rh$^{3+}$ forms octahedral complexes and structures [30]. Hence Rh$_2$O$_3$ shares the same octahedral structure (i.e. hcp) with α-Al$_2$O$_3$ (corundum, see Chapter 2). Rh$^{3+}$ might therefore enter the Al$_2$O$_3$ and TiO$_2$ surface (i.e. it may be embedded into the support surface). Furthermore it is also known that Ti has the electronic configuration [Ar]3d$^2$4s$^2$ (see Chapter 2) which means that as TiO$_2$, it adopts the very stable +4 oxidation state both before and after catalysis (see XPS results in Chapter 6). Ti$^{4+}$ is very stable because it is isoelectronic with Ar (i.e. d$^0$ configuration because two electrons are lost from the 3d orbital and two electrons are lost from the 4s orbital). However TiO$_2$ can be reduced and be involved in the reaction.

The pulse results in Chapter 4 showed that Rh$^0$ or Rh$_2$O$_3$ decomposes CH$_4$ pulses more than CO$_2$. This is because C-H bonds (from CH$_4$) are easier to break than C-O bonds (in CO$_2$) with bond strengths of 414 kJmol$^{-1}$ and 803 kJmol$^{-1}$ respectively. CH$_4$ is thought to produce C (see Raman data in Chapter 6) on the Rh$_2$O$_3$. The Raman data
was obtained for the most active catalyst (0.5 wt % Rh/TiO₂ (SG)). The pulse results indicates that CO₂ dissociates but the CO does not desorb. It was also interesting to note that CH₄ does not fragment without the presence of CO₂; which indicates that O from CO₂ must be present to initiate the CH₄ dissociation. As mentioned earlier, this further justifies the experimentally observed H₂ selectivity.

TP continuous work in Chapter 4 have shown that no reaction was observed during the α-stage until the β-stage. At temperatures greater than 900 K deactivation of the catalysts was noticeable and this was thought to be caused by sintering, structure collapse and C species (see Raman Spectroscopy results in Chapter 6), and hence the loss in surface areas after catalysis (see BET results in Chapter 6).

7.4. Mechanism for N₂O decomposition

The mechanism of N₂O decomposition can be thought to be Langmuir-Hinshelwood in terms of a unimolecular process (see Chapter 2) [31]. Here the adsorption of N₂O and electron transfer ensures that the decomposition occurs [32]:

\[
\begin{align*}
    \text{N}_2\text{O}_2(g) & \rightarrow \text{N}_2\text{O} \\
    \text{N}_2\text{O} + e^- & \rightarrow \text{N}_2\text{O}^- \\
    \text{N}_2\text{O}^- & \rightarrow \text{N}_2(g) + \text{O}^- \\
    \text{O}^- & \rightarrow \frac{1}{2} \text{O}_2(g) + e^- \quad \text{or} \\
    \text{O}^- + \text{N}_2\text{O} & \rightarrow \text{N}_2(g) + \text{O}_2(g) + e^- + 2_-
\end{align*}
\]

Overall this gives 2N₂O(g) → 2N₂(g) + O₂(g). This is sometimes simplified to N₂O₂(g) → N₂(g) + ½ O₂(g). Kapteijn et al [33] indicate a similar mechanism:

\[
\begin{align*}
    \text{N}_2\text{O} + _- & \rightarrow \text{N}_2\text{O} \\
    \text{N}_2\text{O} & \rightarrow \text{N}_2 + \text{O} \\
    2\text{O} & \rightarrow \text{O}_2 + 2_- \\
    \text{N}_2\text{O} + \text{O} & \rightarrow \text{N}_2 + \text{O}_2 + _-
\end{align*}
\]
Uetsuka, Yamashita and Tanaka et al [34-36] have also reported similar mechanisms with very slight variations, such as:

\[
\begin{align*}
\text{N}_2\text{O} & \rightarrow \text{N}_2 + \text{O} \\
2\text{O} & \leftrightarrow \text{O}_2 \\
\text{N}_2\text{O} + \text{O} & \rightarrow \text{N}_2 + \text{O}_2 + _-
\end{align*}
\]

Initially there is N\textsubscript{2}O adsorption followed by decomposition on the surface that results in surface O. The O\textsubscript{2} either desorbs after reaction with another surface O, or reacts with another N\textsubscript{2}O and hence forms the products (N\textsubscript{2} and O\textsubscript{2}).

