First-principles based mechanistic understanding of CO$_2$ utilisation reactions over advanced heterogeneous catalysts

A doctoral thesis by

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In partial fulfilment of the requirements for the degree of Doctor of Philosophy (PhD) at Chemical and Process Engineering Department Faculty of Engineering and Physical Sciences University of Surrey

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September, 2018
Abstract

It has become increasingly important to control carbon dioxide (CO\textsubscript{2}) emissions and at the same time generate fuel sources to meet the growing global energy consumption need. CO\textsubscript{2} (dry) reforming of methane (DRM) is a viable process as it generates fuel (syngas) and utilises greenhouse (CH\textsubscript{4} and CO\textsubscript{2}) gas at the same time. The success of this process relies on the development of suitable noble-metal free catalysts. First principle’s based computational methods, such as density functional theory (DFT), has become a powerful predictive tool for catalyst development in modern science. Therefore the main objective of this thesis work has been to investigate suitable catalysts using computational methods for gas–phase CO\textsubscript{2} utilisation reactions.

In this research work, DFT calculations provided us with the fundamental insights into the DRM mechanism over bimetallic Sn/ Ni (111) periodic model surfaces. This analysis showed that low Sn concentration on Ni surface effectively mitigates carbon formation without compromising the CO\textsubscript{2} conversion and the syngas production, showcasing superior characteristics of the bimetallic catalyst towards carbon tolerance stability. Other heterogeneous catalysts such as Ni\textsubscript{2}P and MoP have also been studied in this thesis. Theoretical analysis of DRM reaction on the unexplored nickel phosphide Ni\textsubscript{2}P (0001) surface showcased suitable syngas production under DRM reaction temperatures with low carbon deposition formation on the surface. This was mainly attributed to a lower number of active sites available for carbon adsorption compared to oxygen on the Ni\textsubscript{2}P (0001) surface.

DFT study on activation of CO\textsubscript{2} and CO on MoP (0001) and Ni\textsubscript{2}P (0001) surfaces showcased selective CO production from CO\textsubscript{2} to be possible on both the surfaces. Further, direct CO activation is favoured on the MoP (0001) surface. Surface bounded oxygen removal on Ni\textsubscript{2}P (0001) is reasonably favourable.

Findings from this thesis work will be beneficial in developing more robust catalysts for gas phase CO\textsubscript{2} utilisation reactions and could contribute to a better understanding of CO\textsubscript{2} conversion processes, catalysts deactivation and thus helping to develop new families of powerful catalysts for a greener society.
Acknowledgements

I am very grateful to my supervisor Prof. Sai Gu, for giving me this wonderful opportunity to work on a very interesting subject in my PhD and supporting me throughout my research.

I would also like to express appreciation to my co-supervisors Dr Qiong Cai and Dr Tomas Ramirez Reina, their expertise in the field has helped me greatly with my understanding of several fundamental concepts. I really appreciate that you have been patient with me during the times when I was not producing results. Also, you have given me outstanding guidance (both personally and academically). I have been extremely lucky to have been supervised by both of you. You made this PhD possible for me.

I would also like to thank Dr Jaydeep Mody, for always providing technical support and made it possible to run my simulations on HPC’s. I have learnt a great deal of computing from you and greatly appreciate that you had made my life easier by providing support to the most critical aspect of my PhD.

How can I forget my friends! Thank you all for making me feel welcome in this department and for helping me enjoy myself down here in Surrey. Also, I appreciate their encouragement at some of the more difficult points of my PhD.

I would like to thank my family. They have supported me both financially and emotionally throughout my life and I would certainly not be here now without them.

Finally, I will thank my wife ‘Riya’ for being patient with me, tolerating all my eccentricities and sacrificing a great deal of her happiness to support my endeavours.
Dissemination


Conferences

- **ChemEngDay** Birmingham U.K, 2017- oral and poster presentation
  
  Title: DFT study on carbon monoxide (CO) molecule adsorption over Ni (111) and Sn/Ni(111) surfaces.

  
  Title: Effect of Sn surface alloying with Ni (111) on increased carbon tolerance in dry CO$_2$ reforming of methane to syngas: A DFT study.

- **Eighth Asia Pacific Conference on Theoretical and Computational Chemistry**, Indian Institute of Technology Bombay (India), 2017- poster presentation
  
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<tbody>
<tr>
<td>GHG</td>
<td>Greenhouse gas</td>
</tr>
<tr>
<td>DRM</td>
<td>Dry reforming of methane</td>
</tr>
<tr>
<td>SRM</td>
<td>Steam reforming of methane</td>
</tr>
<tr>
<td>ATR</td>
<td>Autothermal reforming of methane</td>
</tr>
<tr>
<td>WSGR</td>
<td>Water-gas shift reaction</td>
</tr>
<tr>
<td>RWGS</td>
<td>Reverse water gas shift</td>
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<td>PO</td>
<td>Partial oxidation</td>
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<tr>
<td>FTS</td>
<td>Fischer-Tropsch synthesis</td>
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<td>HDS</td>
<td>Hydrodesulfurization process</td>
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<td>HDN</td>
<td>Hydrodenitrogenation process</td>
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<td>HER</td>
<td>Hydrogen evolution reactions</td>
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<td>Density functional theory</td>
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<td>SPARG</td>
<td>Sulfur passivity reforming</td>
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<td>Transition metal phosphides</td>
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<tr>
<td>TMC’s</td>
<td>Transition metal carbides</td>
</tr>
<tr>
<td>PES</td>
<td>Potential energy surface</td>
</tr>
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<td>ZPE</td>
<td>Zero-point energy correction</td>
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<td>TOF’s</td>
<td>Turn-over frequencies</td>
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<td>CASTEP</td>
<td>Cambridge Serial Total Energy Package</td>
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<td>MKM</td>
<td>Microkinetic modelling</td>
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<tr>
<td>HF</td>
<td>Hartree-Fock</td>
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<tr>
<td>MP2</td>
<td>Møller-Plesset second order perturbation theory</td>
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<tr>
<td>CC</td>
<td>Coupled cluster expansion</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
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<tr>
<td>CCSD</td>
<td>Couple cluster singles and doubles</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>Couple cluster singles and doubles with perturbative trebles</td>
</tr>
<tr>
<td>CCSDT</td>
<td>Couple cluster single double triple</td>
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<tr>
<td>LDA</td>
<td>Local density approximation</td>
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<tr>
<td>GGA</td>
<td>General gradient approximation</td>
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<td>Ceperley and Alder’s</td>
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<td>PZ</td>
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<td>Vosko-Wilk-Nusair</td>
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<td>Perdew-Wang 91</td>
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<tr>
<td>PBE</td>
<td>Perdew-Burke-Enzerhof</td>
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<tr>
<td>RPBE</td>
<td>Revised Perdew-Burke-Enzerhof</td>
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<tr>
<td>BZ</td>
<td>First Brillouin zone</td>
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<tr>
<td>MP</td>
<td>Monkhorst and Pack method</td>
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<tr>
<td>fcc</td>
<td>Face centred cubic</td>
</tr>
<tr>
<td>hcp</td>
<td>Hexagonal close-packed</td>
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<tr>
<td>CG</td>
<td>Conjugate gradient</td>
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<tr>
<td>MEP</td>
<td>Minimum energy pathway</td>
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<td>NEB</td>
<td>Nudge elastic band method</td>
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<tr>
<td>LST</td>
<td>Linear synchronous transit</td>
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<tr>
<td>QST</td>
<td>Quadratic synchronous transit</td>
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<tr>
<td>TS</td>
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<tr>
<td>IS</td>
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<tr>
<td>FS</td>
<td>Final state (products) of the reaction</td>
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<td>RDS</td>
<td>Rate determining steps</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>--------------</td>
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<tr>
<td>DOS</td>
<td>Density of states</td>
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<tr>
<td>PDOS</td>
<td>Partial density of states</td>
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<tr>
<td>SCF</td>
<td>Self-consistency field</td>
</tr>
<tr>
<td>BFGS</td>
<td>Broyden-Fletcher-Goldfarb-Shanno algorithm</td>
</tr>
<tr>
<td>ASE</td>
<td>Atomic simulation environment</td>
</tr>
<tr>
<td>ML</td>
<td>Monolayer of modelled catalyst surfaces</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning tunneling microscopy</td>
</tr>
<tr>
<td>LEED</td>
<td>Low energy electron diffraction</td>
</tr>
<tr>
<td>$E_{\text{ads}}$</td>
<td>Adsorption energy (eV)</td>
</tr>
<tr>
<td>$E_{a,f}$</td>
<td>Forward activation energy (eV)</td>
</tr>
<tr>
<td>$E_{a,b}$</td>
<td>Backward activation energy (eV)</td>
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<td>$\Delta G$</td>
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Chapter 1: Introduction and background study

1.1 General introduction and background

The exponential increase in carbon dioxide (CO$_2$) emissions coupled with the ever-growing demand for energy resources, presents challenges towards maintaining sustainable global growth and simultaneously restricts environmental pollutant emissions. Additionally, a higher emission of CO$_2$, which is a prominent greenhouse gas (GHG), has a detrimental effect on Earth’s atmosphere. Furthermore, the anthropogenic use of fossil fuels has chiefly spurred the growth in CO$_2$ emissions [1-5]. One of the major sources of CO$_2$ emission comes from natural gas (primarily methane), consumption [1, 2]. For instance, between (2007-2012) CO$_2$ emissions from flaring of natural gas on average has increased by 2 % each year [1]. Furthermore, surplus global natural gas reserves for example, 1688 trillion cubic meters (Russia) [1], 1187 trillion cubic meters (Iran) [1] and 280 million cubic feet (U.S) [3] is available. This scenario, on one hand, provides a valuable option to meet the global energy demand, but on the other hand, emissions occurring from the usage of natural gas present adverse environmental effect. Interestingly, this interplay between CO$_2$ emissions and natural gas availability, especially methane (CH$_4$), can be effectively combined to generate value-added chemicals and fuels [1-5].

Syngas (mixture of CO$_2$ and H$_2$) generation from the reforming of CO$_2$ with CH$_4$, commonly known as dry reforming of methane (DRM) is a viable alternative [3]. Further syngas can be produced from other existing processes such as steam reforming of methane (SRM), autothermal reforming (ATR) and partial oxidation (PO) [1, 3]. However, DRM has shown to function at 20% less operating cost compared to other reforming processes [3]. Furthermore, the syngas produced with low H$_2$/CO ratio (~1) in DRM, increases the selectivity towards long chain hydrocarbons in the Fischer-Tropsch (FT) synthesis [3]. One of the major problems found in DRM is the inevitable catalytic deactivation due to coking [1-5]. Thus, the need to develop more carbon resistant and thermally stable noble metal-free catalysts has become essential, to make the DRM process more economically attractive for commercialization. This has been a major focus in the present thesis.

Direct conversion of CO$_2$ by hydrogenation (using of H$_2$ as reducing gas) $\textit{via}$ Reverse water gas shift (RWGS) [3] coupled with FT or CO$_2$ hydrogenation to methanol [3], has immense
potential in producing value-added chemicals and hydrocarbons. Here also, one of the main focus is to develop catalysts which readily activates CO₂ for selective conversion to CO, which is important for RWGS process and thereafter activation of CO essential, in the FT process. Theoretical methods such as Density Functional Theory (DFT), helps in the understanding of atomic and electronic structure properties of molecules and solids. This understanding of the properties at the atomic level leads to the eventual development of the chemical process, which is generally difficult to achieve by using various experimental techniques. The atomic scale knowledge of the catalytic reaction processes enables a target driven design of catalysts, thereby increasing the overall efficiency of the chemical process. Therefore, catalyst development through computational analysis is a focal point in the present thesis. Further computational tools were used to analyse unexplored catalysts for DRM and CO₂, CO activation reactions.

From here on in this chapter, the background research on catalyst development in gas phase-CO₂ utilisation reactions has been elaborated.

1.2 Insights on DRM

The oxidation of methane (CH₄) with carbon dioxide (CO₂) is commonly termed as dry reforming of methane (DRM) [1-5]. The beneficiation of the DRM process stems from its ability to combining two major greenhouse pollutants to generate, a more desirable product as syngas (CO +H₂) equation 1.1;

\[
\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2 \quad \Delta H_{298K} = +247 \text{ kJ/mol} \quad (1.1)
\]

However it may be argued that the endothermic nature of the DRM process (equation 1.1), makes it less desirable for large scale industrial implementation compared to industrially matured syngas producing processes such as autothermal reforming (ATR) where direct oxidation of methane with oxygen takes palace and steam reforming of methane (SMR), where methane is oxidised by steam (H₂O) [1, 2]. But the ability to combine one mole of CO₂ with the one mole of CH₄ makes DRM a beneficial process to generate valuable syngas with (H₂/CO =1) ratio [1-3]. The syngas generated from DRM has found application in the CALCOR (Caloric Gmbh) process [2, 6], sulfur passivity reforming (SPARG) [2, 7, 8] and Fischer-Tropsch synthesis (FTS) [3-5] as well as hydroformylation reactions.
However even with aforementioned benefits of the DRM process in providing opportunities towards remedying CO\textsubscript{2} impact and the applicability of the syngas in variety of industrial processes, it is still not considered to be a mature industrial process mainly due to suffering from catalyst deactivation, owing to its endothermic nature resulting in inevitable carbon deposition at high reaction temperatures [3-5].

1.2.1 DRM reaction chemistry and coking

![Figure 1.1 Possible reactions during DRM from ref [5, 9]](image)

The endothermic nature is mainly attributed to the combining of two stable forms of carbon, reduced form CH\textsubscript{4} and oxidised form CO\textsubscript{2} [5]. The combination of these two molecules comprises of several intermediate reactions resulting in a complicated reaction network. Nikoo et al. [9] on the basis of thermodynamic equilibrium analysis and the standard Gibbs free energy analysis in the temperature range of (573-1473) K, studied different reactions which may be involved in DRM, shown in Figure 1.1. The thermodynamic analysis conducted by
Nikoo et al. also revealed that (R3-R5) will be less favourable to the formation of ethane or ethylene and will require a highly active catalyst for its formation [9]. Further methanol and dimethyl ether formation (R10-11, R15) is not favourable at the DRM temperature range, which is typically between (923-1273K) and will favour at lower temperatures as the reactions are more exothermic [1, 9]. Therefore, essentially at DRM temperature range the reactions that will be observed would be reverse water gas shift (RWGS) (R2), methanation reactions from CO₂ (R16) and CO (R17) hydrogenation [1, 9]. Also due to their exothermic nature (R16-R17), may also occur at lower temperatures below 800 K [5]. From equilibrium calculations Nikoo et al. determined that high conversion of CH₄ can only be achieved above 1273 K at stoichiometric feed concentration [9], similar observations were reported by Wang et al. [10] Bradford and Vannice [11] Istadi et al. [12]. Further equilibrium studies also confirmed that a higher CO₂/CH₄ ratio between (~2-5) is required to achieve good CH₄ conversion at low temperatures (below 923 K) and for CO₂/CH₄ ratio ~1 will require temperatures up to 1273 K to maintain high CH₄ conversion [9, 12, 13].

1.2.2 DRM reaction mechanism

![Overall DRM reaction mechanism scheme](image)

**Figure 1.2** Overall DRM reaction mechanism scheme adapted from ref [5, 14]
The DRM reaction mechanism proposed by Papadopoulou et al. [14], which was further summarized by Aramouni et al. [5] is shown in Figure 1.2. Essentially the DRM mechanism is divided into four main blocks, wherein the initial step gas phase DRM reactants CH$_4$ and CO$_2$ gets activated. This activation largely depends upon the surface properties of the catalyst [5]. For instance, DFT calculations have shown that at same particle size dispersion noble metals like Ru and Rh are more active towards CH$_4$ activation compared to Pd, Pt and Ni [3, 15]. Additionally, in CH$_4$ activation, it is generally accepted that CH$_4$ dissociates sequentially forming, CH$_x^*$(x=0-4) intermediates to atomic carbon C* and H* on the catalyst surface and has been found to be rate determining step in the DRM process [3, 5].

Activation of CO$_2$ is generally accepted to occur on the catalyst surface, either directly forming carbon monoxide (CO) or oxygen (O) or CO$_2$ gets hydrogenated from the surface H* generates during the CH$_4$ dissociation [3, 16-18]. Further, the type of activation mechanism again depends upon the catalyst surface. For instance O'Connor et al. [16] on Pt/Al$_2$O$_3$ found CO$_2$ to be activated by H* forming CO* and OH* on the catalyst surface. Similar observation was reported by Bradford and Vannice [11] and Maestri et al. [18]. Direct dissociation of CO$_2$ has been found to occur mainly on metal supports like CeO$_2$, Al$_2$O$_3$ and ZrO$_2$, to name a few [3, 19]. Additionally, direct dissociation of CO$_2$ was also found to occur on Rh which was oxidized to Rh$^{3+}$ [17] and over Ru/SiO$_2$ [18].

Overall the main oxidiser for the DRM reaction comes from CO$_2$ activation in the form of O*, OH* and CO* species.

In the final phase of the mechanism the oxidisers generated from CO$_2$ activation reacts with the intermediates generated from the CH$_4$ dissociation steps, such that the CH$_X$ species to form CH$_X$O* or CH$_X$OH* species which dissociates to give CO and H$_2$ gas in the DRM reaction [3, 5, 11, 20, 21].

### 1.2.3 Catalyst deactivation in DRM from carbon formation

Carbon formation on catalyst surfaces presents the most impendence to the development of the DRM process [3]. Although catalyst deactivation in DRM may occur from several processes such as sintering [3, 22] and active metal encapsulation by reducible supports such as ZrO$_2$, TiO$_2$ and La$_2$O$_3$ [3, 23, 24]. However, among these processes catalyst deactivation due to carbon formation has been found to be most significant [3, 5]. Therefore, research has focussed on developing catalysts to be more resistant towards carbon formation.
Aramouni et al. [5], described that carbon formation may occur primarily through four main carbon formation mechanisms in DRM, shown in Figure 1.1, (i) sequential CH₄ dissociation [R6], (ii) CO disproportionation [R12] and CO and CO₂ hydrogenation [R13-R14] respectively. Among these reactions, carbon formation at high temperature range, at typical DRM conditions (923-1273 K), occurs due to [R6] CH₄ dissociation [1-3]. While carbon formation from the reactions [R12-R14] occurs at lower temperatures below 800 K [5]. Further Pakhare and Spivey [3], mentioned [R6 and R12] to be more significant for carbon formation where at high operating pressures CO disproportionation [R12] becomes prominent, which leads to the formation of additional carbon on the surface [3, 25]. Additionally, Pakhare and Spivey [3], in their review paper, summarised, that rate of carbon formation is related to the balance between, carbon formation occurring from [R6/R12] to that of oxidation of the surface formed carbon by CO₂ activation reaction. Further, the morphology of the carbon formed in DRM may differ [3, 5, 19, 26-28].

(i) Amorphous (most reactive form of carbon oxidising at temperatures ~100°C)
(ii) Polymeric (less reactive than amorphous but can be oxidised under mild reaction conditions)
(iii) Graphitic (comprising mainly of poly-nuclear aromatics which oxidises at high reaction temperatures.)

These forms of carbon can be ranked in terms of their detrimental effect in reforming reactions as follows: Graphitic > Polymeric > Amorphous. In this scenario, it seems clear that avoiding the formation of graphitic carbon on the catalyst surface is vital to achieving high catalytic performance for long term runs.

1.3 Nickel catalyst in DRM

Catalysts found to be active in DRM are usually transition metals such as Pt, Pd, Ni, Co, Rh and Ru [29]. Among these, noble metal catalysts especially Rh and Ru have showcased to possess high catalytic activity and are very resistant towards carbon formation [29]. However, from an industrial standpoint, noble metals are unlikely to be used due to their high cost and low availability [29, 30]. Therefore, much of the research focus has been devoted towards developing noble metal-free catalysts for DRM. Among the available transition metal catalysts, Nickel (Ni) has found popularity in industrial use and academic research due to its low cost and ready availability [29, 30]. In the last decade, Ni and Ni supported catalysts have been
widely studied for DRM and they have been found to exhibit catalytic activity close to that of noble metals [30, 31]. However, deactivation of Ni based catalysts due to coke deposition during the DRM process has largely affected the usability of Ni catalysts [29-31].

To understand the underlining mechanism for carbon formation and overall DRM mechanism on Ni catalyst, density functional theory (DFT) based microkinetic studies have been widely used [32-36]. Further, systematic DFT studies conducted by Wang et al. [34], have shown that the open and stepped sites Ni (100), Ni (110) and Ni (221) respectively, are more susceptible towards carbon formation compared to the closed packed facets like Ni (111). Additionally, a DFT based microkinetic study of a multi-facet Ni system performed by Fan et al. [35], revealed that CH₄ activation first occurs over the stepped or open sites of the Ni surface which gets blocked quickly due to carbon formation and thereafter the reaction moves to the closed packed sites. Further, DFT studies by Foppa et al. [36], also revealed that C atom diffusion C-C bond formation is thermodynamically easier on Ni (111) compared to Pd and Pt plane surfaces [33, 36]. From these theoretical studies, a general understanding has been developed indicating that carbon affinity on Ni surface is majorly due to the availability of active three fold sites which facilitate sp² hybridization of carbon, thereby facilitating carbon stability on the Ni surface [32-34]. Further, carbon formation basically occurs from the CH₄ dissociation and CO disproportionation reactions on Ni [32-34, 36].

Over the years various catalyst surface modification strategies have been developed to decrease carbon formation on the catalyst surface namely sulfur passivation which has been commercially used in the SPARG process [37], alkali (K, Na) [37, 38] or alkali metals (Ca, Mg) [37, 39] which promotes carbon removal from the catalyst surface due their basicity and alloying or bimetallic systems [37]. Here we focus upon the later surface modification strategy.

1.3.1 Alloying of Nickel surface

Essentially introduction of a second metal to the Ni surface modifies the surface geometric and electronic properties which in return increases the carbon tolerance potential of Ni [37]. Further Trimm et al. [40], found the ‘ensemble effect’ (decrease in active surface sites), introduced due to the addition of second metal, is a major factor for increased carbon resistance on Ni surface. Several bimetallic combinations of Ni with noble metals Ni-M (M= Rh, Pd, Pt, Au) [29, 37, 40] and non-noble metals (M=Cu, Fe, Co, Mn, Sn) [29, 37, 41], have been tried with positive
results. For instance, small addition of noble metals such as Ru, Pd and Pt to Ni supported catalysts not only increased carbon resistance but also enhanced the catalytic activity in DRM [42, 43]. In comparison noble metal free–Ni bimetallic such as Ni-Co does not enhance catalytic activity but increases carbon tolerance without deterring the performance of Ni catalyst [29, 44, 45]. In a comparative experimental study performed by Ay et al. [44] on Ni/CeO$_2$ and Ni-Co/CeO$_2$ (Ni:Co=1:1), reported addition of cobalt to increase the carbon tolerance significantly compared to the Ni/CeO$_2$ without sacrificing catalytic performance of Ni. Similar catalytic performance of bimetallic Ni-Co with (Ni: Co =1:1 and 1:2) ratio was reported by Gonzalez-de la Cruz et al. [45]. Further, as previously mentioned, CH$_4$ dissociation contributes greatly to carbon formation on during DRM [46], DFT studies for CH$_4$ dissociation on bimetallic models Ni-Cu [47] and Ni-Au [48] showed higher carbon resistance of the bimetallic surfaces. For instance, DFT calculations performed by An et al. [47], showed the energy barrier for CH* cracking reaction to atomic C* an H* on Cu/Ni (111) surface to be 1.8 times higher compared to plane Ni (111) surfaces. This increase in energy barrier for CH* cracking step in CH$_4$ dissociation reflects the carbon tolerance level of the Ni or Ni alloyed catalyst surfaces [47, 48]. Here DFT may be a useful method to screen bimetallic Ni catalysts for DRM.

1.3.2 Alternative catalyst materials for DRM

In an effort to develop efficient catalysts for DRM, interesting approaches have been explored in recent studies. One such approach has been devoted towards rare earth metals oxides or pyrochlores, which are highly crystalline fluorite oxides with high thermal stability [31, 49, 50]. Le Saché et al. [50] developed a Ni-doped pyrochlore-perovskite structure, that has shown to have high carbon tolerance with long term stability and good catalytic activity in DRM even at low temperatures ~650 °C. Further, Zhang et al. [31] found Ni substituted defective fluorite structure (Ni/Y$_2$Zr$_2$O$_7$) to exhibit high activity and carbon stability in steam reforming of methane.

Another group of inexpensive catalytic materials which has been largely remained unexplored in regard to DRM are the transitional metal phosphides (TMPs). Despite the early findings for TMPs potentiality for hydrogenation [51, 52], it has only found prominence in recent times [51, 53, 54]. Especially TMPs has been found to be active and stable under feed mixtures
comprising of sulfur and nitrogen such that, hydrodesulfurization (HDS), hydrodenitrogenation (HDN) processes [51, 53, 54]. Further, the activity of the TMPs catalysts in hydroprocessing of compounds such as dibenzothiophene in (HDS) and quinoline in (HDN) is reported to follow the order of Fe₂P < CoP < MoP < WP < Ni₂P [51, 53]. In an earlier study by Burns et al. [55] for the synthesis of binary MoP from CH₄, showcased the potentiality of TMPs in DRM and RWGS process. Further, the same authors found the major gas-phase products evolved from the synthesis process to be CO and H₂ [55]. More recently, Yao et al. [56] performed a comparative study of MoP and Ni/Mo₂C catalysts for DRM, which showcased some interesting findings. For instance, from TSPR analysis of CH₄ on MoP and Ni/Mo₂C indicated, CH₄ conversion to H₂ formation to be more significant on MoP with increasing temperature (above 750 °C) [56]. Further MoP catalyst was found to be resistant towards bulk oxidation by CO₂ to form MoO₂ and activates CO₂ to CO at higher temperature (above 850 °C) [56]. Also, catalyst lifetime tests showcased long duration in a catalytic stability test for MoP [56].

What makes these TMPs an attractive option for DRM comes from their ability to promote oxygen interaction on the catalyst surface [57, 58]. This is especially useful for DRM, as an oxygen rich catalytic surface will allow for gasification of carbon thereby deterring carbon nucleation and increasing catalyst stability [59]. Liu et al. [58], in their combined theoretical and experimental study of Ni₂P (001) catalyst surface in water gas shift reaction (WSGR) found to have greater activity compared to conventional Cu (100) surface, with higher oxygen saturation coverage on Ni₂P (001) which facilitates WGSR both directly and indirectly [58]. This strong oxygen interaction with the Ni₂P (001) surface arises from the strong binding of O with P [58]. Further, the special catalytic properties of TMPs may be attributed to ensemble effect or ligand effects (small charge transfer from parent metal to P) [60]. Therefore, it appears to be worthwhile to investigate these alternative TMP materials in the context of DRM.

1.4 CO₂ and CO activation on catalysts

CO₂ conversion to hydrocarbons can be achieved chiefly through two routes [61];

(i) The direct route where CO₂ is first reduced to CO via the RWGS process followed by subsequent CO hydrogenation to hydrocarbon via FTS process.
(ii) CO₂ hydrogenation to methanol with subsequent transformation of methanol to hydrocarbons in a two-stage process.

The direct route has been found to be more environmentally friendly [61]. Essentially for the direct conversion route multifunctional catalysts are required, on which both CO₂ and CO may be hydrogenated [61]. Iron and copper-based catalyst are popular in RWGS and FTS process owing to significant conversion of CO₂ or CO to C₂⁺ - C₅⁺ hydrocarbons with lower CH₄ selectivity [61-64]. Further, activation of CO₂ on catalyst surfaces depends upon charge transfer from the surface to the CO₂ moiety [65]. For instance, from DFT calculations of CO₂ activation on Ni, Fe, Co and Cu (100) has shown that spontaneous chemisorption of CO₂ depended upon charge transfer from the specific metallic surface [65]. Further Brønsted–Evans–Polanyi (BEP) between reaction energies and energy barriers revealed C-O bond scission to be most favourable on Fe (100) surface [65]. Additionally, Bendavid et al. [66], in their DFT studies found CO₂ adsorption over CuO₂ (111) surface occurs through charge transfer from surface copper atoms rather than surface oxygen anions [66]. In alternative catalyst materials, major focus has been given to Mo-carbides for selective CO₂ reduction to CO and hydrogenation reactions [67]. Liu et al. [67] from their experimental and theoretical analysis found, polycrystalline hexagonal α-Mo₂C to possess high selectivity to CO (~99.5%) at 673 K in RWGS reaction [67]. Further in a combined experimental and DFT study of CO₂ hydrogenation to methanol on β-Mo₂C and Cu/β-Mo₂C (001) ortho-rhombic surface found evidence of suitable CO₂ activation with products (CO, CH₄ and CH₃OH) formation occurring on the Mo-terminated plane of β-Mo₂C (001) [68]. Further addition of Cu increases to β-Mo₂C (001) surface increases methanol selectivity [68]. In comparison to the metal carbides, limited information on TMPs for CO₂ and CO hydrogenation is available. However, a DFT study of syngas conversion on a molybdenum phosphide cluster model (Mo₆P₃) reported low activation energy barriers for CH₄ formation compared CH₃OH resulting in possible methane formation on Mo-phosphides [69]. However the same authors in a later experimental study of syngas conversion on K promoted MoP/SiO₂ catalyst found, the K promoter to suppress the methane formation and increase the selectivity towards C₂⁺ oxygenates [70].

1.5 Computational Catalysis

In modern science, computational methods have become the cornerstone to heterogeneous catalyst design [71, 72]. Among the several computational chemistry methods available [72],
DFT has become a popular method, due to the balance between acceptable time and accuracy [71, 73]. Further due to the advent in computational architecture and increased processor speeds, studying of more complex catalyst model systems such as metal alloys, perovskites, zeolites etc., has become possible [71]. However, catalyst surface models studied with DFT are simple slab models of low Miller index surfaces [71], which in the real heterogeneous catalyst are very complex systems. But the purpose of DFT studies comes from an understanding of underlying catalytic phenomenon rather than exploring new catalytic preparation routes [74]. For instance, development in descriptor based linear correlation techniques such as BEP relationships have made it possible to screen a large number of potential catalysts using few descriptors [74]. Furthermore, the kinetics of a particular chemical process can be determined from DFT. Where, DFT calculated potential energy surfaces (PES) describe the elementary reaction mechanism at 0K and 0bar, to which thermodynamic corrections, such as zero-point energy correction (ZPE), entropic and enthalpy corrections for higher temperature and pressures can be added. Thereafter, rate constants and turn over frequencies (TOF’s) of the chemical process can be determined [71]. A detailed description of the DFT method and microkinetic formulation is given in Chapter 2.

1.6 Research Problem

From the background studies, it is evident that to achieve industrial growth of the DRM process is largely dependent upon the development of heterogeneous catalysts. Highly active and stable catalysts in the DRM process will contribute greatly to the higher production of syngas. Ideally, noble metal-based catalysts such as Ru and Rh may resolve this issue but it’s not suitable for industrial usage due to higher costs. Therefore, major research focus has been given to Ni-based catalysts due to its comparable activity to noble metals in DRM. However, developing suitable strategies to overcome Ni catalyst deactivation due to coking under DRM reaction conditions is a major challenge.

In the present research, one of the catalyst development strategy identified is surface alloying. Where the main focus is towards studying noble-metal free bimetallic catalysts. Ni-Sn is a promising bimetallic catalyst suitable for DRM application; however, the understanding towards its bimetallic composition influencing catalytic activity in DRM is still debatable. For instance, in Ni-Co bimetallic catalyst, higher percentage composition of Co on the Ni surface
may deter the activity of the catalyst to a large extent [44, 59]. Similarly, it is key to understand the composition and catalytic performance of the Ni-Sn catalyst.

Another group of catalysts which has largely remained unexplored in the context of DRM are TMPs. With only experimental investigation performed on MoP catalyst showcasing promising activity and catalyst stability in DRM [56]. In this research, the focus has been given to investigating Ni$_2$P catalyst. As no known previous literature either theoretical or experimental was found, discussing the catalytic potential of the Ni$_2$P catalyst in DRM.

In the final part of this research, attention has been given towards to, the direct syngas production route via the reverse water gas shift RWGS reaction. Here the catalyst development is again key to achieve good product conversion rates. In RWGS reaction CO$_2$ activation is a key step on catalyst surfaces [67]. Among non-precious advanced catalytic material’s molybdenum carbide (Mo$_2$C) have been found to be good in RWGS [67]. However, studies on TMPs (Ni$_2$P, MoP) on RWGS are limited, therefore it’s worthwhile to understand the potentiality of these catalytic materials in CO$_2$ utilisation reactions.

1.6.1 Research Hypothesis

To design suitable heterogeneous catalysts for CO$_2$ utilisation reactions mentioned in the research problem, the approach that has been followed is computational driven catalyst design. The last 20 years have witnessed tremendous growth in first-principles based methods, which has made it possible to study complex catalyst systems and large reaction networks, leading computational driven catalyst design [75].
A schematic overview of a closed loop computational approach implemented in this work is shown in Figure 1.3. Reliable catalyst surface models are developed to study interaction molecules and intermediates of a particular reaction at an atomic level. A wealth of information such as adsorption energies of intermediates, formulation of complex reaction mechanisms networks, electronic properties etc. is gained from first-principles simulations. Thereafter this data can further be used is steady-state microkinetic models to calculate reaction rates, intermediate concentrations and various other kinetic parameters, across an extensive number of catalyst surfaces under realistic reaction temperatures and pressures [76, 77]. Further, the data obtained from the kinetic analysis may be further used in experiments to develop real heterogeneous catalysts suitable for particular reactions.

In regards to CO$_2$ to utilization reactions, especially for DRM, this type of catalyst design approach has been successfully implemented to design Rh doped pyrochlore (LRhZ) catalyst [78], understanding the activity and behaviour of coking on nickel carbides [34] and understanding DRM mechanisms multi-facet nickel plane surfaces [35].
1.6.2 Research Objectives

The main focus of this thesis has been to gain fundamental insights into CO$_2$ utilisation reactions on novel catalyst materials using computational techniques. In this context, the main objectives of the thesis are to contribute towards the understanding of catalytic materials such as Ni-based alloys and TMP’s for DRM and RWGS reactions. The general objectives of this work are outlined below;

- Understanding the fundamental DRM reaction mechanisms on the mono-metallic Ni surface facet.
- Increasing the stability of Ni catalysts towards carbon formation during DRM by using surface alloying strategy with inexpensive metals.
- Exploring the potentiality of interstitial catalyst materials such as Ni$_2$P for potential applications for DRM.
- Exploring the potentiality of TMP’s (MoP and Ni$_2$P) for CO$_2$ and CO activation reactions.
- Using theoretical techniques, DFT and MKM to perform computational screening of catalysts for CO$_2$ utilisation reactions.

1.6.3 Research Scope

In this thesis computational method such as density functional theory (DFT) and steady-state microkinetic modelling (MKM) is used to design noble-metal free heterogeneous catalysts for CO$_2$ utilisation reactions. The scope of this thesis work is outlined below;

- DFT based MKM study of plane Ni (111) periodic surface to develop an understanding of the DRM reaction mechanism behaviour and ascertain the main CO production route. Further analysis of carbon formation behaviour on the catalyst.
- Ni-Sn alloy, catalyst development for DRM using DFT based MKM study. Atomic and kinetic catalytic performance comparison between Ni (111) and Ni-Sn surface
models. Ascertaining carbon tolerance potentiality of the alloyed catalysts form the above analysis.

- Detailed theoretical analysis of Ni2P (0001) catalyst surface using DFT and MKM approach assessing its potentiality in DRM process.

- DFT analysis of two TMP surface models, MoP (0001) and Ni2P (0001), for reverse water gas-shift (RWGS) and CO activation reactions.
Chapter 2: Computational theory and methods

2.1 Introduction

In modern science, computational methods have greatly contributed to developing our understanding of materials and chemical processes by providing atomic-level information about electronic properties of materials and chemical bonds. These computational techniques are mostly based on first principles methods, which not only can derive electronic properties of solids and gases but also, results obtained from these methods may be used to formulate kinetics for chemical processes.

In this thesis, we have used DFT to study the interaction of various gas phase molecules with selected catalyst models and thereafter develop reaction kinetics using the models. Therefore in this chapter, an overview about the foundations of DFT and microkinetic modelling is presented.

2.2 Schrödinger Equation

To study molecular or solid systems, it requires to solve many-body Schrödinger equation for electrons and nuclei of the system.

The time independent many-body Schrödinger equation can be written as;

$$\hat{H}\Psi (r,R) = E\Psi (r,R) \quad (2.1)$$

Where, the terms $E$ and $\Psi$ represents the energy and wave function of a system respectively, with $(r$ and $R)$ representing the electrons and nuclear co-ordinates respectively. The Hamiltonian, $\hat{H}$ is a combination of kinetic and potential energy terms of the nuclei and electrons;

$$\hat{H}_{tot} = \hat{T}_N + \hat{T}_e + \hat{V}_{ne} + \hat{V}_{nn} + \hat{V}_{ee} \quad (2.2)$$

Here, $\hat{H}_{tot}$ represents the Hamiltonian where, $\hat{T}_N$ and $\hat{T}_e$ are the kinetic energy terms of the nuclei and electrons. The electrostatic interaction between the nuclei and electrons is given by $\hat{V}_{ne}$. Finally, the electrostatic interaction between nuclei and electrons are represented by
\( V_{nn} \) and \( V_{ee} \) respectively. In atomic units, the general form the Hamiltonian may be written as:

\[
\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_{i,l} \frac{Z_l}{|r_i - R_l|} + \frac{1}{2} \sum_{i,j \neq i} \frac{1}{|r_i - r_j|} - \sum_i \frac{1}{2M_i} \nabla_i^2 + \frac{1}{2} \sum_{i,j \neq i} \frac{Z_i Z_j}{|R_i - R_j|}
\]  

(2.3)

Here, \( M_i \), \( Z_i \) and \( R_i \) are the mass, charge and position of the nucleus respectively and the position of the electron is shown by \( r_i \).

However, analytical solution of the Schrödinger equation for many body systems with more than a few electrons is impossible to obtain. For this reason, suitable approximations are made to derive solutions for many body systems.

### 2.2.1 Born–Oppenheimer Approximation

Born–Oppenheimer in 1927 [79], proposed an (adiabatic) approximation, which separates the nuclei from electrons. According to this approximation, electrons are much lighter and faster than the nuclei and so any change in the nuclear position will be instantaneously adapted by the electrons. Therefore, based on Born–Oppenheimer Hamiltonian the Schrödinger equation now becomes:

\[
\hat{H}_e \Psi = E \Psi
\]  

(2.4)

Where, \( E \) corresponds to the electronic energy and \( \Psi \) becomes the many-body wave function which depends upon the position of the nuclei. Further, ignoring the nuclear kinetic energy, the electronic Hamiltonian \( \hat{H}_e \) has only electronic terms and can be written as:

\[
\hat{H}_e = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee}
\]  

(2.5)
Where, $T_e$, $V_{ne}$ and $V_{ee}$, corresponds to the electronic kinetic energy, interaction between nuclei and electrons and the electron–electron Coulomb interaction.

On applying the Born-Oppenheimer approximation, the many-body problem is restricted to the electronic part and can be solved for one-electron systems only. Therefore to solve many-electron systems further approximations are required. Among the various (ab initio) methods available to solve the Schrödinger equation for many-body systems, the wave function based and density based approaches are commonly used.

The Hartree-Fock (HF) theory may be viewed as the basis for the development of electronic structure methods. It essentially assumes each electron in a many-body system will interact in a mean-field originating from all other electrons in the system. The main shortcoming of the HF method is attributed to the absence of electron correlation. Due to this limitation, the energy of a system obtained from HF method will be higher than the exact energy of the system. To overcome this limitation of the HF method many new approaches known as post-Hartree-Fock methods had been developed such as, Møller-Plesset second order perturbation (MP2) theory [80], coupled cluster expansion (CC), CC singles and doubles (CCSD), CCSD with perturbative triples CCSD(T) and CC single double triple CCSDT [81, 82]. However, for the calculations of catalytic systems, most of these methods are computationally expensive shown in Table 2.1.

**Table 2.1** List of scaling order $O( )$ with system size $(N)$ for commonly used approximations to solve the Schrödinger equation.

<table>
<thead>
<tr>
<th>ab initio Methods</th>
<th>Scaling relations</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT</td>
<td>$O(N^3)$</td>
</tr>
<tr>
<td>HF</td>
<td>$O(N^3)$</td>
</tr>
<tr>
<td>MP2</td>
<td>$O(N^5)$</td>
</tr>
<tr>
<td>CSSD</td>
<td>$O(N^6)$</td>
</tr>
<tr>
<td>CSSD(T)</td>
<td>$O(N^7)$</td>
</tr>
<tr>
<td>CSSDT</td>
<td>$O(N^8)$</td>
</tr>
</tbody>
</table>
From the Table 2.1, it may be seen that the computational time for ab initio methods increases with system size \( N \), where \( N \) represents number of electrons and \( O() \) denotes the order of the scaling behaviour \([82, 83]\). Therefore, post-Hartree-Fock methods are computationally more expensive. In comparison density functional theory (DFT) scales \( O(N^3) \) comparable to HF theory and also accounts for electronic correlation \([83]\). Therefore, in regards to the balance between computational cost and chemical accuracy DFT is the preferred method, which have been used for calculations of electronic and geometrical properties of solid surfaces and molecules. Therefore, in the present thesis, all the calculations are performed using DFT.

2.2.2 Density Functional Theory Formulation

Density functional theory (DFT) is the most widely used method for calculating the electronic structure of a system. The theoretical formulation of DFT rests on the two theorems presented by Pierre Hohenberg and Walter Kohn in 1964 \([84]\).

- The first theorem states that, the ground state electron density \( n(r) \) can uniquely determine any many-electron system moving with an external potential \( v_{\text{ext}}(r) \). Hence, if the ground state density of many-electron system is known then it becomes possible to calculate other ground state properties and the total energy of the system.

- The second theorem states that, the ground state energy of a many-electron system \( E [n(r)] \) can be calculated by the ground state density and this ground state density is determined by the universal functional \( F [n(r)] \) following the equation (2.6);

\[
E [n(r)] = F [n(r)] + \int v_{\text{ext}}(r)n(r)dr \tag{2.6}
\]

where, \( v_{\text{ext}}(r) \) is an external potential imposed by the nuclei at point \( r \). Further, \( F [n (r)] \) contains the terms \( T [n (r)] \) and \( V_{\text{ee}} [n(r)] \) which represents the kinetic energy and electron-electron interaction;

\[
F [n(r)] = T [n (r)] + V_{\text{ee}} [n(r)] \tag{2.7}
\]
Although the Hohenberg–Khon [84] theorems give formal justification in determining the ground state electron density, however it does not provide a way to find the analytical solution for the universal $F [ n(r) ]$ and hence the ground state energy of a system cannot be determined.

In 1965, Kohn and Sham [85] proposed a practical method to find the ground state energy of a system. Kohn and Sham considered a fictitious system of $N$ electrons which are non-interacting having the same ground state as the real system of interacting electrons. In this ground state, the electrons remain in lowest energy orbitals where the ground state density can be written as

$$n(r) = \sum_{i=1}^{N} |\psi_i(r)|^2$$

(2.8)

The ground state energy of the fictitious system of $N$ electrons can be divided into the following terms:

$$E[n(r)] = T[n(r)] + \int v_{ext}(r)n(r)dr + E_H[n(r)] + E_{XC}[n(r)]$$

(2.9)

Here, the term $T[n(r)]$ represents the kinetic energy of the electrons of the fictitious system;

$$T[n(r)] = -\frac{1}{2} \sum_{i=1}^{N} \langle \psi_i | \nabla^2 | \psi_i \rangle$$

(2.10)

$E_H[n(r)]$, represents the Hartree energy term related to classical Coulomb repulsion between all electrons:

$$E_H[n(r)] = \frac{1}{2} \int \int \frac{n(r)n(r')}{|r-r'|} drdr'$$

(2.11)

And, the term $E_{XC}[n(r)]$ is the exchange correlation which is the difference between universal functional term $F[n(r)]$ with the kinetic $T[n(r)]$ and the $E_H[n(r)]$ energy terms of the
fictitious system. The exact functional of the \( E_{XC} [n(r)] \) is unknown therefore it has to be approximated.

The Kohn-Sham equation [85] for a fictitious system (non-interacting electrons) \( i \), can be written as:

\[
\left[-\frac{1}{2} \nabla_i^2 + V_{\text{eff}}(r_i)\right] \psi_i = \varepsilon_i \psi_i \tag{2.12}
\]

Where,

\[
V_{\text{eff}}(r) = v_{\text{ext}}(r) + \int \frac{n(r')}{|r-r'|} \, dr' + V_{xc}(r) \tag{2.13}
\]

Here, \( V_{\text{eff}}(r) \) is the effective potential which is the sum of the external potential \( v_{\text{ext}}(r) \), Hartree term \( \int \frac{n(r')}{|r-r'|} \, dr' \) and the exchange-correlation potential \( V_{xc}(r) \) is given by equation (2.14);

\[
V_{xc}(r) = \frac{\delta E_{xc}[n(r)]}{\delta n(r)} \tag{2.14}
\]

The first step towards solving the Kohn-Sham equations (2.12), (2.13) and (2.14), starts from an initial guess density \( n(r) \) which then determines \( V_{\text{eff}} \) and thereafter calculates a new \( n(r) \). This procedure is repeated self-consistently until \( n(r) \) converges and the ground state of the system is obtained. Further, the Kohn-Sham equations can find the exact ground state of the system provided the exact form of the \( E_{XC} \) is known. However, this is not the case and the exact form of \( E_{XC} \) is usually unknown. Therefore, in practical electronic structure calculations, the exchange-correlation term is approximated commonly that includes local density approximation (LDA) and generalized gradient approximation (GGA).

### 2.2.3 Exchange-Correlation Functionals

To determine the exchange-correlation functional, LDA is a simple approximation, considers only the electron density \( n(r) \) with respect to position. Further, the exchange part of the functional is an exact expression derived for a homogeneous gas equation (2.15):
\[ E_{xc}^{LDA} [n(r)] = \int n(r) \varepsilon_{xc}^{hom} n(r) dr \]  
(2.15)

Where, the homogenous electron gas exchange energy given by:

\[ \varepsilon_{xc}^{hom} = \frac{-e^2}{4\pi \varepsilon} \frac{3}{4} \left( \frac{3n}{\pi} \right)^{1/3} \]  
(2.16)

All the developed, LDA correlation functionals are on the basis of Ceperley and Alder’s (CA’s), Monte Carlo (MC) calculation of the uniform electron gas with varying densities [86]. Also, different fits of the CA data corresponds to LDA functional such as Perdew-Zunger (PZ) [87], Perdew–Wang (PW) [88] and Vosko-Wilk-Nusair (VWN) [89].

GGA improves the inadequacies of LDA by adding a gradient of the density \(|\nabla n(r)|\) (2.17);

\[ E_{xc}^{GGA} [n(r)] = \int n(r) \varepsilon_{xc} |\nabla n(r)| dr \]  
(2.17)

The GGA approximations have been seen to give better results for geometry optimization, vibrational frequencies and binding energies compared to that of LDA approximations [90]. Some of the popular GGA functionals are Perdew-Wang 91 (PW91) [91], Perdew-Burke-Enzerhof (PBE) [91], Revised Perdew-Burke-Enzerhof (RPBE) [92].

The choice of a functional to obtain reliable and accurate results is mostly system dependent, such as molecular or solid state systems. Among the GGA functionals, the PBE functional have been extensively tested for molecular systems and found to obtain reliable atomization energies [93]. For solids, PBE functional obtains good results for solids comprising of 3d-transition metals and alkaline earth- metals (Ca, Sr and Ba) [90, 94]. Therefore in the present thesis, all calculations have been carried out using PBE functional.

2.3 Periodic Systems and Bloch’s Theorem

To study surface specific properties of crystalline solids such as adsorption and catalytic reactions a slab or supercell approach is required. Crystalline solids or extended systems are complex and comprise of an infinite number of electrons, calculating this type of systems with
DFT is a formidable task. However, by assuming the structure of the extended systems to be periodic and by applying Bloch’s theorem \[95, 96\], the complexity of the calculation reduces.