The results in Chapter 3 for N\textsubscript{2}O decomposition were in agreement with these mechanisms. On effective catalysts, the pulse work clearly indicates that there is N\textsubscript{2}O adsorption followed by decomposition on the surface leading to gaseous products (N\textsubscript{2}(g) and ½ O\textsubscript{2}(g) – of which ½ O\textsubscript{2} was detected).

TOFs for N\textsubscript{2}O decomposition has a similar expression to the dry reforming case:

\[
\text{TOF} = \frac{((\text{flow rate of N}_2\text{O}(\text{cm}^3/\text{s})/V_M) \times \text{L} \times (\% \text{ N}_2\text{O conv.}/100))}{[((\text{wt. of sample} \times \% \text{ Rh or Ir}/100) / \text{ram of Rh or Ir}) \times \text{L}]} 
\]

Here too the molar volumes were taken to be 22 414 cm\textsuperscript{3} mol\textsuperscript{-1} at 273 K and 101 kPa. Table 7.2 shows activation energies (kJmol\textsuperscript{-1}) and apparent TOFs (s\textsuperscript{-1}) for N\textsubscript{2}O decomposition.

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Table 7.2 - \( E_a \) and TOFs for \( \text{N}_2\text{O} \) decomposition at 973 K for different catalysts.

<table>
<thead>
<tr>
<th>( \text{N}_2\text{O}, E_a (\text{kJmol}^{-1}) )</th>
<th>apparent TOF (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 29.4± 1.0</td>
<td>0.44± 0.01</td>
</tr>
<tr>
<td>2 72.7± 2.5</td>
<td>2.59± 0.01</td>
</tr>
<tr>
<td>3 156± 5.4</td>
<td>2.88± 0.01</td>
</tr>
<tr>
<td>4 198± 6.9</td>
<td>0.08± 0.01</td>
</tr>
<tr>
<td>5 69.6± 2.4</td>
<td>4.43± 0.01</td>
</tr>
<tr>
<td>6 52.6± 1.8</td>
<td>0.48± 0.01</td>
</tr>
<tr>
<td>7 302± 10.6</td>
<td>1.29± 0.01</td>
</tr>
<tr>
<td>8 208± 7.3</td>
<td>0.07± 0.01</td>
</tr>
</tbody>
</table>

where 1 = 5 wt. % Rh/Al\(_2\)O\(_3\) pellets, 2 = 0.5 wt. % Rh/TiO\(_2\) (SG), 3 = 0.5 wt. % Rh/TiO\(_2\) (SG, IMP), 4 = 0.5 wt. % Rh/TiO\(_2\)(SG-80%)/Al\(_2\)O\(_3\) (CF, IMP), 5 = 0.5 wt. % Rh/TiO\(_2\) (Degussa, P25, IMP), 6 = 5 wt. % Rh/TiO\(_2\) (Degussa, P25, IMP), 7 = V-Rh/Al\(_2\)O\(_3\) and 8 = 36 wt. % Ir/Al\(_2\)O\(_3\) pellets (Shell 405). \( E_a \) values were taken from page 126 (see Chapter 3).

Apparent TOFs are expressed in terms of the apparent number of \( \text{N}_2\text{O} \) molecules converted at 973 K per second per Rhol\(_{\text{total}}\) atom. Here too, the TOF values were in good general agreement with the literature.

Kinetic data in this area are scarce. Nevertheless TOFs for \( \text{N}_2\text{O} \) decomposition were generally in agreement with the literature value of 0.24 s\(^{-1}\) [37]. Here 0.5 wt % Rh/TiO\(_2\) (Degussa P25, IMP) (no. 5) was the best catalyst for \( \text{N}_2\text{O} \) decomposition with a TOF of 4.43 s\(^{-1}\) and 95 % \( \text{N}_2\text{O} \) conversion, but it was not effective in dry reforming (i.e. partial oxidation reaction occurred (see Chapter 4)). 0.5 wt % Rh/TiO\(_2\) (SG, IMP) (no. 3) deactivated at high temperatures even though its TOF was higher than that of 0.5 wt % Rh/TiO\(_2\) (SG) (no. 2). Shell 405 (no. 8) had 90 % \( \text{N}_2\text{O} \) conversion and relatively moderate \( E_a \) (which was in agreement with the literature values of ~ 250 kJmol\(^{-1}\)). Its TOF however was relatively very poor with only 0.07 s\(^{-1}\). 0.5 wt. % Rh/TiO\(_2\)(SG-80%)/Al\(_2\)O\(_3\) (CF, IMP) (no. 4) shared a similar TOF value of 0.08 s\(^{-1}\) with almost 100 % \( \text{N}_2\text{O} \) conversion at 973 K although it activated above 820K (see Chapter 3). Its \( E_a \) was also favourable at only 198 kJmol\(^{-1}\). In contrast 5 wt % Rh/Al\(_2\)O\(_3\) pellets (IMP) (no. 1) had 75 % \( \text{N}_2\text{O} \) conversion but an \( E_a \) of only 48 kJmol\(^{-1}\) and TOF of 0.44 s\(^{-1}\). In addition it was thermally more stable at high temperatures by
7. Discussion.