### 2.3.1 Bloch’s Theorem

According to Bloch’s theorem, for a periodic system the electronic wave function \( \psi_{n,k} \) can be written as the product of a plane wave \( e^{i \mathbf{k} \cdot \mathbf{r}} \) and a periodic function \( u_{n,k}(r) \) leading to;

\[
\psi_{n,k}(r) = e^{i \mathbf{k} \cdot \mathbf{r}} u_{n,k}(r) \tag{2.18}
\]

Where in equation (2.18), \( \mathbf{k} \) is the wave vector and it lies inside the first Brillouin zone (BZ). The index \( n \), is known as the band index that labels the wave function for each \( \mathbf{k} \). The wave function \( u_{n,k}(r) \) has the periodicity of a lattice. Further, \( u_{n,k}(r) \) can be further expanded using plane wave vectors comparable to reciprocal lattice vectors \( \mathbf{G} \) for unit cell of the crystal.

\[
u_{n,k} = \sum_{\mathbf{G}} C_{i,G} e^{i \mathbf{G} \cdot \mathbf{r}} \tag{2.19}\]

Where, the reciprocal lattice vectors \( \mathbf{G} \) fulfils the boundary conditions of the unit cell, such that \( \mathbf{G} \cdot \mathbf{L} = 2\pi m \), where \( \mathbf{L} \) is the length of the real-space lattice vector and \( m \) is an integer. \( C_{i,G} \) is the plane–wave expansion coefficient.

Therefore from equations 2.18 and 2.19, therefore, the wave function for plane-wave basis set in reciprocal space may be written as;

\[
\psi_{n,k}(r) = \sum_{\mathbf{G}} C_{i,k+G} e^{i (\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}} \tag{2.20}\]

In principle, to represent a wave the basis set should be complete. But this will require an infinite number of plane waves, therefore the basis set is truncated using a kinetic energy cut-off \( E_{\text{cut-off}} \), in order to have a finite number of plane waves.

\[
\frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \leq E_{\text{cut-off}} \tag{2.21}\]

In the simulations using plane waves, the ground state energies and electron densities convergence depends upon the \( E_{\text{cut-off}} \) and \( \mathbf{k} \) points. This shows that higher the kinetic energy
cut-off the accuracy of the result increases, however, the simulation becomes expensive. Also, \( \mathbf{k} \) points are continuous in the BZ, with good simulation results are achieved with \( \mathbf{k} \)-point sampling. This \( \mathbf{k} \) point sampling can be achieved using Monkhorst and Pack (MP) method [97] which generates a \( \mathbf{k} \)-point grid in the BZ. In this thesis work, the MP method has been used in all DFT surface calculations.

### 2.3.2 Pseudopotential

The characteristics of valance and core electrons are different. For instance, core electrons are chemically inert being localized and tightly bound to the nucleus whereas the valence electrons are the chief architect in defining the electronic and chemical properties of an atom. Pseudopotentials create a partition between the core and valence electrons. This is an effective way of electronic structure calculation because the valence electrons are mainly responsible for describing the properties as the core electrons are independent to the external environment. Further, during calculations, the core electrons are not considered and only the valence electrons are treated with the full wave function. An added benefit is, that the orbitals can be represented with lower energy cut off. Further energy cut-off may depend upon the type of pseudopotential being used. As a norm-conserving [98] pseudopotential will require higher energy cut-off compared to Vanderbilt ultrasoft pseudopotential [99].

### 2.3.3 Surface Modelling

To understand the electronic structure and catalytic properties of periodic systems in plane-wave methods, a supercell approach is required. In this kind of approach, a computational surface model is constructed by truncating the primitive bulk unit cell of a periodic solid system into possible crystallographic directions [100]. Thereafter the periodicity of the 3D surface is broken in the \( Z \) direction forming layers of surface slabs.
In Figure 2.1 (a), the unit cell is shown with rectangular dashed lines. These slab layers are separated by vacuum (Vac) in the Z direction, firstly to maintain the periodicity of the system and secondly, to avoid interactions between the periodic images of the constructed slab in both top and bottom directions. Therefore the width of the Vac should be sufficiently large (above 10 Å). Additionally, the slab layers formed should be thick enough to reproduce, bulk properties of the periodic system. This is mainly system dependent and may vary between 4-20 atomic layers.

Figure 2.1(b) shows the top view of the modelled 3 ×3 unit cell of Ni (111) surface slab, where the f, t, h and r, represents face centred cubic (fcc), top, hexagonal closed packed (hcp) and bridge high symmetry adsorption sites. These high symmetry sites provide insights into the bonding and energies between defined molecules or atoms with surface slabs.

2.4 Transition state

For a chemical reaction to take place it will form a minimum of three (reactant, transition and product) states. Among these states, the reactant state is considered to an initial state of a chemical reaction while the product is the final state of the reaction. In between these two states occurs the transition state, which is required to understand the mechanism of the chemical process. The location of the transition states for a particular reaction may be achieved by constructing a potential energy surface (PES). Where a minimum energy path connecting the
reactant and product structures can be mapped out [101, 102]. Further, the difference between the energies of reactant and product states gives the enthalpy of the reaction \( (\Delta H_r) \), where the value may be negative or positive describing the reaction to be either exothermic or endothermic respectively. Also, the difference between the reactant or initial state to that of the transition state provides the activation energy barrier(\( \Delta E_a \)).

To locate the minimum energy paths (MEPs) there are a number of transition state methods available such as, nudge elastic band method (NEB) [103], dimer method [104] and linear synchronous transit (LST) and quadratic synchronous transit (QST) , commonly known as LST/QST method [102]. We will focus on the later method as all the transition state calculations in this thesis work were done using LST/QST.

![Flow chart of transition state LST/QST algorithm adapted from Govind et al. [102]. In the flow diagram converged refers to simulation goes below the force tolerance user-defined value Analysis is vibration frequency analysis.](image)

**Figure 2.2** Flow chart of transition state LST/QST algorithm adapted from Govind et al. [102]. In the flow diagram converged refers to simulation goes below the force tolerance user-defined value Analysis is vibration frequency analysis.
The LST/QST method is explained with a flow chart shown in Figure 2.2. In the first step, the method computes the energies of the reactant and products. In the next step between the reactant and product points, the maximum along the LST path is searched. During the LST search if the maximum is found then the conjugate gradient (CG) optimization of the structure is performed until the forces on the structure fall below the given tolerance value. If the forces are found to be below the tolerance, then the calculation is considered to be converged and can be used for further analysis. Otherwise, a new maximum is searched along the QST path. This path connects the reactants, products with an intermediate structure close to the transition state. After maximum for QST is found, the CG step is again performed until it converges to the force tolerance value.

For the converged transition state structure obtained, either from the LST or QST searches is then undergoes vibration frequency analysis. From this analysis, the transition state structure obtained should have one negative frequency (imaginary mode), which corresponds to a saddle point on the energy hypersurface [102].

2.4.1 Microkinetic Modelling

Microkinetic modelling is a valuable predictive technique to understand the behaviour of complex reactions at high temperature and pressure conditions. This type of modelling works in conjunction with DFT calculations, where ground state properties are obtained (0 K, 0 bar). To effectively analyse the behaviour reactions over catalysts at real reaction conditions, thermodynamic properties such as Gibbs free energy $\Delta G(T, P)$ can provide a proper estimate at high temperature and pressures. These thermodynamic properties can be further used to determine the kinetics of a process using microkinetic modelling.

In this thesis, for microkinetic modelling, we have used the Catalysis Microkinetic-analysis package (CatMAP) [105], which has been widely used to predict catalytic trends on heterogeneous catalysts. CatMAP is a descriptor based mean-field microkinetic package which provides steady-state solutions for elementary reaction steps using the following equations (2.22-2.25) [105, 106];

$$ r_i = k_i^+ \prod_j \theta_{ij} \prod_j p_{ij} - k_i^- \prod_l \theta_{il} \prod_l p_{il} $$ (2.22)
\[ k_i^+ = \frac{k_B T}{h} \exp \left( -\frac{\Delta G_{a,i}^+}{k_B T} \right) \] (2.23)

\[ k_i^- = \frac{k_B T}{h} \exp \left( -\frac{-(\Delta G_{a,i}^- + \Delta G_{a,i}^+)}{k_B T} \right) \] (2.24)

\[ \frac{\partial \theta_i}{\partial \tau} = \sum_j s_{ij} r_j \] (2.25)

Where in equation (2.22), \( r_i \) is the rate for each elementary step, \( k_i^+ \) and \( k_i^- \) shows the forward and reverse rate constants which are calculated using the transition state theory. Where, \( \Delta G_{a,i}^+ = G_{TS} - G_{IS} \) and \( \Delta G_{a,i}^- = G_{FS} - G_{IS} \), \( k_B \) and \( h \) are the Boltzmann and Planck constants. Further \( G_{IS}, G_{TS} \) and \( G_{FS} \) are the Gibbs free energies for the initial, transition and final states respectively. These Gibbs free energies are computed from DFT obtained formation energies with thermodynamic corrections (enthalpy and entropy). The thermodynamic corrections are computed using harmonic approximation for adsorbates and gases. \( \theta_{ij} \) and \( \theta_{il} \) indicates the surface concentration for reactant and products for the elementary step \( i \). Also, \( p_{ij} \) and \( p_{il} \) are the unit less pressures of the gas phase reactants for elementary step \( i \). Here the sum of all the coverages for each type of adsorption site is constrained to be 1. Further, \( s_{ij} \) in equation, represents the coefficients for stoichiometry species \( i \) in elementary step \( j \). These set of non-linear differential equations are solved using a modified Newton’s method of root finding algorithm which should satisfy the equation (2.26).

\[ \frac{\partial \theta_i}{\partial \tau} = 0 \] (2.26)

Which must be solved subject to site conservation constraint, equation (2.27):

\[ \sum_i \theta_i = \theta^{TOT} \] (2.27)

Here, \( \theta^{TOT} \) is the normalized surface area.
Chapter 3: DFT based microkinetic study of CO$_2$ dry reforming of methane (DRM) on Ni (111)

**Short abstract:** To further the development of Ni-based catalysts in perspective of CO$_2$ dry reforming of methane (DRM) it is imperative to first develop a detailed mechanistic understanding of DRM process on plane Ni surfaces. Here in first the CO formation pathways were envisaged on Ni (111) facet using DFT analysis, where the oxidation pathway of CH-O resulted to be most favourable. This prediction was further confirmed with microkinetic analysis, where the calculated forward reaction rates showcased the CH-O pathway to be 1.66 times faster than the C-O oxidation pathway. Furthermore, at higher DRM temperature above 1000 K, the oxidation pathways are rate-determining steps. Finally, microkinetic studies also revealed, atomic carbon coverage to be more and increases at higher DRM temperatures compared to oxygen, thereby forming coke precursors on Ni (111) surface.

3.1. Introduction

Nickel (Ni) based catalysts have received a general acceptance among the scientific and industrial community as reference materials for CO$_2$ dry reforming of methane (DRM), due to their high activity, selectivity, availability and low cost [50, 107-109]. However, Ni undergoes severe coke deposition and sintering at high reaction temperatures during the DRM process which eventually leads to catalyst deactivation [50, 110]. To improve the carbon stability of the Ni catalyst various strategies like yolk-shell structures and surface alloys has been previously investigated. Most recently synthesis of new yolk-shell based Ni catalysts has shown to reduce sintering and increase carbon resistance during DRM [111]. Price et al. used a ZnO/Ni@m-SiO$_2$ yolk–shell catalyst for DRM observing long term stability of the catalyst with high CO$_2$/CH$_4$ conversion, but with some coking [111]. Zhao et al. using a NiCe@m-SiO$_2$ yolk-shell structure, with a combination of Ni nanoparticle and CeO$_2$ encapsulated inside silica shells restricted carbon formation during DRM [112]. In surface alloying, enhanced carbon tolerance of the Ni catalyst has been reported, especially when alloying with noble metals such as Ru, Rh, Pd and Pt, both activity and stability of the Ni catalyst has increased considerably in comparison to mono-metallic Ni catalysts [113]. Although these various attempts to improve Ni-based formulations have shown some promising findings, the approach remains on trial and error. Therefore, it is of vital importance to first explore the underlining reaction mechanisms and kinetics on Ni single surfaces under realistic reaction conditions to
develop a more consistent methodology to achieve highly robust Ni catalysts for reforming processes. However, the large number of elementary reaction steps involved in the DRM reaction mechanism network makes it difficult to investigate the rate-determining steps (RDS). One way to achieve the detailed understanding of reaction mechanisms is through Density functional theory (DFT), which is well known to be a reliable method to explore the atomic understanding of gas-phase molecules to surface interaction [72]. For instance Wang et al. in their theoretical studies of detailed DRM reaction mechanism on Ni (111) surface found the C-H activation to be the RDS and CH-O oxidation route is more favourable than C-O route [32, 33]. Following this Zhu et al., conducted DFT based thermodynamic calculations on Ni (111) at, comprising of the detailed DRM reaction network and found that at 973 K, CO formation favours the CH–O oxidation pathway and both the oxidation steps were identified as RDS [114]. In addition, the possible oxidation route during DRM occurs via, the CH₄ sequential dissociation to CH, thereafter oxidation of CH with O [32, 114]. From the studies conducted by Wang et al. and Zhu et al., it is seen that the CO formation occurring through the CH oxidation route however there remains some contradiction. Fan et al. conducted investigation of the DRM reaction mechanisms using DFT based microkinetic study wherein through the analysis of the forward reaction rates they found C oxidation (C-O) path to be mainly responsible for CO formation with both oxidation paths (C-O) and (CH-O) to be RDS at DRM [35]. In other microkinetic studies of DRM reaction mechanism over Ni (111) by Zhi et al [115] and Foppa et al. [36] found the CH-O path to be favourable towards CO formation. Among the two DRM reactants (CH₄ and CO₂) Wei and Iglesia through Isotopic and kinetic analysis reported the DRM reaction rate to depend upon C-H bond activation without influence of the co-reactant [116]. Additionally, C-H bond activation is an RDS at lower DRM temperatures [114, 115].

In this chapter, firstly the stability of DRM intermediates on different adsorption sites of Ni (111) is studied systematically using DFT. Thereafter, both DFT and MKM is used to elucidate the most likely CO formation pathway in DRM on Ni (111) surface. From the key insights developed in the DFT and microkinetic studies, the coke formation on Ni (111) is analysed.
3.2. Computational Methods

3.2.1 DFT calculations

In this chapter, periodic spin-polarized DFT calculations are performed using the Cambridge Sequential Total Energy Package (CASTEP) [117]. The calculations use the generalized gradient approximation (GGA) and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [118]. The plane wave kinetic energy cut-off 400 eV is used in all the calculations. Gaussian smearing method [119] is used to determine the electron occupancies with a smearing value of 0.2 eV. Brillouin zone sampling is performed using the Monkhorst–Pack method [97] 3 × 3 × 1 k-points grid for the Ni (111) slab. Convergence tests of CO adsorption on Ni (111) slab with denser k point grid (5×5×1) is performed, resulting in adsorption energy change below 0.04 eV. Additionally, dipole correction to the energy is applied self-consistently in the z-direction. The geometry of isolated species was optimized in a cubic box of 15 Å × 15 Å × 15 Å. Adsorption energy (E_{ads}) of the surface adsorbed species is defined by

\[ E_{ads} = E_{\text{species+slab}} - E_{\text{slab}} - E_{\text{species}} \]  

(3.1)

where \( E_{\text{species+slab}} \) represents the energy of the adsorbed species on the modelled surface, \( E_{\text{slab}} \) total energy of the clean surface slab and \( E_{\text{species}} \) corresponds to the energy of the gas phase molecules.

The transition state (TS) searches are performed using the same level of theory for those applied to the reactants and products with the complete linear synchronous transit (LST)/quadratic synchronous transit (QST) method [102]. The convergence criterion for the transition state search is set to be 0.25 eV/Å root-mean-square forces on atoms. The uniqueness of the (TS) structures was confirmed using vibrational frequency analysis using the finite displacement method [120].

3.2.2 Microkinetic calculations

The microkinetic analysis to examine the activity of the Ni (111) catalyst surface was performed using a descriptor based microkinetic model package CatMAP [105]. The rates for the elementary reactions of DRM considered in this work are determined by solving differential equations numerically at steady state approximation. In CatMAP the free energies for the
adsorbates and the gas phase entropies and enthalpies are calculated using ideal gas thermochemistry as implemented in ASE. Free energies and rate constants are calculated from DFT obtained activation energies using the harmonic transition-state theory.

3.3. Results and discussions

3.3.1 Surface properties

Based on our DFT calculations the lattice constant for the Ni (fcc) bulk crystal is calculated to be of 3.525 Å in good agreement with the experimental value of 3.52 Å [121]. Additionally, the magnetic moment for the bulk Ni atoms is calculated to be 0.66 which is in reasonable agreement with the experimental value of 0.61 [122]. Further, the distance between the bulk atoms (Ni-Ni) is calculated to be 2.49 Å.

To develop the Ni (111) surface a 4-layer infinite periodic slab thickness with 9 atoms per layer is used where bottom 2 layers of the surfaces were kept fixed to their bulk position during all geometry optimizations. The surface formation energy for the first two layers is calculated to be 2.01 J/m² in close agreement with experimental values of (2.38 J/m²) [123]. The distance
between the Ni atoms for the constrained layers is similar to the bulk and for the surface layer, it slightly reduces by 0.02 Å. Further the Ni (111) surface comprises of four unique adsorption sites shown in Figure 3.1, namely three-fold hollow sites fcc and hcp with bridge and top sites.

### 3.3.2 Adsorption of the DRM species

Figure 3.2 Shows the most stable surface sites for adsorption of CHx (x=0-4) species, atomic and molecular hydrogen on Ni (111). H (white atom), C (dark grey) and Ni (green).
Table 3. 1 Adsorption energies ($E_{\text{ads}}$) in eV and adsorption sites for the CHx and hydrogen species involved in DRM on Ni (111) surface. The $E_{\text{ads}}$ in bold denotes the most stable sites of particular species for adsorption on Ni (111).

<table>
<thead>
<tr>
<th>Species</th>
<th>$E_{\text{ads}}$ (eV)</th>
<th>q (e)</th>
<th>Bond</th>
<th>Bond length (Å)</th>
<th>Ref [E_{ads}] (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$ -top</td>
<td>-0.02</td>
<td>-0.18</td>
<td>C-H</td>
<td>1.11, 1.11, 1.11, 1.11</td>
<td>-0.02 [114, 115]</td>
</tr>
<tr>
<td>CH$_3$-fcc</td>
<td>-2.02</td>
<td>-0.63</td>
<td>C-H</td>
<td>1.12, 1.13, 1.13</td>
<td>-1.91 [114], -1.81 [32]</td>
</tr>
<tr>
<td>CH$_3$-hcp</td>
<td>-1.98</td>
<td>-0.63</td>
<td>C-H</td>
<td>1.12, 1.12, 1.13</td>
<td>-1.78 [32]</td>
</tr>
<tr>
<td>CH$_3$-bri</td>
<td>-1.79</td>
<td>-0.55</td>
<td>C-H</td>
<td>1.11, 1.11, 1.14</td>
<td>-</td>
</tr>
<tr>
<td>CH$_3$-top</td>
<td>-1.62</td>
<td>-0.41</td>
<td>C-H</td>
<td>1.11, 1.11, 1.11</td>
<td>-1.55 [32]</td>
</tr>
<tr>
<td>CH$_2$-fcc</td>
<td>-4.10</td>
<td>-0.64</td>
<td>C-H</td>
<td>1.11, 1.17</td>
<td>-4.01 [114], -4.02 [48]</td>
</tr>
<tr>
<td>CH$_2$-hcp</td>
<td>-4.02</td>
<td>-0.64</td>
<td>C-H</td>
<td>1.11, 1.17</td>
<td>-3.83 [32]</td>
</tr>
<tr>
<td>CH-fcc</td>
<td>-6.50</td>
<td>-0.52</td>
<td>C-H</td>
<td>1.11</td>
<td>-6.43 [114] -6.27 [32]</td>
</tr>
<tr>
<td>CH-hcp</td>
<td>-6.47</td>
<td>-0.54</td>
<td>C-H</td>
<td>1.11</td>
<td>-6.48 [32]</td>
</tr>
<tr>
<td>C-fcc</td>
<td>-6.67</td>
<td>-0.45</td>
<td>C-Ni</td>
<td>1.76, 1.76, 1.77</td>
<td>-6.52[32]</td>
</tr>
<tr>
<td>C-hcp</td>
<td>-6.72</td>
<td>-0.47</td>
<td>C-Ni</td>
<td>1.76, 1.76, 1.76</td>
<td>-6.78 [114], -6.61 [32]</td>
</tr>
<tr>
<td>H-fcc</td>
<td>-2.78</td>
<td>-0.27</td>
<td>H-Ni</td>
<td>1.70, 1.71, 1.71</td>
<td>-2.81 [114]</td>
</tr>
<tr>
<td>H-hcp</td>
<td>-2.77</td>
<td>-0.26</td>
<td>H-Ni</td>
<td>1.71, 1.71, 1.71</td>
<td>-2.76 [32]</td>
</tr>
<tr>
<td>H-top</td>
<td>-2.19</td>
<td>-0.10</td>
<td>H-Ni</td>
<td>1.47</td>
<td>-2.22 [32]</td>
</tr>
<tr>
<td>H$_2$-top</td>
<td>-0.31</td>
<td>-0.18</td>
<td>H-H</td>
<td>0.89</td>
<td>-0.22 [32]</td>
</tr>
</tbody>
</table>
3.3.2.1 Adsorption of CHx species

The adsorption of CHx$_{(x=0-4)}$ species, monoatomic carbon (C), hydrogen (H) and molecular hydrogen (H$_2$), on all the available sites on the Ni (111) surface is shown in Table 1 and the optimised figure for the most stable adsorption sites are shown in Figure 3.2 (i-xiv).

The most stable adsorption configuration of CH$_4$, with three hydrogen atoms pointing towards the Ni (111) surface is found to physisorb with $E_{\text{ads}}$ of -0.02 on the top site, agreeing closely with previous theoretical studies [114, 115]. The net charge on the CH$_4$ molecule is 0.18 e with uniform C-H bond lengths stretches from 1.09 Å in the gas phase to 1.11 Å on adsorption. CH$_3$ showcases favourable adsorption on all the available sites with the most stable site being fcc with $E_{\text{ads}}$ of -2.02 eV, which is marginally higher than previous studies [114]. The net charge on the CH$_3$ atom on the fcc site is 0.63 e with one C-H bond shortening to 1.12 Å from 1.13 Å found in gas phase molecule. Further CH$_3$ adsorption on the hcp site is similar to that on fcc site with $E_{\text{ads}}$ difference of 0.04 eV and comparatively weak adsorption of CH$_3$ is observed on the top site with $E_{\text{ads}}$ difference of 0.36 eV compared to the fcc site. CH$_2$ prefers both the hollow sites (fcc and hcp) to form a stable adsorption configuration. The adsorption on fcc site ($E_{\text{ads}}$) - 4.10 eV is slightly higher compared to the hcp site by -0.08 eV. Further, the CH$_2$ adsorption energy obtained in this compares very well with previous work [114]. Additionally, the net charge on the adsorbed CH$_2$ atom on the stable fcc site is found to be similar by 0.64 e with a uniform C-H bond stretching of 1.17 Å on both the hollow sites. Again for CH, the preferential sites are the hollow sites (fcc and hcp), with fcc being the most stable adsorption site. CH adsorbs on the fcc site with $E_{\text{ads}}$ of -6.50 eV, similar to previous studies [114]. Interestingly the net charge on the CH atom is slightly higher on the hcp site with 0.54 e which has also been reported in a previous study [32]. Similar to CH, C also prefers to occupy the hollow sites with bridge and top sites being unstable for C adsorption. The hcp site binds C more strongly with $E_{\text{ads}}$ of -6.72 eV compared to -6.67 eV on the fcc site. Notably, among the CHx species, atomic carbon interacts strongly with Ni (111) surfaces and may be a primary cause for carbon formation on Ni surfaces, this has been also reported elsewhere [32, 114]. Atomic hydrogen (H) prefers three adsorption sites (fcc, hcp and top) with strong $E_{\text{ads}}$ of -2.78 eV and -2.77 eV on fcc and hcp respectively. Compared to fcc and hcp the top site is less favourable with $E_{\text{ads}}$ of -2.19 eV. Additionally, the energy values obtained for atomic hydrogen adsorption closely compare with previous works [114]. Similar to previous findings, H$_2$ exhibits dissociative
adsorption onto the hollow sites (fcc and hcp) [32]. The molecular adsorption of H$_2$ is only encountered on the top site, where the obtained E$_{ads}$ of -0.30 eV is slightly higher compared to the previous reported value of -0.22 eV [114].

### 3.3.2.2 Adsorption of the oxygenated species

![Figure 3.3](image)

Figure 3.3 Shows the most stable surface sites for adsorption of oxygenated species which includes CO$_2$, CO, CHO and O on Ni (111). O (red atom), C (black), H (white) and Ni (green).
Table 3. 2 Adsorption energies ($E_{ads}$) in eV and adsorption sites for the oxygenated species involved in DRM on Ni (111) surface. The $E_{ads}$ in bold denotes the most stable sites of particular species for adsorption on Ni (111).

<table>
<thead>
<tr>
<th>Species</th>
<th>$E_{ads}$ (eV)</th>
<th>q (e)</th>
<th>Bonds</th>
<th>Bond length (Å)</th>
<th>Ref [E$_{ads}$] (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$phisorb - top</td>
<td>-0.02</td>
<td>-0.04</td>
<td>C-O</td>
<td>1.18, 1.18</td>
<td>-0.02 [114]</td>
</tr>
<tr>
<td>CO$_2$chemisorb - off - top</td>
<td>0.38</td>
<td>-0.39</td>
<td>C-O</td>
<td>1.21, 1.27</td>
<td>0.31 [124]</td>
</tr>
<tr>
<td>CO-fcc</td>
<td>-1.82</td>
<td>-0.39</td>
<td>C-O</td>
<td>1.19</td>
<td>-1.89 [115]</td>
</tr>
<tr>
<td>CO-hcp</td>
<td>-1.83</td>
<td>-0.42</td>
<td>C-O</td>
<td>1.20</td>
<td>-</td>
</tr>
<tr>
<td>CO-bri</td>
<td>-1.72</td>
<td>-0.33</td>
<td>C-O</td>
<td>1.18</td>
<td>-</td>
</tr>
<tr>
<td>CO-top</td>
<td>-1.51</td>
<td>-0.09</td>
<td>C-O</td>
<td>1.16</td>
<td>-</td>
</tr>
<tr>
<td>CHO-fcc</td>
<td>-2.28</td>
<td>-0.48</td>
<td>C-O</td>
<td>1.29</td>
<td>-2.26 [114]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C-H</td>
<td>1.11</td>
<td></td>
</tr>
<tr>
<td>CHO-hcp</td>
<td>-2.26</td>
<td>-0.47</td>
<td>C-O</td>
<td>1.29</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C-H</td>
<td>1.11</td>
<td></td>
</tr>
<tr>
<td>CHO-bri</td>
<td>-2.27</td>
<td>-0.47</td>
<td>C-O</td>
<td>1.29</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C-H</td>
<td>1.11</td>
<td></td>
</tr>
<tr>
<td>O-fcc</td>
<td>-5.62</td>
<td>-0.63</td>
<td>O-Ni</td>
<td>1.84</td>
<td>-5.67$^{12, 28}$</td>
</tr>
<tr>
<td>O-hcp</td>
<td>-5.49</td>
<td>-0.57</td>
<td>O-Ni</td>
<td>1.84</td>
<td>-</td>
</tr>
</tbody>
</table>

The gas phase CO$_2$ molecule has a linear structure Figure 3.2 (i) which physisorbs onto the Ni (111) surface on the top site with $E_{ads}$ of -0.02 eV. However previous theoretical studies have predicted that covalent bonds of CO$_2$ are only formed during the chemisorption state [124, 125] of the molecule. Where to achieve the chemisorbed state, the CO$_2$ gas phase molecule has to be bent artificially form its stable linear form. We have reproduced this configuration Figure 3.2 (ii) and found that CO$_2$ adsorbs on the two-fold bridge site, annotated as (off-top) site in...
this case. Our calculated adsorption energies were found to be endothermic, 0.38 eV on Ni (111) surface, which is marginally higher than the $E_{ads}$ value calculated by Wang et al. 0.31 eV [124]. Additionally, the net charge on the CO$_2$ molecule increases from physisorbed structure 0.04 $e^-$ to 0.39 $e^-$ during chemisorption state. CO molecule interaction with the hollow sites Figure 3.2 (iii-iv) showcases the strongest adsorption energies with the hcp site being the most stable by -1.83 eV ($E_{ads}$) closely followed by the fcc site with $E_{ads}$ of -1.82 eV, the energies are found to be slightly lower than that previous studies [115] but higher than the experimental value of 1.35 eV [126]. Further, the C-O bond of the CO molecule at the most stable site (hcp) elongates to 1.20 Å from 1.14 Å in the gas phase. CHO is found to adsorb on three stable sites hcp, fcc and bridge. Where CHO binds strongly to the fcc site with $E_{ads}$ on -2.28 eV, which compares closely with the previous result of -2.26 eV [114]. Further, the C-O (1.29 Å) and C-H (1.11 Å) bond lengths of CHO molecules are found to be uniform on the stable adsorption sites. Finally, atomic oxygen prefers to chemisorb only on the hollow sites with fcc site being the most stable with ($E_{ads}$) of -5.62 eV, which compares closely with a previous reported value of -5.67 eV [114].

In summary, the three-fold hollow sites (fcc and hcp) are the most preferred sites for adsorption for most of the DRM species on Ni (111) surface.

3.3.3 DRM reaction mechanism

![Image of DRM reaction mechanism]

**Figure 3.4** DRM reaction mechanism scheme followed in this work with subtraction and addition of hydrogen and oxygen atom on the required reaction steps shown in green and red colours respectively.
A schematic representation of the DRM reaction mechanism followed in this work is shown in Figure 3.4. Essentially the considered reaction mechanism scheme may be broadly divided into four categories, where the first two categories comprise of the mechanisms for methane and carbon dioxide activation, where methane activates on the catalyst surface via sequential CH$_4$ dehydrogenation CH$_x$(0-4) leading to formation of atomic carbon and hydrogen while for CO$_2$ activation the direct dissociation route to CO and O is considered. Additionally activation of CO$_2$ may occur through two other routes by combing with the surface H to form hydroxyl carboxyl (COOH) or formate (HCOO) intermediates which further decompose to form CO and OH or HCO and O. However, Fan et al. [35], in their microkinetic study on Ni (111) reported that the forward reaction rates for the latter two CO$_2$ activation routes to be much slower and negligible in case of the COOH intermediate compared to the direct dissociation rate. In the last two, categories the reactions for the oxidation of the main carbon intermediates (CH and C) leading to the formation of CHO intermediate and eventually CO. Further, the two CO forming routes are on the basis of previous theoretical findings [32, 34, 35, 114], CH-O and C-O routes have been found to be RDS in DRM with some contradiction on the favourability of the CO formation route. We have systematically investigated these reaction steps on Ni (111) surface, where the transition state parameters shown in Table 3.3, transition state configurations for CHx species in Figure 3.5 (R1–R4)) with PES (Figure 3.6), hydrogen formation in Figure 3.7 (R5), CO$_2$ activation [Figure 3.8 (R6)] and CO formation reactions [Figure 3.9 (R7–R9)]. Further, the vibration frequencies for adsorbates and transition states on Ni (111) are given in appendix A (A1).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH$_r$ (eV)</th>
<th>ΔE$<em>{a,f}$ (ΔE$</em>{a,b}$) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>-0.08</td>
<td>1.10 (1.18)</td>
</tr>
<tr>
<td>R2</td>
<td>0.13</td>
<td>0.71 (0.58)</td>
</tr>
<tr>
<td>R3</td>
<td>-0.34</td>
<td>0.32 (0.65)</td>
</tr>
</tbody>
</table>

*Table 3.3* Elementary reactions of DRM on Ni (111) surface with an activation energy of the forward (ΔE$_{a,f}$) and backward (ΔE$_{a,b}$) reactions and reaction energy (ΔH$_r$).
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction Equation</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R4</td>
<td>CH* + * → C* + H*</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.41 (0.79)</td>
</tr>
<tr>
<td>R5</td>
<td>H* + H* → H₂*</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.90 (0.77)</td>
</tr>
<tr>
<td>R6</td>
<td>CO₂* → CO* + O*</td>
<td>-1.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.59 (1.60)</td>
</tr>
<tr>
<td>R7</td>
<td>C* + O* → CO* + *</td>
<td>-1.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.37 (2.96)</td>
</tr>
<tr>
<td>R8</td>
<td>CH* + O* → CHO* + *</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.31 (1.06)</td>
</tr>
<tr>
<td>R9</td>
<td>CHO* + * → CO* + H*</td>
<td>-1.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.32 (1.55)</td>
</tr>
</tbody>
</table>

### 3.3.3.1 CH₄ activation (R1-R4)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(IS)</th>
<th>(TS)</th>
<th>(FS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td>C-H = 1.11 Å</td>
<td>C-H = 1.65 Å</td>
<td>C-H = 3.11 Å</td>
</tr>
<tr>
<td>R2</td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td>C-H = 1.13 Å</td>
<td>C-H = 2.37 Å</td>
<td>C-H = 3.15 Å</td>
</tr>
<tr>
<td>R3</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td>C-H = 1.17 Å</td>
<td>C-H = 1.71 Å</td>
<td>C-H = 2.96 Å</td>
</tr>
</tbody>
</table>
Previous experimental investigation by Wei and Iglesia [116] has shown that the forward reaction rates of the DRM reaction greatly depend on the C-H bond activation whereas the concentration of the co-reactant (CO₂) does not influence the reaction rates.

In our DFT calculations for the first sequential step for CH₄ activation in Figure 3.5(R1), shows the (IS) structure of physisorbed configuration of methane on the top of a Ni atom, where the C-H bond of adsorbed methane molecule is found to be 1.11 Å. Further, in the FS co-adsorbed structure CH₃ and H occupy the fcc and hcp sites respectively, with the distance between carbon and detached hydrogen atom (C-H) is 3.11 Å. In the TS geometry, the C-H bond of CH₄ stretches to 1.65 Å and the detached CH₃ and H are on top of a Ni atom. Additionally, the calculated forward activation energy barrier (Eₐ,f) is 1.10 eV which is lower than the previously reported DFT value of 1.18 eV [32] and higher than the value of 0.91 eV reported in [114]. Also, the reaction is found to be slightly exothermic by -0.08 eV (ΔHᵣ).

The (TS) structure for the next sequential reaction step (R2) is shown in Figure 3.5 (R2), where the stable chemisorbed configuration of CH₃ adsorbed on the fcc site is considered as the (IS) and for (FS), co-adsorbed structures of CH₂ on fcc and H on hcp sites is considered. In the (TS) structure the distance between the C-H bond increases from 1.13 Å in (IS) to 2.37 Å in (TS). The activation energy barrier (Eₐ,f) for the reaction is 0.71 eV matching closely with previous DFT value of 070 eV [114]. Additionally, the reaction is found to be endothermic by 0.13 eV (ΔHᵣ).

For, the third sequential reaction step (R3) shown in Figure 3.5 (R3), CH₂ adsorbed on the fcc site is selected to be the (IS) and co-adsorbed CH at fcc and H at hcp sites is taken to be the (FS). The reaction is found to be exothermic by -0.34 eV (ΔHᵣ), with forward activation energy
(E_{a,f}) barrier decreasing significantly from the previous steps to be 0.32 eV, which matches well with the previous reported value of 0.35 eV [114]. Also in the (TS) configuration, the C-H bond stretches from 1.17 Å found for the chemisorbed CH₂ structure to 1.71 Å in the (TS).

**Figure 3.6** Potential energy surfaces (PES) for CHx (x=1-4) dehydrogenation mechanism on Ni (111). Here the contribution of the H atom at each sequential step to the PES is omitted for the sake of simplicity.

Finally, the dehydrogenation of CH* (R4) shown in Figure 3.5 (R4) is an important step, as it governs the formation of atomic carbon on the catalyst surface [32, 114]. In the transition state reaction, CH occupies the fcc site in the (IS) structure with the co-adsorbed C and H on the fcc and hcp hollow sites chosen as the (FS). During (TS) the C atom prefers to stay at the fcc site while the H moves to the Ni top site forming a C-H bond distance of 1.77 Å. A high forward activation energy barrier (E_{a,f}) of 1.41 eV is obtained for this step with the reaction energy being the most endothermic by 0.62 eV (ΔH_r) among the dehydrogenation steps.

It has been observed previously that the carbon deposition on the catalyst surface during DRM generally occurs during CH₄ dehydrogenation, which is a major source for atomic carbon [32, 33, 114], with the activation energy barrier of the CH cracking step (CH* + *→C* + H*) being an primary indicator for the kinetic and thermodynamic possibility of atomic carbon formation in DRM. In Figure 3.6, the potential energy surface (PES) CH₄ dehydrogenation on the Ni (111) surface is shown, where the initial (R1) and final (R4) sequential reaction steps are the
most energy demanding steps with the (R4) having the highest activation energy barrier. The CH* cracking step on Ni surface facets has been found to be structure sensitive, where low coordinate Ni facets such as Ni (100) and Ni (221) have lower activation energy barriers. This may be the reason why Ni surfaces are susceptible to carbon formation from CH₄ dehydrogenation, mainly attributed to low coordinate Ni facets [34, 35]. Further, on Ni (111) facet, CH becomes the most stable intermediate whereas for low coordinated facets atomic C is the most stable intermediate.

3.3.3.2 Hydrogen formation (R5)

The formation of the hydrogen molecule (R5) occurs from the adsorbed hydrogen atoms on the Ni (111) surface contributed chiefly through the methane dehydrogenation reactions (R1-R4). From Figure 3.7 (R5), the hydrogen atoms adsorbed on parallel hcp sites are considered to be the (IS) with the (FS) configuration forming on the top site of a nickel atom. The H-H bond length at (TS) is 1.25 Å. The forward activation energy barrier (E_{a,f}) for H₂ formation is calculated to be 0.90 eV with the reaction energy being slightly endothermic 0.13 eV (ΔH_r). Additionally, value of energy barrier compares well with the previously reported value of 0.92 eV [114].
3.3.3.3 CO2 activation (R6)

**Figure 3.8** Transition state configurations including (IS) initial state (TS) transition state (FS) final state for (R6) CO2 activation.

CO2 is the source of atomic oxygen in DRM and therefore the activation of CO2 on the surface of the catalyst is vital to understand the overall reaction mechanisms and ultimately to explain catalytic trends. Both experimentally and theoretically two main dominant routes for CO2 activation on Ni surfaces has been hypothesised namely, (i) direct dissociation of CO2 into CO and O, where the latter intermediate oxidises the CHx (x=0-4) species and (ii) CO2 activation with atomic hydrogen to firstly form COOH intermediate which eventually dissociates yielding CO and H over the surfaces of the catalyst [32, 33, 35, 114]. Here, the latter route (CO2 activation by hydrogen), has been found to be less dominant on all Ni surfaces facets with being a more preferred route on noble metal surfaces in DRM [36]. Therefore in our present calculations, we have focussed on the direct CO2 dissociation route.

For CO2 dissociation (R6), shown in Figure 3.8 (R6) the chemisorbed structure of CO2 on the off-top position on the Ni (111) surface is considered to be the (IS) and the (FS) configuration shows CO adsorbed on the fcc site and O on the opposite bridge site. In the (TS) configuration both CO and O are on the bridge sites opposite to each other with cleaving C-O bond elongated to 1.71 Å. The reaction is found to be highly exothermic with a forward activation energy barrier of 0.59 eV (Ea,f) which is found to be lower compared to previous results 0.67 [114] 0.78 eV [124, 125].
3.3.3.4 CO formation routes (R7-R9)

Although CO formation in DRM reaction may occur through several pathways, oxidation of CH and C intermediates are of primary interest. From our DFT calculations, it has become evident that the source of atomic carbon C formation occurs through sequential C-H bond dissociation (R1-R4). Further previous DFT calculations carried out by Zhu et al. [114], envisaged that among the CHx (x=0-3) oxidation reactions only CH and C are the most likely candidates undergo oxidation on Ni (111) surface. Therefore in the present calculations, we
have only considered the CH and C oxidation pathways to elucidate the most energetically favourable CO forming route.

CO formation by atomic carbon oxidation by O (R7) shown in Figure 3.9 (R7), the (IS) configuration of C is on the fcc site with the atomic O being in the opposite bridge site, which during the (TS) moves to the top site with the distance between C and O decreasing to 1.91 Å from 2.92 Å found during the (IS). The reaction energy is very exothermic by -1.59 eV (ΔH_r). Further the forward activation energy barrier is 1.37 eV (E_a,f), which is lower than the values by 1.59 eV [34], 1.61 eV [34] reported in previous works.

The oxidation of CH species undergoes two reaction steps, where initially CHO intermediate is formed (R8: CH* + O*→CHO* + *) and thereafter, CHO decomposes (R9: CHO* + *→CO* + H*) to form surface available CO* and H*.

CHO formation Figure 3.9 (R8) shows the (IS) configuration of CH occupying the fcc site and O in the adjacent bridge site. During the (TS) similar to C oxidation, the atomic O moves to the top site with C-O distance decreasing from 2.85 Å in the initial state to 1.87 Å. The forward energy barrier obtained for this reaction is 1.31 eV (E_a,f). Further, the endothermicity of CHO formation on Ni (111) has been previously established by Zhu et al. [114], matching perfectly with the value of 0.25 eV (ΔH_r) obtained in our study. In comparison, the CHO decomposition reaction is highly exothermic with a value of -1.23 eV (ΔH_r), accompanied with a low activation energy barrier of 0.32 eV (E_a,f). Figure 3.9 (R9) shows the C-H bond of CHO adsorbed on the fcc site in the (IS) geometry stretches from 1.11 Å to 1.37 Å during the (TS) producing CO and H on the surface during the (FS) of the reaction.
3.3.3.5 Free Energy analysis of DRM reaction mechanism

(a) PES of DRM reaction mechanism

(b) Free energy profile of DRM reaction mechanism and CO formation paths 1000 K and 1 bar.

**Figure 3.10** (a) PES of DRM reaction mechanism (b) Free energy profile of DRM reaction mechanism and CO formation paths 1000 K and 1 bar.
In the previous sections, we have investigated and established the adsorption characteristics and the elementary reaction steps of DRM intermediates on Ni (111). In this section, the DRM reaction routes have been evaluated and rate determining steps using combined DFT and free energy analysis. The free energy profile is drawn considering the thermal energy and entropic corrections for the gas phase and adsorbed DRM species at 1000 K and 1 bar pressure. Further, both energy profiles constructed are limited to the assumption that the elementary steps occur sequentially instead of simultaneously. Further, in the drawn energy profiles, the first step is considered to be the activation step among the main DRM reactants (CH\textsubscript{4} and CO\textsubscript{2}) having the lowest activation energy barrier. From Figure 3.10 (a-b) it is seen that low and high temperatures, CH and C oxidation steps are the rate-limiting steps in DRM. However, among the two CO formation routes considered in this work, the CH oxidation by O to form CHO and thereafter decomposing to CO and H is found to be the most favourable route.

3.3.4 DFT based microkinetic modelling

\[
\begin{align*}
\text{CH}_4(g) + *_s + *_h &\rightarrow \text{CH}_3^* - s + \text{H}^*_h & \text{R1} \\
\text{CO}_2(g) + 2*_* &\rightarrow \text{CO}^*_s + \text{O}^*_s & \text{R2} \\
\text{CH}_3^* - s + *_h &\rightarrow \text{CH}_2^* - s + \text{H}^*_h & \text{R3} \\
\text{CH}_2^* - s + *_h &\rightarrow \text{CH}^* - s + \text{H}^*_h & \text{R4} \\
\text{CH}^* - s + *_h &\rightarrow \text{C}^* - s + \text{H}^*_h & \text{R5} \\
\text{H}^*_h + \text{H}^*_h &\rightarrow \text{H}_2^* - h + *_h & \text{R6} \\
\text{H}_2^* - h + *_h &\rightarrow \text{H}_2(g) & \text{R7} \\
\text{CO}_2(g) + 2*_* &\rightarrow \text{CO}_s + \text{O}_s & \text{R8} \\
\text{C}^* - s + \text{O}^*_s &\rightarrow \text{CO}^*_s + * - s & \text{R9} \\
\text{CH}^* - s + \text{O}^*_s &\rightarrow \text{CHO}^*_s + * - s & \text{R10} \\
\text{CHO}^* - s + *_h &\rightarrow \text{CO}^*_s + \text{H}^*_h & \text{R11}
\end{align*}
\]
\[
\text{CO}^*_s + ^*_s \rightarrow \text{CO} (g) + ^*_s \quad \text{R12}
\]
\[
\text{H}_2\text{O} (g) \rightarrow \text{H}_2\text{O} (g) \quad \text{R13}
\]

The (\(^*_s\)) and (\(^*_h\)) represents open and hydrogen adsorption sites respectively on the Ni (111) surface.

To determine the main CO formation path on the Ni (111) surface on the basis of forward reaction rates, the CH-O and C-O oxidation pathways are further studied with mean-field descriptor based microkinetic modelling. Furthermore, the model also discusses the coverage of the adsorbed DRM species on Ni (111). A DRM reaction mechanism with 13 reaction steps (R1-13) is considered for the microkinetic model. Here as CH\(_4\) and CO\(_2\) have been seen to physisorbed onto the Ni (111) surface in our DFT findings, therefore, it has been considered to be a one-step process R1 and R8 respectively. Additionally, the desorption of the adsorbed species to form product gases H\(_2\) (R7) and CO (R12) has been also considered with the C-H (R10-11) and C-O (R9) as oxidation pathways respectively. R13 is taken to be a dummy reaction due to the H\(_2\)O gas involvement for calculating the formation energies of the gas phase and adsorbed species shown in and does not influence reaction in the present model.

Furthermore, the temperature range considered to study the microkinetics is between (900-1200) K and pressure of 1 bar which are typical conditions on lab-scale experiments. Additionally, the ratio of the concentration of CH\(_4\)/CO\(_2\)/CO/H\(_2\) is set to be 0.5/0.5/0.05/0.05 corresponding to approximately 10 % CH\(_4\) conversion in the present model.

**Table 3.4** Forward reaction rates (\(k_f\)) in s\(^{-1}\) for CH\(_4(g)\) + * →CH\(_3*)+ H* (R1), C-O and CH-O reaction pathways.

<table>
<thead>
<tr>
<th></th>
<th>Forward reaction rate (k_f) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>973.37 K</td>
</tr>
<tr>
<td>(k_f) (R1)</td>
<td>6.32 \times 10^{-1}</td>
</tr>
<tr>
<td>C-O path ((k_f\ C))</td>
<td>1.90</td>
</tr>
<tr>
<td>CH-O path ((k_f\ CH))</td>
<td>3.16</td>
</tr>
</tbody>
</table>
From Table 3.4, the dependence of the DRM reaction rate on the methane activation step is highlighted through calculated forward reaction rates $k_f$ for R1 at variable temperatures. Indeed methane activation is temperature dependent and may be even rate-determining at lower temperatures as observed by Fan et al. [35] and Jones et al. [15] in their microkinetic studies for steam and dry reforming.

The forward reaction rates $k_f$ C and $k_f$ CH for the two CO formation pathways are found to be kinetically involved in the generation of CO on Ni (111). As seen in Table 3.4, the forward reaction rates for both pathways play a key role in CO generation and where good C oxidation rates are required to deter carbon formation on the catalytic surface. However, on the basis of the reaction rates the CH-O oxidation pathway is found to be ~1.66 times more dominant than C-O pathway in temperature ranges between (900-1100) K with reducing slightly to 1.58 times at temperatures above 1100 K. The favourability of CH-O pathway or CO production, matches with our free energy analysis observation and previous theoretical findings [34, 36], thereby establishing the main CO formation route on Ni (111).
Figure 3.11 (a) Coverage of major species on the Ni (111) surface and (b) Coverage of minor species on the Ni (111) surface. All the microkinetic calculations are performed between a temperature range of (900-1200) K and pressure is kept constant at 1 bar.