retaining its surface area and Rh on the surface (see BET and SEM/EDAX results in Chapter 6). Shell 405 was unstable at high temperatures with reduced surface area and loss of surface Ir. Hence in a satellite microthruster application context, 5 wt % Rh/Al₂O₃ was regarded as a better catalyst than Shell 405. It is therefore recommended that with further research and optimisation Rh/Al₂O₃ pellets (IMP) catalyst may be considered a likely competitor against commercial Shell 405 in the longer term. In general, the Eₐs were lower than the typical literature values of 250-270 kJmol⁻¹ (see Chapter 3). Here too there was no correlation between Eₐ and TOF.

Despite Rh₂O₃ and Al₂O₃ sharing the same structure the Rh-O and Ir-O (420 kJmol⁻¹) [38] bonds are easier to break than Ti-O and Al-O. TP continuous work showed that IrO₂ was very active but rather unstable since the SEM/EDAX results (see Chapter 6) showed that the Ir had volatilised, whereas Rh₂O₃ was much more stable as it was retained on or in the support surface. This was because Rh³⁺ is better incorporated and embedded into the Al₂O₃ and TiO₂ structure since they share the same coordination number (i.e. 6) and geometrical structure (i.e. octahedral), whereas Ir⁴⁺ has d⁵ configuration (coordination number 5) which prefers either trigonal bipyramidal or square pyramidal structures. Clearly this cannot be incorporated within the Al₂O₃ structure as easily as Rh³⁺ and therefore is very unstable. Both Rh₂O₃ and IrO₂ shared the same melting point of 1373 K [39-40], but since Rh-O bonds were broken slightly more easily, it is thought that Rh⁶ or Rh³⁺/Rh⁺ after sustained reaction were able to decompose N₂O more effectively from the safety of its position embedded in the oxide surface. Another similarity between Rh³⁺ and Al³⁺ is that they share the same charge whereas Ir⁴⁺ doesn’t, and hence 5 wt % Rh/Al₂O₃ pellets (IMP) appears to be more stable than commercial Shell 405 (36 wt % Ir/Al₂O₃ pellets). The TiO₂ support facilitated the decomposition due to its strong metal-support interaction (see Chapters 2 and 3).

Shell 405 contains Ir⁶ and Ir⁴⁺ as IrO₂ because the +4 oxidation state for Ir is the most stable state. This is because Ir has the electronic configuration [Xe]5d⁷6s² (see Chapter 2) which means that in the +4 oxidation state the 5d orbital minimises electron-electron repulsion by having singly filled d-orbitals (i.e. d⁵ configuration because two electrons are lost from the 6s orbital and two from the 5d orbital).
7. Discussion.

Similarly Al$_2$O$_3$ has Al$^{3+}$ as the most stable oxidation state which is isoelectronic with Ne. In its ground state Al has the electronic configuration [Ne]3s$^2$3p$^1$ (see Chapter 2) which means that in its Al$^{3+}$ state, 2 electrons have been lost from the 3s orbital and 1 from the 3p orbital.

7.5. Suggestions of immediate future work

An accurate assessment of surface sites and species is required including real TOFs. Electron spin resonance (ESR) can be used to monitor TiO$_2$ band gap (see Chapter 5) and Ti oxidation states before and after reaction [41]. CO or H$_2$ chemisorption can be used to determine active surface areas.

7.6. Suggestions for longer term future work

In the light of current findings the following suggestions seem appropriate for future work:

- development of ceramic foam (CF) catalysts for a range of reactions and comparison of the results for the present 5 wt % Rh/Al$_2$O$_3$ pellets (IMP) (see Chapter 9, Appendix III [42]).
- Development of better satellite N$_2$O catalysts than Shell 405.
- Raman spectroscopy to search for levels of C on all catalysts and relate to activity in dry reforming (i.e. concentration of C versus activity).
- Development of catalysts for the synthesis of dimethyl carbonates (DMC) - the production of methanol uses CO$_2$ [43] and dry reforming products (syngas) [44], and this in turn can be reacted with further CO$_2$ to yield DMC [45-53, 54-55]. Methanol is a very useful organic precursor used widely in both industry and academia. DMC has wide commercial applications. These include solvents, intermediates and fuel additives.
- Development of catalysts for conversion of higher alkanes - an abundant supply of C$_2$-C$_5$ alkanes exist but relatively few means of converting them to more useful and valuable products. Methane is predominantly natural gas. However it still contains ethane, propane and butane of which ethane is the
secondary most abundant compound [56]. Hence, it is useful to develop reactions with these alkanes in order to determine whether they are also useful in terms of producing valuable products via synthesis gas as a result of dehydrogenation reactions [57], e.g. alkane/CO\textsubscript{2} experiments. Similar products may also be formed via oxidative dehydrogenation reactions [58-59] e.g. alkane/O\textsubscript{2} experiments. Furthermore, reactions may occur via the hydrogenolysis route whereby a C-C bond is broken principally to generate methane and other alkanes or alkenes e.g. propane hydrogenolysis may result in methane and ethene [57] - useful starting materials in the chemical industries. Ethene is expected to be produced on ‘dry reforming’ of ethane and this must mean (as in methanol synthesis over Cu) that CO\textsubscript{2} produces O (and CO) which reacts with adsorbed C\textsubscript{2}H\textsubscript{6} to give ethene and H\textsubscript{2}O or that O controls the build-up of carbonaceous deposits.

It is expected that the reactivity increases across the series CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6} and C\textsubscript{3}H\textsubscript{8}. This is because of the increased stability of the corresponding free radicals, which determine the C-H bond strengths and also the C-C bond strengths. Radical stability increases along the series from primary to secondary to tertiary. Consequently the energy required to produce them decreases. This implies that the C-H bonds are weaker in ethane (410 kJmol\textsuperscript{-1}) than in methane (439 kJmol\textsuperscript{-1}) [60], and therefore requires less energy to break the C-H bonds in ethane than in methane for example.

• An interesting use of CO\textsubscript{2} was reported by Asami and Co [61]. The following reaction was reported to explain the formation of ethene:

\[
2\text{CH}_4 + 2\text{CO}_2 \rightarrow \text{C}_2\text{H}_4 + 2\text{CO} + 2\text{H}_2\text{O}
\]

Ethene can subsequently be used to form benzene [62]:

\[
2\text{C}_2\text{H}_4 + 3\text{CO} \rightarrow \text{C}_6\text{H}_6 + \text{CO}_2 + \text{H}_2\text{O} \ (\Delta G = -183.2\text{KJmol}^{-1} \text{ at } 1113\text{K})
\]

This is another area that may be of interest.
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- Since the dry reforming of methane is highly endothermic, high temperatures may be avoided by allowing the reaction to occur at high pressure together with an effective catalyst. Economically however, the costs could be the same as the high temperature case since specialised equipment will be required in either case to withstand high temperatures or pressure. In this regard, the use of photocatalysts, consisting of TiO$_2$ based catalysts for example as semiconductors using UV appears to be an interesting alternative. This is because the required energy is provided for the reaction to occur without the need to use high temperatures and/or pressures.

- Isothermal experiments at 900 K as a function of reactant concentrations and time to determine rates and orders of the reactions.

7.7. Conclusions

Technologies and developments were considered for the control of GHGs (i.e. CO$_2$, CH$_4$ and N$_2$O). Of the options available, dry reforming of methane and N$_2$O decomposition were considered to be useful for the control and reduction of these gases (see Chapter 1).

The main conclusions derived from the research may be summarised as follows:

- TiO$_2$ (SG) was an effective support although at high temperatures its structure changed from anatase to rutile.

- 0.5 wt. % Rh/TiO$_2$ (SG) was the most effective catalyst for CO$_2$-CH$_4$ in terms of activity and selectivity for H$_2$ production (see Chapters 3 and 4). It also deactivated the least at high temperatures and was most resistant to sintering effects. TiO$_2$ as a support facilitated the reactions better than SiO$_2$ (SG) and SiO$_2$-TiO$_2$ (SG). It appeared that the presence of SiO$_2$ in SiO$_2$-TiO$_2$ inhibited the performance of TiO$_2$ (see Chapter 3).

- 5 wt. % Rh/Al$_2$O$_3$ (pellets, IMP) was shown to be a viable competitor for commercial Shell 405 (36 wt. % Ir/Al$_2$O$_3$) in terms of N$_2$O decomposition as a monopropellant fuel for satellite microthrusters. Weight for weight metal, Rh was more active than Ir and was also retained on the surface after repeated use.