Among the surface coverage of adsorbed DRM species, CO is found to have the major coverage on the surface Figure 3.11 (a), which is found to reduce with increasing temperature forming CO gas. Further hydrogen maintains a steady coverage but much lower than CO. CH coverage tends to increase at higher temperatures (above 1000K) owing to the delayed activation of methane at high temperatures. In regard to the concentration of the minor species (below $10^{-4}$), carbon coverage Figure 3.11 (b) tends to increase with temperature and eventually might compete with CH species at higher DRM temperatures leading to blocking of active sites which results in eventual catalyst deactivation. Although Ni (111) surfaces are closed packed Ni crystal facets and in DRM carbon formation are more prone to occur onto coordinated or stepped Ni crystal facets due to their higher binding strength with carbon [34], the available active sites will shift to the closed packed Ni crystal planes [35]. Therefore Ni (111) plane acts as a good indicator towards carbon nucleation which has become clear from Figure 3.11(b), where even at low coverage, atomic carbon is found to be higher than atomic oxygen.
3.5 Coking on Ni (111) surface

The DRM is a complicated reaction network where coke formation on a catalytic surface might occur through coupling of between CH\textsubscript{x} species [34]. However primarily, the formation of atomic carbon in DRM on a particular catalyst’s surface may be considered to be a reliable measure for coking due to the tendency of carbon atoms to be precursors for graphene growth on catalyst surface [127]. Therefore we have performed DFT calculations shown in Figure 3.12,

\[ E_{a,f} = 0.36 \text{ eV} \]
\[ \Delta H_f = 0.04 \text{ eV} \]

**Figure 3.12** Transition state configurations including (IS) initial state (TS) transition state (FS) final state for (R6) carbon atom diffusion on Ni (111).

to measure the diffusion of single carbon atoms between highly stable hollow sites (hcp, fcc). The activation energy obtained for such a reaction was found to be 0.36 eV \((E_{a,f})\) with very low endothermicity. As a comparison the diffusion of carbon atoms becomes difficult on the noble metal surface. For instance, Pt (111) has larger activation energy barrier 0.90 eV \((E_{a,f})\) [36]. This showcases that mobility of carbon atoms to nucleate on Ni (111) surface to form graphene is much greater. Furthermore from our DFT calculations and microkinetic investigations it has been evidenced that sequential dissociation of CH\textsubscript{4} contributes largely to the formation of atomic C, where CH\textsuperscript{*} (CH\textsuperscript{*} + *→C\textsuperscript{*} + H\textsuperscript{*}) cracking reaction step is responsible for controlling carbon formation. In addition Fan \textit{et al.} and Wang \textit{et al.} calculated CH cracking step is much faster on stepped Ni facets Ni (221) [34, 35], which confirms the step facets on Ni particle to be deactivated first. Another source of carbon formation may stem
from CO₂ dissociation to CO and thereafter dissociation to C and O. The reverse of this reaction step also may be responsible to reduce coking were the rate of atomic carbon oxidation becomes important. The calculated kinetic values for forward reaction rate for C oxidation is found to be lower than rates of CH₄ dissociation reactions which indicates the Ni (111) surface to be prone to coking during DRM.

3.6 Conclusions

A systematic detailed DFT based microkinetic study on Ni (111) was carried out to investigate DRM reaction mechanism. Our DFT calculation firstly showcased the stable active sites for the DRM intermediates to react. Where the threefold (fcc and hcp) sites was preferred by most of the adsorbates with CH₄ only physisorbing. Further, the linear configuration of CO₂ molecule also physisorbs with low charge transfer from the surface. However, CO₂ was found to chemisorb with a bent structure, where the charge transfer from the surface increases. Additionally, in regards to the adsorption energies calculated, atomic carbon and oxygen species are the most stable on Ni (111).

To predict the CO formation the pathways both DFT based PES and Free energy analysis was explored. Where the CH-O oxidation pathway compared to C-O was found to be more favourable. However, both oxidation pathways were found to energetically demanding at low and higher temperatures. This was also ascertained by microkinetic study, where the reaction rate for CH-O was found to lower that C-O pathway. Further, the concentration of carbon was found to be higher than oxygen Ni (111) surface with C coverage increasing with temperature. We further analysed this observation with DFT analysis of atomic carbon diffusion between two adjacent sites, which showed that atomic carbon requires a low energy barrier to diffuse between sites on Ni (111). From the above analysis, it may be concluded that to negate atomic carbon formation the CH species stability on the Ni (111) surface is important.
Chapter 4: Effect of tin (Sn) in improving Ni catalyst stability in DRM

Short abstract:
Nickel catalysts in DRM fail to overcome the stability requisites in terms of resistance to coking and sintering. In this scenario, the use of Sn as a promoter of Ni leads to more powerful bimetallic catalysts with enhanced stability which could result in a viable implementation of the reforming technology at a commercial scale. This chapter uses a combined computational (DFT based microkinetics) and experimental approaches, to address the fundamental aspects of mitigation of coke formation on the catalyst’s surface during dry reforming of methane (DRM).

4.1 Introduction

The inherent ability of nickel (Ni) based catalysts to be active towards the production of syngas (CO+H₂) in the CO₂ reforming of methane (DRM) process and at the same time be prone to catalyst deactivation due to coke deposition has increased the importance to develop strategies to improve the carbon resistance of the Ni-based catalyst in DRM [113].

Among the various strategies available for the development of Ni-based catalysts, surface alloying is a promising option [37, 113]. Here in, a monometallic surface can be modified by the introduction of additional metals, thereby changing the surface ensemble of the metal and drastically reducing the potentiality of carbon deposition [113]. This enhanced carbon tolerance of the Ni catalyst has been reported, especially when alloying with noble metals such as Ru, Rh, Pd and Pt, both activity and stability of the Ni catalyst has increased considerably in comparison to mono-metallic Ni catalysts [37]. However, any capable Ni bimetallic catalysts comprising of noble metals is less likely to be implemented in large scale industrial applications due to the trade-off between the cost of the noble metals and the cost of development of the final process product. Therefore, it is important to develop noble metal free bimetallic Ni catalysts for DRM, with comparable carbon tolerance and catalytic properties to that of noble metals.

Tin (Sn) alloyed Ni catalyst is a promising economically viable alternative, which has been previously used in steam reforming reactions [128-131]. During steam reforming of methane
(SRM) Sn alloying with Ni was observed to have a positive effect towards increased catalyst stability by inhibition of carbon nucleation on the active Ni sites [128-130]. In addition, Sn/Ni alloyed catalyst surface exhibits a promoting effect towards carbon oxidation [129]. In the case of DRM, experimental studies conducted by Hou et al. [132], on Sn/Ni alloyed catalyst showcased an increased carbon tolerance and decreased sintering of the Ni catalyst. This attribute of carbon tolerance due to Sn alloying may be due to the tetravalent similarity of electronic structure to that of carbon [40]. Further, small Sn doping on Ni, have shown to increase DRM products conversion [133]. However, there remain some contradictions towards the performance of Sn/Ni catalyst in the DRM process. As, in a recent experimental study on silica-supported Ni nano-particles, the doping of Sn at various concentrations, was not able to restrict coke formation and also had an adverse effect in decreasing activity of the Ni catalyst [134]. A similar loss in catalyst activity at higher Sn concentrations on Ni surface in DRM was observed in other experimental investigations [135].

To have a clear picture of the effect of Sn alloying with Ni in DRM process, it has become imperative to develop a detailed mechanistic understanding leading to experimental investigation, which may provide vital insights to explain the aforementioned effects Sn/Ni alloy in improved carbon resistance and loss in catalyst activity due to higher tin concentration on the Ni Surface.

Therefore, in this chapter a step forward approach for the catalysts design for the DRM reaction, by combining DFT based microkinetic studies. In fact, this chapter reveals through DFT studies: (i) the fundamental aspects of DRM in terms of mechanistic information, where catalyst models of a low and high Sn concentration is used to investigate the C-H bond activation and carbon resistance, (ii) the optimised Sn concentration model is used to ascertain key pathways for CO₂ activation, CH and C oxidation compared to Ni (111) surface examined in the previous chapter. From the key insights developed in our DFT and microkinetic studies. Using this catalyst development approach key insights towards Sn/Ni bimetallic catalysts development with potential applicability has been established.

4.2 Methods

The computational methods used are the same as in Chapter 3 section (3.2.1)
4.3 Results and discussions

4.3.1 Surface properties of Ni-Sn models

To study DRM reaction mechanisms on Sn/ Ni (111) bimetallic surfaces, two surface models were developed shown in Figure 4.1 (a,c). Further, the Sn-Ni bimetallic surfaces are referred to as NiSn₁ (Figure 4.1a) and NiSn₂ (Figure 4.1c) and are modelled by replacing one and two Ni atoms within the outermost surface with Sn atoms respectively. The two surface models
with variable Sn coverage of 1/9 ML and 2/9 ML represent low and high Sn concentration on the Ni surface respectively.

Additionally, Figure 4.1(a) shows that the NiSn$_1$ surface comprises of high symmetry three-fold hollow Ni sites denoted as fcc and hcp respectively and Ni-Sn three-fold hybrid sites denoted as fcc-1 and hcp-1 respectively.

We first investigated the segregation effect that Sn atoms have on Ni (111). The segregation energy is calculated using equation (4.3);

$$E_{\text{seg}} = E_I - E_{\text{bulk}}$$  \hspace{1cm} (4.3)

Here, $E_I$ represents the total energy of Ni-Sn surfaces with Sn located in 1$^{st}$ or 2$^{nd}$ layer of the NiSn$_1$ and NiSn$_2$ surfaces, and $E_{\text{bulk}}$ is the total energy of the surface with the Sn atom in the 3$^{rd}$ layer. Under this definition, a negative $E_{\text{seg}}$ indicates the Sn atom prefers to stay on the surface to form a surface alloy, otherwise a bulk alloy is preferred [136].

**Table 4.1** Segregation energy ($E_{\text{seg}}$) of Sn over (Ni 111) surface

<table>
<thead>
<tr>
<th>Surface</th>
<th>1$^{st}$ atomic layer (eV)</th>
<th>2$^{nd}$ atomic layer (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSn$_1$</td>
<td>-1.83</td>
<td>-0.20</td>
</tr>
<tr>
<td>NiSn$_2$</td>
<td>-2.66</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Table 4.1 indicates that Sn prefers to segregate onto the outermost layer of the Ni (111) surface rather than staying in the bulk. This observation is consistent with a previous reported experimental and thermodynamic study that at low Sn concentrations Ni/Sn surface alloy is thermodynamically preferable [128]. Furthermore, the segregation energies on the outermost layer of the Ni-Sn surfaces increase with an increase in the concentration of Sn, corresponding to -2.66 eV on NiSn$_2$ and -1.83 eV on NiSn$_1$. A similar effect of Sn segregating onto the Ni outer surface was found in the Ni$_3$Sn$_5$ bulk alloy phase [137]. The same authors mentioned that a large number of Sn atoms on the surface may have an adverse effect due to the atom induced stress to the surface lattice. This is evident in the present study during the geometry optimization of the NiSn$_1$ surface, the Sn atom is found to move outward by 0.48 Å Figure
4.1(b) which is slightly higher than reported experimental value of 0.44 Å [48]. This is mainly due to the atomic radius of Sn being larger than that of Ni and the Sn atoms buckle upwards to compensate for the surface strain. Additionally, the thermodynamic stability of the Ni-Sn surface is further assessed by considering the feasibility of a single Sn atom being doped onto the top most layer of the Ni (111) surface. This methodology has been previously followed by Fu and Luo [138], to calculate the stability of transition metals on Cu (111) surface. Here first the adsorption of a Sn atom on the Ni (111) surface is calculated according to equation 4.4, where $E_{\text{vac}}^{\text{Ni}(111)}$ represents the energy of the Ni (111) surface with a single Ni vacancy, $E_{\text{Sn-atom}}$ the energy of a single Sn atom and $E_{\text{NiSn}_1}$ the energy of the NiSn$_1$ surface. To compare the adsorption of Ni atom is calculated by equation 4.5. Additionally, the energy required to substitute a Ni atom on the Ni (111) surface by a Sn atom is calculated by equation 4.6.

\[
E_f^{(\text{Sn})} = E_{\text{vac}}^{\text{Ni}(111)} + E_{\text{Sn-atom}} - E_{\text{NiSn}_1} \quad (4.4)
\]

\[
E_f^{(\text{Ni})} = E_{\text{vac}}^{\text{Ni}(111)} + E_{\text{Ni-atom}} - E_{\text{Ni}(111)} \quad (4.5)
\]

\[
\Delta E_d = E_f^{(\text{Sn})} - E_f^{(\text{Ni})} \quad (4.6)
\]

From the above considerations, the adsorption energy of Sn $E_f^{(\text{Sn})}$ is calculated to be 5.81 eV and that of $E_f^{(\text{Ni})}$ is 0.73 eV. Hence, the substitution energy $\Delta E_d$ is calculated to be 5.08 eV. Here a positive value of the $\Delta E_d$ showcases the energy gained by the Ni (111) surface on Sn substitution on the topmost layer [138], indicating the stability of the Sn atom on the outer layer of Ni (111) surface.
4.3.2 Electronic structure of Ni-Sn

To understand the behaviour and chemical activity of the developed NiSn surfaces we have performed electronic structure analysis comprising of total density of states (DOS), as shown in Figure 4.2 (a-c), and partial density of states (PDOS), as shown in Figure 4.2(d-f) for three surfaces of Ni (111), NiSn₁ and NiSn₂. The metallic characteristic of the mentioned surfaces may be understood through the DOS plots, where \( N(E_F) \) represents the value of the concentration of electrons of the specific surface. Here a larger value of \( N(E_F) \) showcases a higher concentration of electrons and therefore better metallic characteristics of the concerned surface [139]. In our DOS calculations, the \( N(E_F) \) value for Ni (111) is obtained to be 10.18
states/eV which is slightly less on NiSn1 by 8.04 states/eV and it further decreases to be 0.01 states/eV on NiSn2. Therefore it is evident from the DOS analysis that the metallic characteristic of Ni (111) decreases at higher Sn concentration on the surface. Further, the PDOS is calculated by projecting the s and p states on a surface Sn atom and d states are projected onto a Ni atom of NiSn1 and NiSn2 Figure 4. 2 (e-f) surfaces. Additionally, the PDOS for Ni (111) surface is given for comparison Figure 4. 2 (d). It is clear from the PDOS plots that s and p states of Sn dominates between the range below -6 eV with higher s states on NiSn2. Further above -6 eV mainly the p states hybridises with the d states. This hybridization p and d continues above the Fermi level ‘E_F’ similarly found in previous theoretical observations [139]. It may be noted that on Ni (111) plane Ni s and p states have minimal hybridization with d states Figure 4.2 (d).

4.3.3 DRM reaction mechanism

To investigate the DRM reaction mechanism on the Ni –Sn bimetallic surfaces a similar mechanism scheme shown in Figure 3.4 in Chapter 3 is used in the present work. Here the mechanism is divided into three parts (i) CH4 activation (ii) CO2 activation and (iii) CH and C oxidation reactions. Additionally, the discussions on each DRM mechanism is carried out firstly describing the adsorption characteristics of DRM species corresponding to a particular reaction mechanism and thereafter the transition states of the achieved for the reaction on the Ni–Sn surfaces. Additionally, the calculated vibrational frequencies for the adsorbates and transition states on both NiSn1 and NiSn2 surfaces are provided in appendix A (A2-A3) respectively.

4.3.3.1 CH4 activation

To study the CH4 activation we used two Ni-Sn bimetallic surfaces developed shown in Figure 4.1 (a-c), to determine the effect of Sn concentration on CH4 activation.
Figure 4.3 Shows the most stable surface sites for adsorption of CHx (x=0-4) species and hydrogen on NiSn1 (a-f) and NiSn2 (g-l). H (white atom), C (black) and Ni (green).

Table 4.2 Adsorption energies (E_{ads}) in eV and adsorption sites for the CHx(x=0-4) and atomic hydrogen adsorbates involved in DRM on NiSn1, NiSn2 and Ni (111) surfaces

<table>
<thead>
<tr>
<th>Species</th>
<th>E_{ads} (eV)</th>
<th>NiSn1</th>
<th>NiSn2</th>
<th>Ni (111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>-6.58 /hcp</td>
<td>-6.26/ hcp</td>
<td>-6.72 /hcp</td>
<td></td>
</tr>
</tbody>
</table>
Adsorption of CHx\(_{(x=0-4)}\) species and H on the Ni-Sn surfaces

The adsorption configurations of CHx\(_{(x=0-4)}\) and H species is shown in Figure 4.3(a-i), where Figure 4.3(a-f) are adsorption geometries on the NiSn\(_1\) surface and Figure 4.3(g-i) are the geometries of the same species on NiSn\(_2\) surface. Further adsorption energies (E\(_\text{ads}\)) of CHx\(_{(x=0-4)}\) and H species on the NiSn\(_1\) and NiSn\(_2\) surfaces are shown in Table 4.2 with a comparison of the energies of the same species on Ni (111) surface taken from chapter 3.

In our DFT calculations for adsorbate geometry optimization for the CH\(_x\) species on both the Ni-Sn bimetallic (NiSn\(_1\) and NiSn\(_2\)) surfaces, we found the stable adsorption sites for the species to be on the fcc or hcp sites with immediate neighbour atoms being nickel. The adsorption sites fcc-1 and hcp-1 nearby to the Sn surface atoms were found to be unstable due to the alloyed Sn atom breaking the ensemble of the connected Ni (111) surface. Similar observations have been reported for Ni\(_3\)Sn bulk alloy phase [137] and surface alloy configurations of Au-Ni, Ag-Ni and Cu-Ni [48].

Table 4.2 shows that the CH\(_x\) (x=1-4) species are found to be more favourable on the Ni (111) with stronger adsorption energies compared to that on NiSn\(_1\) and NiSn\(_2\) surfaces. Notably, uniform physisorption of the CH\(_4\) gas phase molecule is observed on both the Ni-Sn surfaces with very weak adsorption energies of -0.01 eV for NiSn\(_1\) and -0.001 eV for NiSn\(_2\) and NiSn\(_1\). Figure 4.3 (a and g) shows the C-Ni bond distance for CH\(_4\) molecule to be 3.28 Å on NiSn\(_1\) and 3.96 Å on NiSn\(_2\) showcasing weak methane molecule to surface interaction with increasing Sn concentration Ni (111). This C-Ni bond distance tends to decrease with a decreasing amount of hydrogen atoms for the CH\(_x\) species [Figure 4.3(a-e) and (g-k)]. Additionally, the adsorption energies E\(_\text{ads}\) tends to increase with the loss of H atom, i.e., E\(_\text{ads}\) CH > E\(_\text{ads}\) CH\(_2\) > E\(_\text{ads}\) CH\(_3\) > E\(_\text{ads}\) CH\(_4\), this trend is found to be similar on both NiSn\(_1\) and NiSn\(_2\). However, the E\(_\text{ads}\) of the CH\(_x\) species are stronger on the NiSn\(_1\) compared to NiSn\(_2\) but weaker than that on Ni (111) surface. This showcases the addition of Sn to Ni close-packed plane decrease the stability of C.

<table>
<thead>
<tr>
<th>Specie</th>
<th>Adsorption Energy (E(_\text{ads}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>-2.79 /fcc</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>-0.01 /top</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>-1.80 /fcc</td>
</tr>
<tr>
<td>CH(_2)</td>
<td>-3.91 /fcc</td>
</tr>
<tr>
<td>CH</td>
<td>-6.29 /fcc</td>
</tr>
<tr>
<td></td>
<td>-2.71 /fcc</td>
</tr>
<tr>
<td></td>
<td>-0.001 /top</td>
</tr>
<tr>
<td></td>
<td>-1.50 /fcc</td>
</tr>
<tr>
<td></td>
<td>-3.89 /fcc</td>
</tr>
<tr>
<td></td>
<td>-6.02 /fcc</td>
</tr>
<tr>
<td></td>
<td>-2.78 /fcc</td>
</tr>
<tr>
<td></td>
<td>-0.021 /top</td>
</tr>
<tr>
<td></td>
<td>-2.02 /fcc</td>
</tr>
<tr>
<td></td>
<td>-4.10 /fcc</td>
</tr>
<tr>
<td></td>
<td>-6.50 /fcc</td>
</tr>
</tbody>
</table>
containing species. Further atomic carbon is found to bind strongly to the hcp site on NiSn$_1$ with $E_{\text{ads}}$ of -6.58 eV, while on NiSn$_2$ the C adsorption energy decreases to -6.26 eV ($E_{\text{ads}}$). Comparatively the $E_{\text{ads}}$ of carbon on Ni (111) surface is higher, at -6.72 eV. This signifies that the process of forming carbon nucleated structures on Ni surfaces will be deterred due to the decreasing strength in carbon-nickel bonds in the presence of Sn atoms on Ni (111) surface. The variation in adsorption energies of atomic hydrogen is found to be minimal with values of -2.78 eV on Ni (111), -2.79 eV on NiSn$_1$ -2.71 eV on NiSn$_2$. Overall the CH$_x$$_{(x=0-4)}$ and H species stability based on the adsorption energies calculated prefers, Ni (111) > NiSn$_1$ > NiSn$_2$.

**CH$_4$ sequential dissociation**

**Figure 4.4** Transition state configurations including (IS) initial state (TS) transition state (FS) final state for CH$_x$ ($x=0-4$) species [R1-R4] on (a) NiSn$_1$ and (b) NiSn$_2$ surfaces. H (white atom), C (black) and Ni (green) Sn (grey).
Table 4.3 Elementary reactions of DRM on NiSn₁ and NiSn₂ surfaces with an activation energy of the forward ($\Delta E_{a,f}$) and backward ($\Delta E_{a,b}$) reactions and reaction energy ($\Delta H_r$).

<table>
<thead>
<tr>
<th></th>
<th>NiSn₁</th>
<th>NiSn₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta E_{a,f} (\Delta E_{a,b})$</td>
<td>$\Delta H_r$</td>
</tr>
<tr>
<td>R1</td>
<td>CH₄* + <em>→CH₃</em> + H*</td>
<td>1.43 (1.34)</td>
</tr>
<tr>
<td>R2</td>
<td>CH₃* + <em>→CH₂</em> + H*</td>
<td>0.81 (0.77)</td>
</tr>
<tr>
<td>R3</td>
<td>CH₂* + <em>→CH</em> + H*</td>
<td>0.42 (0.81)</td>
</tr>
<tr>
<td>R4</td>
<td>CH* + <em>→C</em> + H*</td>
<td>1.53 (0.87)</td>
</tr>
</tbody>
</table>

The transition state geometries of CH₄ sequential dissociation on NiSn₁ and NiSn₂ surfaces are shown in Figure 4.4 (a-b). Further, the values of the forward and backward activation energies ($E_{a,f}$ and $E_{a,b}$) with reaction energy ($H_r$) are given in Table 4.3.

R1: CH₄* + *→CH₃* + H*

In the present calculations, the initial state (IS) of CH₄ on both NiSn₁ and NiSn₂ is found to be physisorbed on the top of a Ni atom with very low adsorption energy. In the final state (FS) of the reaction, CH₃ and H occupy the fcc and hcp sites with the distance between the carbon atom of CH₃ molecule and opposite H atom (C-H) being found to be 3.22 Å and 3.83 Å on NiSn₁ and NiSn₂ respectively. In the transition state (TS) geometry the C-H bond is 1.60 Å for NiSn₁ whereas for NiSn₂ it is much higher by 2.41 Å. Further the reaction is endothermic on both the surfaces, however, the endothermicity is higher on NiSn₂ by 0.52 eV ($\Delta H_r$). Due to this higher endothermic nature, the forward activation energy barrier ($E_{a,f}$) on NiSn₂ is very high at 2.69 eV compared to 1.43 eV on NiSn₁. This showcases that higher concentration of Sn on Ni (111) may be detrimental towards CH₄ activation.

R2: CH₃* + *→CH₂* + H*

To find the transition state for the next sequential step, the stable configuration of CH₃ adsorbed on the fcc site is considered as the (IS) and the co-adsorption fragments of CH₂ on the fcc with H on hcp site is considered to be the (FS) on both NiSn₁ and NiSn₂. In the (TS) structure the
C-H bond separation between CH$_2$ and H is 2.37 Å on NiSn$_1$ and is lower on NiSn$_2$ by 1.90 Å. Again the reaction energy ($\Delta H_r$) is found to be endothermic but lesser than the first sequential step on both the surfaces. Additionally the forward activation energy barrier ($E_{a,f}$) for the reaction on NiSn$_1$ 0.81 eV while on NiSn$_2$ its higher by 1.25 eV ($E_{a,f}$).

R3: CH$_2^* + ^* \rightarrow$CH* + H*

For, the third sequential CH$_4$ dehydrogenation step, CH$_2$ adsorbed on the fcc site is selected to be the (IS) and co-adsorbed CH at fcc and H at hcp sites are taken to be the (FS) on both the N-Sn surfaces. In the (TS) configuration the C-H bond distance is found to be identical at 1.55 Å on both NiSn$_1$ and NiSn$_2$. Further, the reaction is found to be exothermic by -0.39 eV ($\Delta H_r$) on NiSn$_1$ and -0.34 eV ($\Delta H_r$) on NiSn$_1$ with the forward activation energy barriers ($E_{a,f}$) decreasing significantly from the previous steps to be 0.41 eV on NiSn$_1$ and 0.63 eV on NiSn$_2$.

Figure 4. 5 Potential energy surfaces (PES) for the comparison of CHx (x=1-4) dehydrogenation mechanism between NiSn$_1$, NiSn$_2$ and Ni (111) surfaces. Here the contribution of H* atom at the sequential step to the PES is omitted for the sake of simplicity.
R4: \( \text{CH}^* + \text{*} \rightarrow \text{C}^* + \text{H} \)

The dissociation of CH is the final and most important step during sequential dehydrogenation of \( \text{CH}_4 \), as it governs the formation of atomic carbon on the catalyst surface. The stable configuration of CH adsorbed at the fcc site is selected as (IS) and C and H co-adsorbed at the fcc and hcp hollow sites are chosen to be the (FS) on NiSn\(_1\) and NiSn\(_2\) surfaces. In the (TS) geometry the C atom prefers to stay at the fcc site while the H moves to the Ni top site with a C-H bond distance of 1.77 Å on NiSn\(_1\) and 1.83 Å on NiSn\(_2\). A very high forward activation energy barrier \( (E_{a,f}) \) of 1.53 eV is obtained on NiSn\(_1\) with the energy barrier further increasing to 1.72 eV on NiSn\(_2\) for this step. Therefore it is found that between CH and C, the former is a more stable intermediate on Ni-Sn bimetallic surfaces.

As mentioned earlier in Chapter 3, that CH\(_4\) dissociation reactions may be considered to be a key contributor towards carbon formation on Ni (111) surface, we have used PES to compare the energy barriers between Ni-Sn bimetallic and Ni (111) surfaces. Also, it may be noted that such kind of comparisons using DFT calculations to screen bimetallic surfaces have been conducted previously such as Ni-Au [48, 140] Ni-Pt [141]. In our DFT calculations it is found that, even a low concentration of Sn corresponding to (1/9 ML) on Ni (111) surface, showed encouraging characteristics towards carbon resistance especially during the CH cracking step, with an elevated activation energy barrier for the formation of atomic carbon and atomic hydrogen on the NiSn\(_1\) surface. To understand further this effect of Sn, we used a higher Sn concentration (2/9 ML) represented as NiSn\(_2\) surface Figure 4.1(c) for CH\(_4\) sequential dehydrogenation reaction and compared the activation energy barriers with Ni (111). Figure 4.5 represents the PES for sequential CH\(_4\) dehydrogenation. It is evident from the calculated activation energies that the activity of CH\(_4\) dissociation decreases on Sn-Ni (111) surfaces with an increasing concentration of Sn. This is observed during the initial de-hydrogenation step \( (\text{CH}_4^* + \text{*} \rightarrow \text{CH}_3^* + \text{H}^*) \) where the activation energy barriers increase by 2.4 times on NiSn\(_2\) to that on Ni (111). Similar behaviour was observed by Liu et al. [135], in their experimental study, where the activity of the Sn/Ni catalyst decreased with an increase in the concentration of Sn on the Ni surface. However, the carbon resistance increases with a higher concentration of the Sn on the surface. This observation is showcased during the CH cracking step \( (\text{CH}^* + \text{*} \rightarrow \text{C}^* + \text{H}) \), where the activation barrier remarkably increases on the NiSn\(_2\) by 1.2 times compared to that on the Ni (111).
4.3.3.2 Hydrogen Formation

**Figure 4.6** (a) Transition state configurations including (IS) initial state, (TS) transition state (FS) and final state for \( \text{H}_2 \) formation (R5) on NiSn\(_{1} \). H (white atom), C (black) and Ni (green) Sn (grey). (b) Potential energy surfaces (PES) for the comparison of \( \text{H}_2 \) formation on NiSn\(_{1} \) and Ni (111) surfaces.

The investigation of hydrogen formation is only performed on the NiSn\(_{1} \) surface where the adsorption energy of \( \text{H}_2 \) is calculated to be -0.22 eV (\( E_{\text{ads}} \)) and the H-H bond stretches from 0.74 Å in the gas phase to 0.95 Å on adsorption. Further, the formation of hydrogen molecule occurs from the adsorbed hydrogen atoms on the NiSn\(_{1} \) surface originating from the sequential dehydrogenation reactions. The hydrogen atoms adsorbed on parallel hcp sites are considered to be the (IS) with the (FS) configuration forming on the top site of a nickel atom (as shown in Figure 4.6 (a). The H-H bond length at (TS) is 1.18 Å. To draw a comparison with Ni (111) the PES is shown in Figure 4.7 (b) shows the reaction to be slightly less endothermic on NiSn\(_{1} \).
surface compared to Ni (111). Further, the activation energy barrier on NiSn$_1$ is 0.94 eV, which is 0.04 eV than on Ni (111).

4.3.3.3 CO$_2$ activation

In sequential methane dissociation reaction, we investigated the two Ni-Sn surface models with variable Sn concentrations of (1/9 ML) and (2/9 ML) corresponding to NiSn$_1$ and NiSn$_2$ respectively. Our findings for CH$_4$ sequential dissociation showed that a higher concentration of Sn such that NiSn$_2$ surface in this case, to have a negative effect towards CH$_4$ activation. Therefore to further investigate the CO$_2$ activation and the following CH and C oxidation reactions we have only considered the NiSn$_1$ surface model.

CO$_2$ adsorption on NiSn$_1$

![CO$_2$ adsorption](image)

(a) CO$_2$ – top
C-Ni = 3.48 Å
C-O= 1.18 Å , 1.18 Å

(b) CO$_2$ – off- top
C-Ni = 1.98 Å
C-O= 1.27 Å ,1.22 Å

**Figure 4.7** Shows the structures of CO$_2$ adsorption for (a) Physisorb (b) chemisorb on NiSn$_1$. O (red atom), C (black) and Ni (green), Sn (grey).

**Table 4.4** Adsorption energies (E$_{ad}$) in eV and adsorption sites for CO$_2$ adsorption on NiSn$_1$.

<table>
<thead>
<tr>
<th>Species</th>
<th>NiSn$_1$</th>
<th>Ni (111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ physisorption</td>
<td>0.02</td>
<td>-0.02</td>
</tr>
<tr>
<td>CO$_2$ chemisorption</td>
<td>0.48</td>
<td>0.38</td>
</tr>
</tbody>
</table>
Similar to our observations made in Chapter 3, to achieve CO$_2$ chemisorption on Ni (111) surface, the linear configuration Figure 4.7 (a) of initial gas phase CO$_2$ molecule was artificially bent Figure 4.7 (b), similarly we reproduced CO$_2$ chemisorbed structure on NiSn$_1$. Further, the linear CO$_2$ molecule structure was found to physisorb on NiSn$_1$ as well. Here also, CO$_2$ chemisorbed structure adsorbs on the two-fold bridge site called as (off-top) adsorption energies are found to be 0.49 eV on NiSn$_1$. Comparatively from Table 4.4 adsorption is less endothermic on Ni (111) 0.38 eV.

Figure 4. 8 (a) Transition state configurations including (IS) initial state, (TS) transition state and (FS) final state for CO$_2$ (R6) dissociation on NiSn$_1$. O (red atom), C (black) and Ni (green) Sn(grey). (b) Potential energy surfaces (PES) for the comparison of CO$_2$ dissociation on NiSn$_1$ and Ni (111) surfaces.

To examine the direct dissociation step for CO$_2$ activation the chemisorbed configuration is considered to (IS) geometry with the (FS) of CO adsorbed on the fcc site and O on the opposite
bridge site shown in Figure 4.8 (a). As shown in Figure 4.8 (a), in the (TS) geometry the C-O bond stretches from 1.27 Å to 1.81 Å. From Figure 4.8 (b), it can be seen that the reaction is exothermic with an activation energy barrier of 0.83 eV on the NiSn1 surface. Further, the reaction is less exothermic on the NiSn1 surface compared to Ni (111).

### 4.3.3.4 CH and C oxidation

To describe the CH and the C oxidation steps on the NiSn1 surface first the adsorption characteristics of the intermediates involved in these reaction steps is discussed in details.

![Figure 4.9](image)

**Figure 4.9** Shows the structures of (a) O (b) CO and (c) CHO adsorption on NiSn1. O (red atom), C (black) and Ni (green), Sn (grey).

<table>
<thead>
<tr>
<th>Species</th>
<th>NiSn1</th>
<th>Ni (111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>-5.58 /fcc</td>
<td>-5.62 /fcc</td>
</tr>
<tr>
<td>CO</td>
<td>-1.74 /hcp</td>
<td>-1.83 /hcp</td>
</tr>
<tr>
<td>CHO</td>
<td>-2.11 /hcp</td>
<td>-2.28 /fcc</td>
</tr>
</tbody>
</table>

**Table 4.5** Adsorption energies ($E_{ads}$) in eV and adsorption sites for O CO and CHO species on NiSn1.

Atomic oxygen prefers to adsorb onto the fcc site of NiSn1 forming O-Ni bond of 1.84 Å Figure 4.9 (a) with an adsorption energy $E_{ads}$ of -5.58 eV, which is slightly lower compared to the value on Ni (111) -5.62 eV. CO binds to the hcp site Figure 4.9 (b), with the C-O bond elongates to 1.19 Å from 1.14 Å in the gas phase, with an $E_{ads}$ -1.74 eV on NiSn1 lower compared to Ni (111). The stable structure of CHO is found to occupy the fcc site Figure 4.9 (c ) with C-O and
C-H bond distances of 1.29 Å and 1.11 Å respectively on the NiSn₁ surface, $E_{\text{ads}}$ on Ni (111) surface is stronger with -2.28 eV compared to -2.11 eV on NiSn₁. Overall the binding strength of the oxygenated species decreases with the introduction of Sn to the Ni (111) surface.

![Transition state configurations including (IS) initial state, (TS) transition state and (FS) final state for (a) C oxidation [R7], (b) CHO formation [R8], (c) CHO dissociation [R9] on NiSn₁ surfaces H (white atom), C (black) and Ni (green) Sn (grey), O (red atom).](image)

**Figure 4.** Transition state configurations including (IS) initial state, (TS) transition state and (FS) final state for (a) C oxidation [R7], (b) CHO formation [R8], (c) CHO dissociation [R9] on NiSn₁ surfaces H (white atom), C (black) and Ni (green) Sn (grey), O (red atom).

**Table 4.** Elementary reactions of DRM on NiSn₁ surface with an activation energy of the forward ($\Delta E_{a,f}$) and backward ($\Delta E_{a,b}$) reactions and reaction energy ($\Delta H_r$).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H_r$ (eV)</th>
<th>$\Delta E_{a,f}$ ($\Delta E_{a,b}$) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R7</td>
<td>-1.59</td>
<td>1.37 (2.96)</td>
</tr>
<tr>
<td>R8</td>
<td>0.25</td>
<td>1.31 (1.06)</td>
</tr>
<tr>
<td>R9</td>
<td>-1.23</td>
<td>0.32 (1.55)</td>
</tr>
</tbody>
</table>
To calculate the activation energy barriers for the C and CH oxidation reaction steps leading to finding the CO formation route on NiSn<sub>1</sub> surface, the transition state geometries are discussed shown in Figure 4.10 (a-c) and the activation energy values given in Table 4.6. Further comparison of the activation energies with Ni (111) is presented with help of PES plots Figure 4.11.

R7: C* + O*→CO*+*

In the (IS) configuration atomic C is on the fcc site with the atomic O being in the opposite bridge site, which during the (TS) moves to the top site Figure 4.10 (a) with the distance between C and O decreasing to 2.05 Å from 3.05 Å during the (IS). Remarkably, the reaction is highly exothermic, with ΔH<sub>r</sub> = -2.47 eV on the NiSn<sub>1</sub> surface, which also indicates that it is unlikely to have coke formation from the backward reaction (CO dissociation). Similarly, the reaction is also exothermic on Ni (111). Further, the activation energy barrier on NiSn<sub>1</sub> surface is 1.36 eV, signifying a thermodynamically more favourable surface for C oxidation compared to Ni (111) Figure 4.11(a).

![Figure 4.11. Potential energy surfaces (PES) for the comparison of (a) C oxidation (b) CHO formation (c) CHO dissociation on NiSn<sub>1</sub> and Ni (111) surfaces.](image-url)
The CH oxidation undergoes two-step reaction process, where firstly it forms (CHO) intermediate thereafter decomposing to CO and H species.

\[ \text{R8: } \text{CH}^* + \text{O}^* \rightarrow \text{CHO}^* + * \]

Figure 4.10 (b) shows the (IS) geometry of CH occupying the fcc site and O in the adjacent bridge site. During the (TS), the atomic O moves to the top site with C-O distance decreasing from 2.85 Å in the initial state to 1.87 Å. Presence of Sn on Ni (111) surface promotes CHO production which is evident from the lower activation energy barrier of 1.22 eV on NiSn\(_1\) compared to 1.31 eV on Ni (111) Figure 4.11 (b). Further, the reaction is found to be more exothermic on the NiSn\(_1\) surface with \(\Delta H_r\) -0.38 eV, thereby making the NiSn\(_1\) surface more favourable to CHO production.

\[ \text{R9: } \text{CHO}^* + * \rightarrow \text{CO}^* + \text{H}^* \]

Figure 4.10 (c) shows the C-H bond of CHO adsorbed on the fcc site during the (IS) slightly stretches from 1.11 Å to 1.19 Å during the (TS) producing CO and H on the surface during the final state of the reaction. CHO decomposition is highly exothermic with a value of -1.30 eV (\(\Delta H_r\)) on NiSn\(_1\), accompanied with low activation energy barriers compared to Ni (111). Interestingly, Figure 4.11 (c) shows that the NiSn\(_1\) surface is marginally favourable, with 0.03 eV for CO formation.

### 4.3.4 Microkinetic analysis

In this section, the microkinetics of the DRM reaction mechanism on the NiSn\(_1\) surface using the CatMAP [105] module is calculated. For the microkinetic analysis the same reaction scheme used for Ni (111) surface (see Chapter 3, section 3.3.4), comprising of 13 elementary DRM reaction steps, is considered in the present analysis. Further, the reaction temperature considered for the analysis is between (900-1300) K and the pressure is kept constant at 1 bar. The reactant feed ratio used for the microkinetic model is CH\(_4\): CO\(_2\)=1, with the partial pressures of the reactant and product P\(_{\text{CH}_4}\)/P\(_{\text{CO}_2}\)/P\(_{\text{CO}}\)/ P\(_{\text{H}_2}\) being in the following ratio 0.5/0.5/0.05/0.05, this corresponds to nearly 10% CH\(_4\) conversion. A low CH\(_4\) conversion has been considered in the previous theoretical study [34] and also in our microkinetic analysis on Ni (111) surface.
Table 4.7 Forward reaction rates (kf) in s⁻¹ for the elementary CH₄(g) + * → CH₃* + H* (R1), C-O and CH-O reaction pathways.

<table>
<thead>
<tr>
<th></th>
<th>1063.27 K</th>
<th>1153.06 K</th>
<th>1202.04 K</th>
<th>1283.67 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>kf (R1)</td>
<td>3.33×10⁻²</td>
<td>7.94×10⁻¹</td>
<td>2.51×10⁰</td>
<td>9.08×10⁰</td>
</tr>
<tr>
<td>C-O path (kf C)</td>
<td>0.10</td>
<td>2.45</td>
<td>7.84</td>
<td>29.67</td>
</tr>
<tr>
<td>CH-O path (kf CH)</td>
<td>0.17</td>
<td>3.91</td>
<td>9.70</td>
<td>43.01</td>
</tr>
</tbody>
</table>

It has been established in previous theoretical work that reaction rates in both DRM and steam reforming of methane (SRM) is controlled through the C-H bond activation [34, 35, 114]. The forward reaction rate of methane activation reaction (R1) on NiSn₁ increases gradually with the rates being lower at even 1063.27 K (Table 4.7). This may be primarily due to the higher methane activation energy barrier of (R1) which is higher at ~0.33eV on NiSn₁ compared to on Ni (111) (see Figure 4.5). Therefore it may be considered that CH₄ conversion rates on Ni-Sn bimetallic catalysts will be lower at low temperatures compared to Ni plane surfaces. Among the CO gas formation pathways considered, the CH-O path is favoured on NiSn₁ with higher forward rates compared to the C-O path.
The coverage of the adsorbed species on the NiSn\textsubscript{1} surface is shown in Figure 4.12 (a-b). In Figure 4.13 (a), the coverage of the major species shows that CO adsorbates dominate the maximum coverage, which decreases with an increase in temperature thereby desorbing as CO gas from the surface. Further, a steady presence of atomic hydrogen at all simulation temperatures is observed, which decreases with the increase of the temperature. The presence
of CH species is also found to have higher coverage than CO temperatures above 1100 K. Figure 4.12(b) represents the coverage of the minor species on NiSn₁. Here, it may be noted that the concentration of atomic C and O is found to be low on well closed packed plane Ni surfaces pertaining to lower binding energies of these adsorbates to surfaces compared to under co-ordinated or stepped surfaces [34, 35]. However, the trends of Sn de-stabilising atomic carbon formation on the closed packed surface is observed in Figure 4.12 (b). Interestingly the concentration of C is less on NiSn₁ compared to Ni (111) and atomic O coverage increases on NiSn₁ at higher temperatures while for Ni (111) coverage shows a decreasing trend. Higher coverage of O is linked to lower coverage of C since a surface rich with O is more prone to oxidise or gasify carbon and deter carbon nucleation on the catalyst surface.

4.4. Conclusions

Sn/Ni as an active phase for a DRM catalyst represents a viable option for chemical CO₂ recycling to produce high-quality syngas. The bimetallic Ni-Sn formulation is superior in terms of activity, stability and selectivity towards syngas compared to the monometallic Ni – observations demonstrated both in model catalytic surfaces. Ni-Sn interaction is vital to achieving excellent levels of CO₂ and CH₄ conversion. The positive effect of Sn is credited to Sn atoms occupying C nucleation sites in the vicinity on Ni atoms, slowing coke formation (i.e. increasing the energy barrier for coke nucleation). The addition of Sn does not fully prevent carbon deposition but it does slow down the carbon formation and it also affects the type of carbon formed over the catalyst’s surface. The optimisation of Sn loading is a key factor since relatively high amounts of Sn impact negatively on the catalytic activity while small amounts of Sn leads to a good compromise between activity and carbon resistance. Along with the exceptional resistance towards carbon deposition, Sn also promotes the oxidation of the key reaction intermediates such as CHO over the catalyst’s surface thus favouring the final products formation as evidenced by the DFT and MKM calculations, overall this chapter illustrates a strategy to develop highly efficient bimetallic catalysts for DRM using DFT and kinetics to guide the development of powder catalysts for realistic applications in reforming units for CO₂ utilisation.
Chapter 5: Theoretical study to explore the potentiality of Ni$_2$P (0001) catalyst for DRM

Short abstract

In this chapter, DFT and microkinetic to examine the suitability of interstitial nickel phosphide Ni$_2$P catalyst in CO$_2$ dry reforming of methane (DRM). Our DFT calculations showed the Ni$_2$P (0001) surface to be active towards adsorption of the DRM species, with the Ni hollow site being the most energetically stable site and Ni-P and P surface sites being active towards adsorption of monoatomic species. Free energy analysis at 1000 K found CH-O to be the main intermediate in the CO formation pathway. Microkinetic calculations found CO gas production to be higher at lower temperatures (below 1000K) with H$_2$ gas production, visible between (1100-1200) K. Further, oxygen is found to have a higher surface coverage than carbon at higher temperatures. Finally, with DFT and microkinetic analysis, it was ascertained that Ni$_2$P (0001) is a robust surface to mitigate carbon deposition due to the lower number of active sites for carbon adsorption compared to oxygen on the Ni$_2$P (0001) surface.

5.1 Introduction

To develop suitable and low-cost stable catalysts for the DRM process, it is worth exploring alternative materials to traditional nickel supported catalysts. In recent years, interstitial compounds of metal carbide, nitride and phosphides have received attention for catalyst development [51]. Amongst these interstitial compounds for DRM, predominant attention has been provided to Mo-based carbide, nitride and phosphide catalysts [56, 142-144]. Especially, extensive studies on Mo$_2$C has shown that this compound has similar activities compared to noble metals (Pd, Pt) at slightly elevated pressures (2 bar) in DRM [142-144]. However, for single metal carbides, high reaction pressures are required to achieve good activity, as at low pressures the catalyst deactivates due to oxidation by CO$_2$ to form ineffective oxides [142, 144]. Recently, Fu et al.[145] showed that bimetallic Ni and Co-doped molybdenum nitrides exhibited high catalytic activity, and are resistant to oxidation at atmospheric pressure [145]. Similarly, an experimental study of DRM with molybdenum phosphate (MoP) catalyst showcased high coke and oxidation resistance with better stability compared to Ni/Mo$_2$C catalyst [56]. Apart from MoP, only one other study of metal phosphide catalyst, tungsten phosphide (WP) has been investigated, which was found to be active for the DRM reaction [56,
Considering the good activity of Ni-based catalysts towards the reactant species (CH$_4$ and CO$_2$) [3], it is worthwhile to investigate nickel phosphide (Ni$_2$P) catalyst, as it has largely remained untouched for exploring its potentiality in DRM.

The versatile nature of the Ni$_2$P family of materials stems from its applicability in important industrial processes such as hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) with high catalytic activity [147, 148]. Furthermore, both theoretical and experimental studies have previously demonstrated higher activity and stability of Ni$_2$P compared to Pt electro-catalyst for hydrogen evolution reactions (HER) [148, 149]. These enhanced catalytic properties of Ni$_2$P have been attributed to the ligand (with minor charge transfer observed between Ni and P), and ensemble (limitation of active metal sites) effects [58, 60]. The phosphorus (P) atoms present in Ni$_2$P catalyst surface dilutes, the Ni concentration resulting in perturbing the electronic structure of nickel slightly [60]. Experimental studies and DFT calculations found most of the phosphorus sites on Ni$_2$P (0001) catalyst surface to be occupied with oxygen, with strong oxygen to phosphorus interactions under water gas shift reaction (WGSR) conditions [58]. Further X-ray photoelectron spectroscopy (XPS) studies of the Ni$_2$P (0001) surface under WGSR reaction conditions indicated the presence of oxygen mostly occupying the P sites without oxidizing the Ni sites. Additionally, a small amount of carbon was found to bind to the Ni$_2$P surface in the same XPS study [58]. Indeed, this oxygen affinity of the Ni$_2$P catalyst surface may be beneficial during DRM reaction conditions by negating carbon growth on the catalyst surface. Furthermore, the presence of oxygen to bind P atoms is another advantage since it avoids any possible oxidation of Ni which must remain in its metallic state to display high activity.

In comparison to Ni$_2$P, traditional, Ni surface facets are known to have severe carbon nucleation problem, which during DRM reaction conditions, is mainly due to CH$_4$ sequential dissociation and CO disproportionate reactions eventually leading to catalyst deactivation [32, 34-36, 114]. Additionally, DFT-based microkinetic studies have established that at high DRM reaction temperatures, the close-packed Ni (111) surface has low oxygen concentration thereby restricting carbon oxidation from the surface [34-36].

In this chapter, we have used DFT-based microkinetic study to investigate the suitability of Ni$_2$P (0001) as a DRM catalyst. This work reveals for the first time, through DFT studies, the fundamental aspects of DRM reaction steps on the Ni$_2$P (0001) surface. From the key insights and data obtained from the DFT investigations, thermodynamic and microkinetic analysis is
performed to ascertain the reaction paths, the behavior of DRM intermediates at high temperatures and coking stability of the Ni$_2$P (0001) surface.

5.2. Computational details

Cambridge Sequential Total Energy Package (CASTEP) [117], which has previously been shown to be suitable for Ni$_2$P bulk and surface studies [60], is used to perform all the DFT calculations in the present work. The exchange-correlation energy was described by generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional [118]. The electron wave functions were expanded in a plane wave basis set with kinetic energy cut off 340 eV for all the calculations, chosen after convergence tests. Further ultra-soft pseudopotentials, introduced by Vanderbilt is considered to describe the ion-electron interaction. Spin polarization is considered for all the calculations. The electron occupancies were determined by the Gaussian smearing method [119] with a smearing value of 0.1 eV. The self-consistency field (SCF) is considered to be converged when the total energy of the system is below the $10^{-6}$ eV/atom. All geometries were optimized using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) [150] algorithm, where the geometries converged until the forces between atoms are less than 0.01 eV/Å.

To model the DRM reaction mechanisms, first, the Ni$_2$P bulk parameters are calculated with a Monkhorst-Pack [97] k-point grid of 4×4×5. Thereafter the optimized bulk was cleaved in the [0001] direction. To model the Ni$_2$P (0001) surface, four layers were used to construct the surface slab in a (2×2) surface supercell, corresponding to a surface coverage of ¼ monolayer (ML), with a vacuum gap of 12 Å to avoid interactions between the slabs. For sampling, the Brillouin zone of Ni$_2$P (0001) surface a k-point grid of 2×2×1 was found to be suitable after convergence tests. Additionally, tests were performed with denser k-point grid of (5×5×1) and kinetic energy cut-off (520 eV) for CO adsorption on Ni$_2$P (0001), the results did not show an appreciable increase in the adsorption energies value. Therefore, a lower k-point grid was considered in this work to save computational expense.