---

7. Discussion.

- Ceramic foam catalysts containing 0.5 wt % Rh/TiO$_2$ (SG) showed moderate activity for N$_2$O decomposition (see Chapter 3).
- During the dry reforming reactions there was build up of carbonaceous species, C on the used catalysts, (i.e. at 973 K).
- Heterogeneous photocatalysis has potential for dry reforming and N$_2$O decomposition. This provided an alternative route to normal high temperature reactions. Hence an important use was made of solar energy (which can potentially lead to global warming).
- TOFs and E$_a$s for dry reforming were generally in good agreement with the literature. Mechanisms agreed with some commentators, where the CO$_2$ adsorbs and dissociates on the surface without CO desorbing. CH$_4$ dissociation and reaction were in agreement with the literature.
- TOFs and E$_a$s for N$_2$O decomposition were in agreement with the literature. E$_a$s in particular were significantly lower than literature values (typically 250 kJmol$^{-1}$ (see Chapter 3)).
- The keynote finding of this research was that catalytic technologies (e.g. dry reforming and N$_2$O decomposition) were used effectively to reduce the environmental impact of GHG emissions; and at the same time provided routes to useful industrial/commercial processes (e.g. N$_2$O as fuel for satellite microthrusters and DMC/oxygenates from dry reforming).

The aims of the programme (see Chapter 1) were therefore largely met.

7.8. References

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8. Appendices.

CHAPTER VIII

Appendices

9.1. Contents (i)


Appendix II – (x) Experimental Rig Design


Appendix I
MATERIAL REDACTED AT REQUEST OF UNIVERSITY
8. Appendices.

Appendix III
Porous Ceramic Foam Catalysts for N₂O-based Satellite Microthrusters

UniS, SSTL and Dytech Corporation

Microthrusters can be based on (i) cold gases [1], (ii) vaporising liquids [2], (iii) low b.pt. liquid propellant [3], (iv) decomposing monopropellants (N₂H₄, H₂O₂ or N₂O) and (v) bipropellants.


N₂O has been suggested as a green monopropellant for N₂H₄ replacement. It has extremely low toxicity and has a higher theoretical IₜRp than for H₂O₂ (i.e. N₂O IₜRp~210s, H₂O₂ IₜRp~180s) [1]


N₂O is thermodynamically unstable (e.g. for its dissociation lnK =+42.0 at 298K), but is kinetically stable, since its bimolecular decomposition only takes place >838K with an activation energy of 245-264kJ/mol, because its conversion is spin-forbidden. N₂O decomposition is exothermic (i.e. ΔH=-82.38kJ/mol at 900K). It is catalysed by a variety of metallic and oxide surfaces. Often the kinetic orders with respect to N₂O and O₂ have been found to be +1.00 and -0.5, although retardation of the rate-determining step (O₂ release from the surface) by O₂(ads) depends on catalyst pre-treatment.

Propellant Properties

<table>
<thead>
<tr>
<th>Propellant</th>
<th>N₂H₄</th>
<th>H₂O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH⁰ (kJ mol⁻¹)</td>
<td>50</td>
<td>54</td>
</tr>
<tr>
<td>IₜRp Theoretical</td>
<td>240</td>
<td>180</td>
</tr>
<tr>
<td>Storability</td>
<td>Storable</td>
<td>Decomposes</td>
</tr>
<tr>
<td>Storage Density @ 273K (kg m⁻³)</td>
<td>1008</td>
<td>1387</td>
</tr>
<tr>
<td>Vapour Pressure @ 273K</td>
<td>15 Pa</td>
<td>3 Pa</td>
</tr>
<tr>
<td>Storage Temp Range (K)</td>
<td>282-355K</td>
<td>266-311K</td>
</tr>
<tr>
<td>Toxicity L.D₅₀ Rabbit Dermal</td>
<td>91 mg/kg</td>
<td>700 mg/kg</td>
</tr>
<tr>
<td>Flammability</td>
<td>Flammable</td>
<td>Strong Oxidiser</td>
</tr>
<tr>
<td>Heritage</td>
<td>Long</td>
<td>Long</td>
</tr>
</tbody>
</table>

Vapour Pressure, Storage Density and Toxicity data for N₂H₄ and H₂O₂ are also provided.
History of N₂O propellant use

- 1930s - early experimentation with N₂O as an oxidiser for bipropellant rockets
- 1950s - NACA* investigated N₂O as a monopropellant
- 1996 - UniS and SSTL consider N₂O for small satellite applications
- 1999 - UOSAT-12 launched with an SSTL N₂O resistojet

* NACA = National Advisory Committee on Aeronautics

The authors are developing catalytic N₂O microthruster nanotechnology for satellites, where the catalysts are active in N₂O decomposition at low temperature (to lower power requirements) and yet stable at the high temperatures produced in the resulting oxidising conditions.