Adsorption energy ($E_{\text{ads}}$) of the surface adsorbed species is defined by $E_{\text{ads}} = E_{\text{species+slab}} - E_{\text{slab}} - E_{\text{species}}$, where $E_{\text{species+slab}}$ represents the total energy of the adsorbed species on the modelled surface, $E_{\text{slab}}$ total energy of the clean surface slab and $E_{\text{species}}$ corresponds to the energy of the gas phase molecules.
Transition state (TS) searches are performed using the same level of theory for those applied to the reactants and products with the complete linear synchronous transit (LST)/quadratic synchronous transit (QST) method [102] as implemented in CASTEP. The convergence criterion for the transition state search is set to be 0.05 eV/Å root-mean-square forces on each atom. The uniqueness of the (TS) structures was confirmed using vibrational frequency analysis using the finite displacement method [120].

The microkinetic analysis to examine the activity of the Ni$_2$P (0001) catalyst surface was performed using the descriptor based microkinetic model package CatMAP [151]. The rates for the elementary reactions of DRM considered in this work are determined by solving differential equations numerically at steady state approximation. In CatMAP, the free energies for the adsorbates and the gas phase entropies and enthalpies are calculated using ideal gas thermochemistry as implemented in ASE [152]. Free energies of TS and rate constants are calculated from DFT obtained activation energies using the harmonic transition-state theory.

5.3 Results and discussions

5.3.1 Bulk and surface models

To develop the Ni$_2$P surface model, a cell optimization of the Ni$_2$P bulk was performed. The Ni$_2$P bulk has a hexagonal structure and belongs to the P6$_2$m space group [153]. The DFT calculated lattice parameters (a=b=5.86 Å and c= 3.37 Å) are in good agreement with previous reported theoretical (a=b=5.88 Å and c= 3.37 Å) and experimental (a=b=5.87 Å and c=5.39 Å) data [154, 155]. Further, the nearest Ni-P distances on the Ni$_3$P$_2$ and Ni$_3$P$_1$ plane in the bulk stoichiometry was calculated to be 2.21 Å and 2.28 Å respectively, which is consistent with previous theoretical findings.
Figure 5.1 (a) Top view of the Ni$_3$P$_2$ surface layer of Ni$_3$P (0001) termination. Numbers denote possible adsorption sites as discussed in Section 5.3.1. (b) Side view of Ni$_3$P (0001) surface with alternating Ni$_3$P$_2$ and Ni$_3$P$_1$ layers (c) Total density of states (DOS) for Ni$_3$P surface. (d) Partial density of states (PDOS) projected onto a Ni and P atom on the outer layer of the Ni$_3$P$_2$ plane in Ni$_3$P (0001). Green spheres represent Ni atoms, and orange P atoms, respectively.

From the optimized bulk parameters, the Ni$_3$P (0001) surface is constructed shown in Figure 5.1(a), with supercell dimension of a=b=11.78 Å and c=18.79 Å, comprising of 72 (48 Ni and 24 P) atoms. Further, the Ni$_3$P (0001) surface is developed with four atomic layers Figure 5.1 (a-b) comprising of alternate Ni$_3$P$_2$ and Ni$_3$P$_1$ atomic layers representing the bulk stoichiometry along [0001] termination. This has been observed in previous scanning tunnelling microscopy (STM) [153], and low energy electron diffraction (LEED) studies [156]. Herein, we have considered the Ni$_3$P$_2$ surface plane shown in Figure 5.1 (a-b) for our calculations, as this plane has been generally considered in catalytic activity investigations for HDS [60] and WGS [58]. Further, the metallic character of the Ni$_3$P (0001) is evident from the total surface density of states (DOS) shown in Figure 5.1 (c), where the highest peaks in the DOS plot represents the d states of Ni without any band gap above the Fermi level. Additionally the partial DOS (PDOS) on a Ni atom of the Ni$_3$P$_2$ plane shows, the overlapping of Ni 3d and P 3p states (1.34 to -8.2 eV) and (-10 to -14.14 eV) P s states. Further, the
Mulliken charges of the surface ions show a slight charge transfer from Ni to P bond (Ni $0.08e$ and P $-0.08e$), consistent with the observations in previous theoretical studies [60].

Further, previous DFT calculations found, in Ni$_2$P (0001) the Ni$_3$P$_2$ terminated plane to be more stable compared to Ni$_3$P$_1$ by 2.75 eV per unit cell [60] with lower surface free energy [157]. Also, Hernandez et al. [158] with dynamical LEED observations found the stability of the Ni$_3$P$_2$ surface plane to increase with the addition of P adatoms onto three-fold hollow sites found on the Ni$_3$P$_2$ plane [158]. This increased surface stability of Ni$_3$P$_2$ is mainly attributed to phosphorus (P) stabilization of the dangling bonds formed due to unbound P (p) and Ni (d) orbitals of Ni$_3$P$_2$ surface plane [159]. Additionally experimental evidence has shown that, during the synthesis of Ni$_2$P –single crystal a phosphorus-poor surface is created by argon sputtering, however, it recovers its original Ni$_2$P stoichiometry by diffusion of phosphorus at low temperature (450 K) [156, 160]. Further, high-temperature annealing induces segregation of the phosphorus to produce a phosphorus-rich well-defined reconstructed surface [160]. Also, P segregation and diffusion to the surface occurs from the bulk at relatively low temperatures ($\sim 450$ K) [160]. This experimental observation was confirmed in a recent DFT study by Conteras-Mora et al., that bulk diffusion of P to surface P vacancy sites occurs through an interstitial-vacancy mechanism [160]. Therefore in light of these observations reported in previous works the formation of P vacancies on the Ni$_3$P$_2$ surface plane is not considered in the present work.

To study the active sites on the Ni$_2$P (0001) surface for the interaction of the DRM species, we have used a similar site annotation approach used in a previous study of water gas shift reaction (WSGR) [58]. Herein six inequivalent surface sites Figure 5.1 (a) are considered to study the adsorption of DRM species, the definition of the sites are given as Ni threefold hollow ‘1’, Ni bridge ‘2’, Ni top ‘3’, Ni-P hollow ‘4’, Ni-P bridge ‘5’ and P top ‘6’.

5.3.2 Adsorption of DRM species on Ni$_2$P (0001) surface

The optimized structures of the DRM species on the Ni$_2$P (0001) surface are shown in Figure 5.2 (a-n) and their corresponding adsorption energies, preferable adsorption sites and calculated bond lengths are reported in Table 5.2. Additionally, the adsorption energies of the species on all the available adsorption sites on the Ni$_2$P (0001) surface are included in Table 5.1 for completeness. Further vibrational frequencies of adsorbates are given in appendix B.
Figure 5.2 Front views of the most stable configurations of the DRM species on the Ni_2P (0001). Additionally, for details of bonds and bond lengths of the adsorbates refer to Table 5.2. Green spheres represent Ni atoms, orange P atoms, grey carbon, red oxygen, and white hydrogen, respectively.

Table 5.1 Adsorption energies in (eV) for DRM species on all possible sites on the Ni_2P plane of Ni_2P (0001) surface. The arrow with site annotation represents the final site the particular species adsorbs after geometry optimization.

<table>
<thead>
<tr>
<th>Species</th>
<th>Ni sites</th>
<th>Ni-P hybrid site</th>
<th>P site</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>C</td>
<td>-6.53</td>
<td>→1</td>
<td>→1</td>
</tr>
<tr>
<td>H</td>
<td>-2.95</td>
<td>→1</td>
<td>→1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>O</td>
<td>-6.00</td>
<td>→1</td>
<td>→1</td>
</tr>
<tr>
<td>OH</td>
<td>-3.63</td>
<td>→1</td>
<td>→1</td>
</tr>
<tr>
<td>H₂</td>
<td>→2</td>
<td>-0.71</td>
<td>-0.71</td>
</tr>
<tr>
<td>H₂O</td>
<td>→3</td>
<td>-</td>
<td>-0.50</td>
</tr>
<tr>
<td>CH₃</td>
<td>-0.02</td>
<td>-0.01</td>
<td>-0.02</td>
</tr>
<tr>
<td>CH₃</td>
<td>-2.14</td>
<td>→1</td>
<td>→1</td>
</tr>
<tr>
<td>CH₂</td>
<td>-4.07</td>
<td>→1</td>
<td>→1</td>
</tr>
<tr>
<td>CH</td>
<td>-6.13</td>
<td>→1</td>
<td>→1</td>
</tr>
<tr>
<td>CO</td>
<td>-1.97</td>
<td>→1</td>
<td>-1.61</td>
</tr>
<tr>
<td>CO₂</td>
<td>→2</td>
<td>-0.05</td>
<td>-</td>
</tr>
<tr>
<td>COOH</td>
<td>→2</td>
<td>-2.26</td>
<td>→2</td>
</tr>
<tr>
<td>COH</td>
<td>-4.27</td>
<td>→1</td>
<td>→1</td>
</tr>
<tr>
<td>CHO</td>
<td>-2.66</td>
<td>-1.80</td>
<td>-2.40</td>
</tr>
</tbody>
</table>
Table 5.2 Adsorption energies ($E_{ads}$) in eV and Bond lengths (Å) of DRM species on the most stable sites on Ni$_3$P$_2$ plane of Ni$_2$P (0001) surface and adsorption energies ($E_{ads}$) in eV, values are taken from Chapter 3 of similar species on Ni (111) for comparison.

<table>
<thead>
<tr>
<th>Species</th>
<th>Preferred site</th>
<th>Ni$<em>2$P(001) $E</em>{ads}$ (eV)</th>
<th>Ni (111) $E_{ads}$ (eV)</th>
<th>Bond lengths of adsorbates on Ni$_2$P (0001) Bonds</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1</td>
<td>-6.53</td>
<td>-6.72</td>
<td>C-Ni</td>
<td>1.81, 1.82</td>
</tr>
<tr>
<td>H</td>
<td>1</td>
<td>-2.95</td>
<td>-2.78</td>
<td>H-Ni</td>
<td>1.79, 1.80</td>
</tr>
<tr>
<td>O</td>
<td>1</td>
<td>-6.00</td>
<td>-5.62</td>
<td>O-Ni</td>
<td>1.92</td>
</tr>
<tr>
<td>OH</td>
<td>1</td>
<td>-3.63</td>
<td>-</td>
<td>O-H / O-Ni</td>
<td>1.0 / 2.04</td>
</tr>
<tr>
<td>H$_2$</td>
<td>3</td>
<td>-0.71</td>
<td>-0.31</td>
<td>H-H / H-Ni</td>
<td>0.91 / 1.59, 1.63</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>3</td>
<td>-0.50</td>
<td>-</td>
<td>O-H / O-Ni</td>
<td>1.01 / 2.13</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>3</td>
<td>-0.02</td>
<td>-0.021</td>
<td>C-H / C-Ni</td>
<td>1.11, 1.12 / 3.45</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>1</td>
<td>-2.14</td>
<td>-1.98</td>
<td>C-H / C-Ni</td>
<td>1.12 / 2.18, 2.19</td>
</tr>
<tr>
<td>CH$_2$</td>
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<td>-4.07</td>
<td>-4.10</td>
<td>C-H</td>
<td>1.11, 1.17</td>
</tr>
<tr>
<td></td>
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<td>C-Ni</td>
<td>1.95, 1.96, 2.12,</td>
</tr>
<tr>
<td>CH</td>
<td>1</td>
<td>-6.13</td>
<td>-6.50</td>
<td>C-H / C-Ni</td>
<td>1.11 / 1.90</td>
</tr>
<tr>
<td>CO</td>
<td>1</td>
<td>-1.97</td>
<td>-1.83</td>
<td>C-O</td>
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</tr>
<tr>
<td>CO</td>
<td>bri</td>
<td>-0.05</td>
<td>-0.02</td>
<td>C-O$_1$ / C-O$_2$</td>
<td>1.31/1.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C-Ni</td>
<td>2.0</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>bri</td>
<td>-0.05</td>
<td>-0.02</td>
<td>C-O$_1$ / C-O$_2$</td>
<td>1.31/1.23</td>
</tr>
<tr>
<td>COOH</td>
<td>OFF-top</td>
<td>-2.27</td>
<td>-</td>
<td>C-O / O-H</td>
<td>1.22 / 1.02</td>
</tr>
<tr>
<td>COH</td>
<td>1</td>
<td>-4.27</td>
<td>-</td>
<td>O-H</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C-Ni</td>
<td>1.90, 1.92, 1.94</td>
</tr>
</tbody>
</table>

85
From Figure 5.2 (a-n), Table 5.1 and 5.2, it is seen that the most preferable adsorption sites for the majority of the DRM species on the Ni$_2$P (0001) surface is Ni ‘1’ site, which is similar to the hollow sites (hcp, fcc) of Ni (111) surfaces found to be active for adsorption of similar species [14-15]. Monoatomic carbon prefers to adsorb on both the available hollow sites (Ni ‘1’ and Ni-P ‘4’) with a stronger binding of -6.53 eV ($E_{ads}$) on the ‘1’ site. Additionally, compared to Ni (111), C adsorption is weaker on Ni$_2$P. Further, in comparison to Ni (111), the binding of atomic O is found to be stronger on Ni$_2$P, at -6.00 eV ($E_{ads}$) on the Ni ‘1’ site. Furthermore, O also showcases adsorption on Ni-P ‘5’ bridge site with $E_{ads}$ of -5.84 eV. The adsorption energy of monoatomic hydrogen (H) was found to be most stable on the Ni ‘1’ site, at -2.94 eV ($E_{ads}$), higher compared to that found on Ni (111). Also, H adsorbs with lower energies onto the P top site ‘6’ at -2.18 eV ($E_{ads}$) and Ni-P bridge site ‘5’ at -2.32 eV ($E_{ads}$).

For the diatomic species, the most preferable adsorption site for OH and CO was found to be Ni ‘1’ hollow site with $E_{ads}$ of -3.63 eV and -1.97 eV respectively. Further OH also adsorbs on the P and Ni –P sites (5 and 6) with lower $E_{ads}$. For CO adsorption only the Ni sites (1-3) are preferred with physisorption of CO being observed on the P site with ($E_{ads}$) of -0.25 eV. H$_2$ preferably adsorbs on the Ni ‘3’ site with $E_{ads}$ -0.71 eV and dissociates on the Ni ‘1’ site, which is found similarly occurring on Ni (111) planes. Overall among the diatomic species, OH was found to have moderate binding on Ni-P and P sites whereas CO and H$_2$ prefer the Ni sites.

The adsorption data of the two main reactants in DRM, CO$_2$ and CH$_4$ indicate physisorption Figure 5.2 (g and l) on the Ni$_2$P surface with very weak adsorption energies of -0.05 eV and -0.02 eV respectively. CO$_2$ was found to chemisorb Figure 5.2 (l) on the Ni ‘2’ site, while the rest of the sites were unfavourable for CO$_2$ adsorption (Table 5.1). Similarly, the CH$_4$ molecule favours the Ni ‘3’ site with one hydrogen atom pointing towards the surface, while the Ni-P and P sites were not favourable towards CH$_4$ adsorption. The most preferential adsorption site for the CH$_x$(x=0-3) species is the Ni’1’ site, and it was found that adsorption energy increases with decreasing x: $E^{CH}_ads > E^{CH_2}_ads > E^{CH_3}_ads$. Additionally, the Ni-P ‘5’ bridge site shows moderate stability with lower binding energies towards the CH$_x$ species (Table 5.1).
Carboxyl (COOH) prefers to only adsorb on the Ni‘3’ site with $E_{\text{ads}}$ of -2.27 eV while Ni-P and P sites being ineffective towards adsorption. Again, for CHO and COH, the Ni ‘1’ site is found to be most stable with $E_{\text{ads}}$ of -2.66 eV and -4.67 eV respectively. However, for COH moderate binding was observed on the Ni-P bridge site while CHO did not bind onto these sites. Finally, H$_2$O was found to be stable only on the Ni ‘3’ site with $E_{\text{ads}}$ of -0.50 eV. From the adsorption energetics of the DRM species, it may be noted that the Ni sites, especially 1 and 3, showcased stronger binding ability with DRM species when compared to other available sites on the Ni$_2$P surface. However, the Ni-P bridge site also exhibits moderate stability in regards to binding characteristics to monoatomic DRM species such as (H, O and OH), which contributes as co-adsorption sites in the DRM reaction steps. Further, this observation also confirms that Ni-P and P sites may actively participate in the reaction.

5.3.3 DRM reaction mechanism on Ni$_2$P (0001)

To gain a proper understanding of the catalytic activity of the Ni$_2$P, the fundamental DRM reaction mechanism scheme described in chapter 3 (Figure 3.4) is considered in this chapter similarly. However, we have also considered additional reaction steps shown in the purple circle in Figure 5.3, which accounts for the reverse water gas shift (RWGS) and CO formation from COH intermediate with OH and H$_2$O formation. Further to develop a fundamental

![Figure 5.3 DRM mechanism scheme considered in the present work on Ni$_2$P (0001).](image-url)
understanding and ascertaining the rate determining steps on the Ni$_2$P (0001) surface, it is important to consider the intermediates of the DRM reactions even if they are not experimentally observable. For instance, in experimental studies, CH$_x$ and CH$_x$O or OH intermediates were not detectable by in situ IR technique [161]. This is due to the rate of decomposition of these intermediates are higher than formation [161]. However, these intermediates influence the eventual products conversion in DRM [38, 161] and have been considered in previous theoretical studies to ascertain the rate determining steps of the DRM reaction on particular catalyst surfaces [35, 36]. Therefore the reaction mechanism scheme in the present chapter essentially comprises of CH$_4$ activation via sequential dissociation, CO$_2$ activation through a direct or hydrogenation route and finally the C and CH oxidation reactions leading to CO formation.

The details about the calculated values of the forward ($E_{a,f}$) and backward activation energies ($E_{a,b}$), reaction energy ($\Delta H_r$) and bond formation or bond scission at transition state of the reaction steps is reported in Table 5.3. Further, the DFT calculated geometries for all the reaction steps considered in the present comprising of initial (IS), transition (TS) and final (FS) states are shown in Figures 5.4-5.7.

**Table 5.3** Elementary reactions of DRM on Ni$_2$P (0001) surface with an activation energy of the forward ($\Delta E_{a,f}$) and backward ($\Delta E_{a,b}$) reactions, reaction energy ($\Delta H_r$).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta E_{a,f}$ ($\Delta E_{a,b}$) [eV]</th>
<th>$\Delta H$ (eV)</th>
<th>Bond</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>CH$_4^<em>$ + -</em>→CH$_3^<em>$ + H</em></td>
<td>1.14 (0.58)</td>
<td>0.56</td>
<td>C-H</td>
</tr>
<tr>
<td>R2</td>
<td>CH$_3^<em>$ + -</em>→CH$_2^<em>$ + H</em></td>
<td>1.00 (0.14)</td>
<td>0.86</td>
<td>C-H</td>
</tr>
<tr>
<td>R3</td>
<td>CH$_2^<em>$ + -</em>→CH* + H*</td>
<td>0.66 (0.12)</td>
<td>0.53</td>
<td>C-H</td>
</tr>
<tr>
<td>R4</td>
<td>CH* + -<em>→C</em> + H*</td>
<td>1.77 (0.28)</td>
<td>1.48</td>
<td>C-H</td>
</tr>
<tr>
<td>R1</td>
<td>CH* + O* → COOH* + *</td>
<td>1.34 (1.85)</td>
<td>-0.51</td>
<td>C-O</td>
</tr>
<tr>
<td>-----</td>
<td>----------------------</td>
<td>-------------</td>
<td>-------</td>
<td>-----</td>
</tr>
<tr>
<td>R2</td>
<td>COOH* → CO* + H*</td>
<td>0.55 (0.82)</td>
<td>-0.27</td>
<td>C-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C-H</td>
</tr>
<tr>
<td>R3</td>
<td>O* + H* → OH* + *</td>
<td>1.55 (0.66)</td>
<td>0.89</td>
<td>O-H</td>
</tr>
<tr>
<td>R4</td>
<td>OH* + H* → H₂O* + *</td>
<td>0.98 (1.04)</td>
<td>-0.06</td>
<td>O-H</td>
</tr>
<tr>
<td>R5</td>
<td>CO₂* → CO* + O*</td>
<td>0.96 (1.57)</td>
<td>-0.61</td>
<td>C-O</td>
</tr>
<tr>
<td>R6</td>
<td>CO₂* + H* → COOH*</td>
<td>1.19 (1.30)</td>
<td>-0.11</td>
<td>O-H</td>
</tr>
<tr>
<td>R7</td>
<td>COOH* → CO* + H*</td>
<td>0.23 (0.74)</td>
<td>-0.51</td>
<td>C-O</td>
</tr>
<tr>
<td>R8</td>
<td>C* + O* → CO* + *</td>
<td>1.18 (3.44)</td>
<td>-2.26</td>
<td>C-O</td>
</tr>
<tr>
<td>R9</td>
<td>C* + OH* → COH* + *</td>
<td>0.94 (2.48)</td>
<td>-1.54</td>
<td>C-O</td>
</tr>
<tr>
<td>R10</td>
<td>COH* + * → CO* + H*</td>
<td>1.04 (1.54)</td>
<td>-0.50</td>
<td>O-H</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C-O</td>
</tr>
<tr>
<td>R11</td>
<td>CH* + O* → CHO* + *</td>
<td>1.34 (1.85)</td>
<td>-0.51</td>
<td>C-O</td>
</tr>
<tr>
<td>R12</td>
<td>CHO* + * → CO* + H*</td>
<td>0.55 (0.82)</td>
<td>-0.27</td>
<td>C-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C-H</td>
</tr>
<tr>
<td>R13</td>
<td>O* + H* → OH* + *</td>
<td>1.55 (0.66)</td>
<td>0.89</td>
<td>O-H</td>
</tr>
<tr>
<td>R14</td>
<td>OH* + H* → H₂O* + *</td>
<td>0.98 (1.04)</td>
<td>-0.06</td>
<td>O-H</td>
</tr>
<tr>
<td>R15</td>
<td>H* + H* → H₂*</td>
<td>0.36 (0.14)</td>
<td>0.22</td>
<td>H-H</td>
</tr>
</tbody>
</table>

5.3.3.1 CH₄ activation (R1-R4)

![Image of CH₄ activation (R1-R4)](image_url)

- C-H = 1.12 Å
- C-H = 1.73 Å
- C-H = 2.76 Å
Figure 5.4 Front view of CH$_4$ activation on Ni$_2$P (0001) surface showing, (R1) CH$_4$* + *→CH$_3$* + H* (R2) CH$_3$* + *→CH$_2$* + H*, (R3) CH$_2$* + *→CH* + H* and (R4) CH* + *→C* + H*. Transition state configurations including (IS) initial state (TS) transition state (FS) final state for CH$_4$ sequential dissociation. Black dashed line indicates C-H bond cleavage distance. Green spheres represent Ni atoms, orange P atoms, grey carbon, and white hydrogen, respectively. * denotes surface adsorbate.

R1: CH$_4$* + *→CH$_3$* + H*: The first sequential step of CH$_4$ activation. The stable structure of CH$_4$ on site 3 is considered as the IS and co-adsorbed CH$_3$ and H as FS [Figure 5.4 (R1)]. The TS for the reaction occurs on top of a Ni atom where the C-H bond stretches from 1.12 Å in the IS to 1.73 Å during the TS. The calculated $E_{a,f}$ is 1.14 eV with the step being endothermic 0.56 eV ($\Delta H_r$).

R2: CH$_3$* + *→CH$_2$* + H*: In the next sequential step [Figure 5.4 (R2)], CH$_3$ dehydrogenates to CH$_2$ and H with $E_{a,f}$ of 1.00 eV. The reaction is found to be endothermic by ($\Delta H_r$) 0.86 eV. The C-H bond length at the TS is 1.97 Å, which in the IS geometry is 1.12 Å.
R3: CH\textsubscript{2}* + *\rightarrow CH* + H*: The C-H bond length of the IS structure of CH\textsubscript{2} is 1.17 Å which stretches to 1.95 Å during the TS [Figure 5.4 (R3)]. The endothermicity of the reaction is considerably lower (\(\Delta H\)) 0.53 eV compared to the previous steps, and \(E_{a,f}\) required obtained for this step is 0.66 eV.