N₂O decomposition on platinum metals:

\[
\begin{align*}
N_2O + _- &\stackrel{k_1}{\Rightarrow} N_2 + O \\
2O &\stackrel{k_3}{\Rightarrow} O_2 + 2_- \\
N_2O + O + _- &\stackrel{k_2}{\Rightarrow} N_2 + O_2 + _- \\
O_2 + _- &\Rightarrow O_2
\end{align*}
\]

can be studied by continuous T-programmed and isothermal (1073K) pulse methods [1]. This approach is used here.

Shell 405 Results

Shell 405™ (29.7%Ir/Al₂O₃; 115 m²/g; pore volume 0.18 cm³/g; Ir area 33 m²/g; spheres 0.6-0.8 mm) was developed for catalyse hydrazine decomposition at around 293K [1] (although as a result the catalyst temperature rises to 748K).

Now new catalysts are being sought with low temperature activity and high temperature stability.

Rh/TiO₂ (SG) Results

0.5 wt % Rh/TiO₂ (SG IMP) involved RhCl₃ impregnation of sol-gel titania.

0.5wt % Rh/TiO₂ P25 was produced by RhCl₃ in ethanol impregnation of a commercial TiO₂ (Degussa AG, P25).
XPS for 0.5wt % Rh/TiO₂ (SG)

Reduction *  
N₂O decomposition **

Rh3d₅/₂ 306.8eV (Rh₀)  
Ti2p₃/₂ 458.2eV (Ti⁴⁺)

309.6eV (Rh³⁺)  
458.6eV (Ti⁴⁺)

* in an atom ratio Rh: Ti: O = 1: 315: 833 (i.e. 0.07at%Rh)
** in an atom ratio Rh: Ti: O = 1: 343: 990 (i.e. 0.05at%Rh)
Rh/TiO$_2$ (SG)/Ceramic Foam

Results

0.5wt % Rh/TiO$_2$ (SG:80 %)/Al$_2$O$_3$ (ceramic foam:CF). White Al$_2$O$_3$ ceramic foam (CF; Hi-Por alumina (Dytech Corporation Ltd) was acid etched (3M HNO$_3$, 200 cm$^3$) three times for 15h. TiO$_2$ (SG) in ethanol was coated onto CF blocks (1 x 1 x 3 cm) and dried for 16h. This was then impregnated with RhCl$_3$ in ethanol and dried at 373 K for 24h.
Ea (%) conv TOF*(kJ/mol) at (s⁻¹) at 900K

IR/Al₂O₃ Shell 405 205 92.4 0.15
IR/Al₂O₃ (IMP) 241 31.5 0.48
Rh/TiO₂ (P25) 50 12.7 0.78
Rh/TiO₂ (SG) 159 15.2 9.27
Rh/TiO₂/Al₂O₃ (CF) 217 15.2 9.27

* the apparent TOF was measured as the number of O₂ molecules produced from N₂O at 900K per second per Rh or Ir atom.

Ceramic foams are now being nanoengineered from PMMA microspheres with sol-gel oxide overcoats [1]


Scale bar=0.5mm

High throughput and factorial design will be applied to optimise these catalysts [1], but a decision needs to be made as to whether DSC or RGA evidence is stronger.


Do these catalysts work in N₂O microthruster prototypes?
The present authors have taken the first steps to determine whether a Rh/TiO₂/ceramic foam (CF) low power catalytic N₂O microthruster could be developed.

It is possible that with TiO₂ overcoats and a flux of UV radiation (e.g. UVA at 320-385nm and UVB at 290-320nm) rises with altitude from the Earth that they may operate as photo-initiated microthrusters. Konstantin Tsiolkovsky suggested that a focussed mirror on a spacecraft or satellite would produce a temperature of 5300-6300K from solar energy.

This catalytic technology can be used in environmental monitoring (e.g. the coccolithophore bloom off the coasts of Cornwall and Brittany seen on 18/6/04)
Conclusion: green catalytic microthrusters can be developed for nanosatellites

Merci