R4: CH* + *\rightarrow C* + H*: The final sequential dissociation step is the most energy demanding step with an \(E_{a,f}\) of 1.77 eV and (\(\Delta H\)) being highly endothermic 1.42 eV. The C-H bond stretches from 1.11 Å in the IS to 1.95 Å during the TS, Figure 5.4 (R4). The crucial reaction mechanism of methane activation is found to be mostly endothermic on the Ni\textsubscript{2}P (0001) surface, however, the final step showcases the difficulty of atomic carbon formation on the surface due to high energy barriers.

5.3.3.2 CO\textsubscript{2} activation (R5-R7)

To study the CO\textsubscript{2} activation on Ni\textsubscript{2}P (0001) surface two reaction routes namely (i) direct dissociation (R5), and (ii) CO\textsubscript{2} hydrogenation (R6-R7) are considered in the present work. While the former requires a single step to form CO and O (R6), the latter comprises of two reactions (R7) for the formation of CO and OH.
Figure 5.5 Front views of CO$_2$ activation reactions on Ni$_2$P (0001) surface showing, (R5) CO$_2$* $\rightarrow$ CO* + O* (R6) CO$_2$* + H* $\rightarrow$ COOH* and (R7) COOH* $\rightarrow$ CO* + H*. Transition state configurations including (IS) initial state (TS) transition state (FS) final state for CO$_2$ activation reaction. Black dashed line indicates C-O and O-H bond breaking or forming distances. Green spheres represent Ni atoms, orange P atoms, grey carbon, and red oxygen, white hydrogen, respectively. * denotes surface adsorbate.

R5: CO$_2$* $\rightarrow$ CO* + O*: The direct dissociation route Figure 5.5 (R5), for CO$_2$ activation is the main source of oxygen formation on the Ni$_2$P (0001) surface, similarly to Ni monometallic surfaces [14-15]. The reaction occurs via C-O bond scission, where the C-O bond distance increases from 1.31 Å in the (IS) to 2.31 Å during the (TS). The reaction is exothermic (ΔH$_r$) by -0.61 eV with an E$_{a,f}$ of 0.96 eV.

R6: CO$_2$* + H* $\rightarrow$ COOH*: The CO$_2$ hydrogenation occurs via the combination of carbon dioxide and hydrogen to form a carboxyl intermediate species on the catalyst surface. On Ni$_2$P (0001) the formation of this carboxyl occurs with the decrease in the O-H bond distance from 2.70 Å in the IS to 1.50 Å in the TS [Figure 5.5 (R6)]. The (ΔH$_r$) is less exothermic compared to the direct dissociation route (R5) by -0.11 eV, with an E$_{a,f}$ of 1.19 eV.

R7: COOH* $\rightarrow$ CO* + H*, dissociation of the carboxyl intermediate Figure 5.5 (R7) occurs easily with an E$_{a,f}$ of 0.23 eV and exothermic reaction energy (ΔH$_r$) by -0.51 eV. In the dissociation geometry Figure (5c), the C-O bond length of 1.44 Å for the carboxyl molecule shown in the IS geometry stretches to 2.59 Å in the TS to form CO and OH on the Ni$_2$P (0001) surface.

5.3.3.3 C and CH oxidation (R8 – R12)

The main source for the formation of CH and C species on the Ni$_2$P (0001) surface is through the methane dehydrogenation reactions (R1-R4). In previous theoretical studies on monometallic Ni and other transition metal surfaces, the oxidation reactions of the above-mentioned
species influence the formation of CO on the catalyst surfaces both thermodynamically and kinetically [34-36]. Therefore, in this section, we have studied the mechanism of C oxidation by O forming CO (R8), C oxidation by OH forming COH (R9) and subsequent reaction of COH dissociation to CO and H (R10). Further, the oxidation of CH species with O is studied via reaction (R11) where CHO is formed, thereafter the dissociation of CHO to CO and H (R12).
Figure 5.6 Front view of C and CH oxidation reactions on Ni$_2$P (0001) surface showing, (R8) C$^*$ + O$^*$→CO$^*$ + *, (R9) C$^*$ + OH$^*$→COH$^*$, (R10) COH$^*$→CO$^*$ +H$, (R11) CH$^*$ + O$^*$ → CHO$^*$ and (R12) CHO$^*$ →CO$^*$ +H$. Transition state configurations including (IS) initial state (TS) transition state (FS) final state for C and CH oxidation reactions. Black dashed line indicates C-O, O-H, C-H bond breaking or forming distances. Green spheres represent Ni atoms, orange P atoms, grey carbon, and red oxygen, white hydrogen, respectively.* denotes surface adsorbate.

R8: C$^*$ + O$^*$→CO$^*$ + *: In the IS [Figure 5.6 (R8)] configuration of the co-adsorbed C and O is separated with a bond distance of 3.03 Å, which in the TS shortens to for form CO bond of 1.80 Å. The ($\Delta H_r$) is highly exothermic by -2.26 eV and an $E_{a,f}$ of 1.18 eV.

R9: C$^*$ + OH$^*$→COH$^*$ + *: The IS geometry is similar to (R8) where, the co-adsorbed species of C and OH (IS) are separated by a distance of 3.04 Å, which in the TS, C-OH bond distance shortens to 2.32 Å Figure 5.6 (R9). Again ($\Delta H_r$) is found to be highly exothermic by -1.54 eV with $E_{a,f}$ of 0.94 eV.

R10: COH$^*$ + *→ CO$^*$ + H$^*$ dissociation of COH occurs with the stretching of the O-H bond from 1.01 Å in the IS to 1.36 Å in the TS, Figure 5.6(R10). The reaction is exothermic by -0.50 ($\Delta H$) and of 1.04 eV.

R11: CH$^*$ + O$^*$→CHO$^*$ + *: In the IS geometry the C-O bond distance between the co-adsorbed CH and O is 2.90 Å, which during the formation of CHO shortens to 1.73 Å in the TS, Figure 5.6 (R11). The $E_{a,f}$ required for the reaction is 1.34 eV and the reaction is exothermic -0.51 eV ($\Delta H_r$) in nature.

R12: CHO$^*$ + *→CO$^*$ + H*: After the formation of CHO, it dissociates with an energy barrier of 0.55 eV ($E_{a,f}$ ) and the reaction is exothermic by -0.27 eV ($\Delta H_r$). CO and H formation occur with the stretching of the C-H bond from 1.12 Å in the initial state to 1.20 Å TS and the shortening of the C-O bond from 1.31Å in the IS to 1.27Å TS [Figure 5.6 (R12)].
5.3.3.4 OH, H\textsubscript{2}O and H\textsubscript{2} formation (R13 – R15)

R13: O* + H*→OH* + *, OH forms with the combination of the adsorbed atomic oxygen and hydrogen species which requires a high \(E_{a,f}\) of 1.55 eV with the reaction (\(\Delta H_r\)) endothermic by 0.89 eV. In comparison, the formation of H\textsubscript{2}O (R14: OH* + H*→H\textsubscript{2}O* + *) is exothermic by -0.06 eV (\(\Delta H_r\)) with a much lower energy barrier (\(E_{a,f}\)) of 0.98 eV. In the TS configurations Figures, 5.7(R13-14) for both the reactions the O-H bond formation is similar by 1.61 Å and 1.64 Å respectively.

**Figure 5.7** Front view of OH, H\textsubscript{2}O and H\textsubscript{2} formation on Ni\textsubscript{3}P (0001) surface showing, (R13) O* + H*→OH* + *, (R14) H* + OH*→H\textsubscript{2}O* and (R15) H* + H* → H\textsubscript{2}*. Transition state configurations
including (IS) initial state (TS) transition state (FS) final state for OH, H₂O and H₂ formation. Black dashed lines indicate O-H and H-H bond breaking or forming distances. Green spheres represent Ni atoms, orange P atoms, grey carbon, and red oxygen, white hydrogen, respectively.* denotes surface adsorbate.

(R15: H* + H *→H₂*), atomic hydrogen formed during the sequential dissociation steps (R1-R4) contributes towards the process of forming molecular hydrogen on the Ni₂P (0001) surface, which is easier with an Eₐ,f of 0.36 eV and the corresponding reaction energy (ΔH_r) slightly endothermic at 0.22 eV. The TS of the reaction occurs on top of a Ni atom where the H-H bond distance is 1.26 Å, which decreases from 2.04 Å in the IS geometry [(Figure 5.7 (R15)].

In summary, the above-reported reaction energies and activation energies showcase the active nature of the Ni₂P (0001) surface towards the DRM reaction steps. Further, the catalyst activity and the reaction pathways have been examined using free energy analysis in the next section.

5.3.4 Free energy analysis

In the previous section, we have developed a mechanistic understanding of the DRM reaction steps on the Ni₂P (0001) surface using DFT calculations. Building on this knowledge, in this section we have further assessed the thermodynamic characteristics of the DRM reaction on Ni₂P with the help of free energy (ΔG) analysis. It is to be noted that the free energy profiles are calculated assuming the reaction steps are sequential rather than simultaneous. The temperature and pressure considered for the free energy analysis are 1000 K and 1 bar respectively, similar to previous theoretical studies of DRM [34, 36] and our analysis on Ni (111) and NiSn surfaces in Chapter 3 and 4 respectively.
Figure 5.8 Free energy profile diagrams for (a) CH₄ sequential dissociation (b) CO₂ activation paths (c) Reverse water gas shift (RWGS) reaction and (d) DRM reaction paths for syngas formation on Ni₂P (0001) surface at 1000 K and 1 bar.

The CH₄ activation on Ni catalyst has previously been shown to influence the DRM turnover rates greatly, and simultaneously remaining unaffected with co-reactant (CO₂) concentration
Herein, Figure 5.8a shows the CH₄ activation on Ni₂P (0001) surface, where the first (CH₄(g) → CH₃* + H*) and the final (CH* → C*+ H*) sequential steps are the most energy demanding with (ΔG) of 2.43 eV and 1.67 eV respectively. Figure 5.8 (b) shows the two reaction paths for CO₂ activation on the Ni₂P (0001) surface, where thermodynamically and energetically the direct dissociation path is favoured over the CO₂ hydrogenation route. The free energy barrier for the direct route is 2.26 eV (ΔG) compared to carboxyl (COOH*) reaction is 3.32 eV (ΔG). Interestingly, the bond cleavage of the carboxyl intermediate to form CO* and OH* occurs at a much lower energy 0.14 eV (ΔG). Further, the direct CO₂ decomposition path has been found to be favourable on closed packed Ni (111) surface while CO₂ hydrogenation path is more favoured on noble metal surfaces especially on Pd (111) and Pt (111) surfaces [36]. We have also considered the reverse water gas shift (RWGS) reaction Figure 5.8 (c), which is a competing reaction with DRM and occurs due to the hydrogenation of CO₂ to produce CO and H₂O gas [36]. RWGS on Ni₂P (0001) surface occurs through the direct CO₂ dissociation route with the free energy barrier for H₂O formation by combination of OH and H on the surface is less than the CO formation steps in both the routes. This may affect the H₂/CO ratio on the Ni₂P due to the hydroxyl (OH) and available surface hydrogen (H) combination during RWGS reaction.

We have considered three reaction routes for CO formation on Ni₂P (0001) surface shown in the free energy profiles in (Figure 5.8d); (i) C oxidation by O (ii) C oxidation by OH and (iii) CH oxidation by O. Here in the free energy profile, CO₂ gets activated before CH₄ owing to the lower energy barrier. Among the considered routes, the CH oxidation route is found to be most favourable for CO formation compared to the C oxidation route by O and OH. This route has been found to be favourable on Ni surfaces in previous studies [32, 34, 36, 114].

5.3.5. Microkinetic analysis

In the previous sections, we performed DFT calculations, and thermodynamic free energy analysis for the DRM reaction mechanism scheme (Figure 5.3) to understand the reactivity of the Ni₂P (0001) surface towards DRM. In this section, we further study DRM performance on Ni₂P catalyst using microkinetic analysis. For our kinetic model, a total of 17 elementary DRM reactions steps (R1-R17) were used, including the essential CH₄ and CO₂ activation steps, syngas (CO and H₂) formation pathways, and H₂O and H₂ formation steps.
\[ \text{CH}_4(g) + *_{\text{s}} + *_{\text{h}} \rightarrow \text{CH}_3*_{\text{s}} + \text{H}^*_{\text{h}} \]  
R1

\[ \text{CO}_2(g) + 2*_{\text{s}} \rightarrow \text{CO}^*_{\text{s}} + \text{O}^*_{\text{s}} \]  
R2

\[ \text{CH}_3*_{\text{s}} + *_{\text{h}} \rightarrow \text{CH}_2*_{\text{s}} + \text{H}^*_{\text{h}} \]  
R3

\[ \text{CH}_2*_{\text{s}} + *_{\text{h}} \rightarrow \text{CH}^*_{\text{s}} + \text{H}^*_{\text{h}} \]  
R4

\[ \text{CH}^*_{\text{s}} + *_{\text{h}} \rightarrow \text{C}^*_{\text{s}} + \text{H}^*_{\text{h}} \]  
R5

\[ \text{H}^*_{\text{h}} + \text{H}^*_{\text{h}} \rightarrow \text{H}_2(g) + 2*_{\text{h}} \]  
R6

\[ \text{CO}_2*_{\text{s}} + \text{H}^*_{\text{h}} \rightarrow \text{COO}^*_{\text{s}} + *_{\text{h}} \]  
R7

\[ \text{COOH}^*_{\text{s}} + *_{\text{h}} \rightarrow \text{CO}^*_{\text{s}} + \text{H}^*_{\text{h}} \]  
R8

\[ \text{O}^*_{\text{s}} + \text{H}^*_{\text{h}} \rightarrow \text{OH}^*_{\text{s}} + *_{\text{h}} \]  
R9

\[ \text{OH}^*_{\text{s}} + \text{H}^*_{\text{h}} \rightarrow \text{H}_2\text{O}_s + *_{\text{h}} \]  
R10

\[ \text{H}_2\text{O}_s \rightarrow \text{H}_2\text{O}_g + *_{\text{s}} \]  
R11

\[ \text{C}^*_{\text{s}} + \text{O}^*_{\text{s}} \rightarrow \text{CO}^*_{\text{s}} + *_{\text{s}} \]  
R12

\[ \text{C}^*_{\text{s}} + \text{OH}^*_{\text{s}} \rightarrow \text{COH}^*_{\text{s}} + *_{\text{s}} \]  
R13

\[ \text{COH}^*_{\text{s}} + *_{\text{h}} \rightarrow \text{CO}^*_{\text{s}} + \text{H}^*_{\text{h}} \]  
R14

\[ \text{CH}^*_{\text{s}} + \text{O}^*_{\text{s}} \rightarrow \text{CHO}^*_{\text{s}} + *_{\text{s}} \]  
R15

\[ \text{CHO}^*_{\text{s}} + *_{\text{h}} \rightarrow \text{CO}^*_{\text{s}} + \text{H}^*_{\text{h}} \]  
R16

\[ \text{CO}^*_{\text{s}} + *_{\text{s}} \rightarrow \text{CO}(g) + *_{\text{s}} \]  
R17

The (*_s) and (*_h) represents open and hydrogen adsorption sites respectively on the Ni$_2$P (0001) surface.

The CatMAP [105] code is used to perform all microkinetic calculations in this work. In the microkinetic model all the DRM species, adsorbed on the Ni$_2$P (0001) surface competes for a free site (*_s) expect for hydrogen, which occupies a special site (*_h), known as the ‘hydrogen reservoir site’. The consideration of a special site for hydrogen arises due to the smaller size
scale of hydrogen compared to other adsorbates, which enables it to adsorb during high coverages of other adsorbates [162, 163]. From this definition, it may be considered that hydrogen adsorbs onto a separate lattice [162, 163]. In the present calculations, the coverage of all adsorbates on Ni₃P (0001) surface and hydrogen sites are constrained to 1.

The reactant gas feed ratio considered for the kinetic model used in our calculations is CH₄: CO₂ = 1, which is typical in DRM [10, 36], and the product (H₂ and CO) gas concentrations were taken as 10% of CH₄ conversion. Here, we have not considered the dependence of products concentration on CO₂ conversion, as Wei and Iglesia in their kinetic and isotopic study on Ni/MgO catalyst found the forward turn-over rates for the DRM reactants to depend only upon the CH₄ partial pressures [116]. Further, a low CH₄ conversion of (10%) was considered to provide kinetic control for the reaction as well as avoid reverse methanation reaction on the Ni₃P (0001) surface, which occurs due to higher H₂ partial pressures on Ni-based catalysts [34, 38]. Also, formation energies of the adsorbates and gas phase species were calculated relative to gas phase energies of CH₄, H₂O and H₂.
Figure 5.9 (a) Production rate in (TOF s⁻¹) of CO, H₂ and H₂O gas production on Ni₂P (0001) surface. (b) Coverage of major species on the Ni₂P (0001) surface, and (c) Coverage of minor species on the Ni₂P (0001) surface. All the microkinetic calculations are performed at a temperature range of 900-1300 K with a constant pressure of 1 bar.

For the microkinetic calculations, a temperature range of (900 – 1300) K is considered with pressure kept constant at 1 bar. Figure 5.9a shows the production rate in (TOF s⁻¹) of CO, H₂ and H₂O gases on the Ni₂P (0001) where the rates for CO and H₂O gas production are observed at lower temperatures of (900 - 1050 K). However, the rates for H₂ gas is not observed at this temperature range and requires higher temperatures >1050 K. Further, the H₂/CO ratio obtained from our calculations from 1100 -1300 K is in the range of 0.68 -0.86, whereas below <1100 K the H₂/CO ratio is low ~0.63. From these calculated values it may be considered that high temperatures will be required to get good product conversion (and high-quality syngas) on Ni₂P (0001) surface. This has also been observed during catalytic activity tests on molybdenum phosphide (MoP) in DRM where the reactant and product conversion greatly dependent on temperature [56]. One reason may be due to the endothermic nature of the CH₄ activation mechanism on Ni₂P, shown in our DFT and free energy analysis. As the CH₄ activation is the main source for hydrogen and carbon species, a delayed CH₄ activation slows down H₂ gas production rate. Another reason may be due to reverse water gas shift (RWGS), which has been seen to affect H₂/CO rates at low CH₄ conversions (>15%) on Ni (111) surface and the RWGS was found to reach equilibrium without kinetic limitation [36]. In fact, the presence of the
RWGS imposes a pathway for hydrogen consumption and leads to H₂-poor syngas with an H₂/CO ratio below 1. Additionally, similar to Ni (111) [36], in the present calculations, minor amounts of H₂O gas production (<10⁻²) is observed, confirming the influence of the RWGS.

Coverage of the adsorbed species on the Ni₂P surface in the microkinetic model is divided into two categories – major coverage Figure 5.9 (b), and minor coverage Figure 5.9 (c). (Here it should be mentioned that we have not considered the effect of lateral interactions of the surface adsorbed species in both our DFT and microkinetic study. From Figure 5.9b, the major coverage on the Ni₂P (0001) surface is that of CO and H which gradually decreases with increasing temperature, and participates in the formation of CO and H₂ gas kinetically. Further, CH maintains a relatively uniform coverage of (~10⁻²) in the calculated temperature range. Among minor coverage species, the carbon concentration is lower compared to the oxygen concentration indicating the possibility of less coking on the Ni₂P (0001) surface during DRM. Furthermore, oxygen concentration increases with increasing temperature. The higher oxygen concentration is consistent with an experimental XPS study performed by Liu et al. [58] where it was found that oxy phosphides were formed on the Ni₂P surface under WGSR conditions [58]. In other words, P act as an oxygen sink due to its ability to interact with oxygen, this is very helpful in DRM since an oxygen-rich surface is less prone to coking. Also, the preferential interaction of O with P (P-O) maintains O far from Ni atoms avoiding their oxidation. This is again another advantage of our engineered model catalysts since Ni must remain reduced (metallic) to achieve high performance in reforming reactions.

5.3.6 Coking stability

It has been well established previously that nickel-based catalysts are prone to coking at high DRM reaction conditions [34, 36, 114]. The mechanisms mainly responsible for coking on Ni catalysts are essentially driven by the reaction steps of (i) sequential dissociation of CH₄ to atomic C and H (R1-R4) and (ii) CO dissociation to C and O (R8), where carbon atoms are considered to be precursors to carbon growth on the catalyst surface [36, 128].
In our DFT adsorption energy analysis of the DRM species on Ni$_2$P (0001), we found atomic carbon to have the strongest adsorption energy ($E_{\text{ads}}$) with the surface followed closely by atomic oxygen (see Table 5.2). This is also shown in Figure 5.10 (a-b) where the p orbitals of C has stronger overlap with the d orbitals of a Ni atom below the Fermi level ($E_F$) on Ni$_2$P (0001) at the three-fold hollow Ni ‘1’ site. In comparison, the p orbitals of an O atom adsorbed on the same surface site also overlaps with the d orbital of the Ni atom Figure 5.10 (b) but to a lesser extent and hence C is more stable than O on Ni ‘1’ site. However atomic O is also found to be stable on the Ni-P bridge site ‘5’ where the p orbitals of O overlaps with the p orbitals of P and Ni Figure 5.10 (c). Additionally, the p orbital overlapping of O with P Figure 5.10 (c) is much stronger, which is in good agreement with previous findings by Liu et al. [58]. Further, in our DFT calculation, we have found C to be unstable on the Ni-P ‘5’ and P ‘6’ sites. Therefore from this analysis, it may be considered the available stable adsorption sites for C.

**Figure 5.10** Partial density of states (PDOS) (a) C adsorbed on Ni site ‘1’ (b) O adsorbed on Ni site ‘1’ and (c) O adsorbed on Ni-P site ‘5’.
formation are fewer than those for O adsorption on Ni₃P (0001) surface and adsorbed oxygen on the Ni-P site '5' will propagate carbon oxidation during the DRM reaction hence negating carbon growth to a larger extent on Ni₃P. To analyze the mobility of the C atoms on Ni₃P we performed similar DFT calculation used in Chapter 3 (Section 3.3.5).

![diagram](Image)

**Figure 5.11** Transition state configurations including (IS) initial state (TS) transition state (FS) final state for carbon atom diffusion from stable Ni site ‘1’ to Ni-P site ‘4’ on Ni₃P (0001) surface.

<table>
<thead>
<tr>
<th>Surfaces</th>
<th>Adsorption site</th>
<th>Adsorption energy (E_{ads}) in eV</th>
<th>C migration E_a,f (eV)</th>
<th>ΔH (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₃P (0001)</td>
<td>1</td>
<td>-6.53</td>
<td>1.34</td>
<td>0.38</td>
</tr>
<tr>
<td>Ni (111)</td>
<td>hcp</td>
<td>-6.72</td>
<td>0.31</td>
<td>-0.04</td>
</tr>
</tbody>
</table>

Table 5.4 DFT energy barriers for single C adsorption and diffusion on Ni₃P (0001) and Ni (111).

Figure 5.11 shows the DFT calculations of carbon diffusion from one stable adsorption site ‘1’ to a less stable site ‘4’ on Ni₃P (0001) and we have also compared C atom diffusion with our findings on Ni (111) shown in Table 5.4. In both surfaces, the hollow adsorption site is preferred for C adsorption hcp for Ni (111) and Ni ‘1’ for Ni₃P (0001). Further, the carbon diffusion on Ni₃P (0001) is found to be more energy demanding with (E_{a,f}) being 1.34 eV compared to 0.31 eV on Ni (111). This analysis shows the mobility of C atoms will be difficult and C will be constrained to the hollow site ‘1’ on Ni₃P (0001). This may represent an ensemble effect (decrease in active sites for adsorption), similar to our findings in Chapter 4, where Sn also decreases C formation by reducing active hollow sites on Ni (111).
In regards to carbon stability on Ni$_2$P (0001), our microkinetic calculations showcased lower carbon coverage compared to increasing coverage of oxygen with temperature (Figure 5.9c). The increasing O coverage at higher reaction temperature agrees well with our hypothesis made earlier, of carbon oxidation (C-O) compared to C-C bonds on Ni$_2$P (0001). Additionally, CO* is found to be the most abundant species at DRM reaction conditions on Ni$_2$P (0001) Figure 5.9(b) and the probability of carbon formation from its dissociation is less due to its high backward activation energy barrier of 3.44 eV (E$_{a,b}$) found in our DFT calculation. Additionally, CH cracking (R4: CH* → C*+ H*) during CH$_4$ dissociation contributes to coke formation. However, on the Ni$_2$P (0001) surface the CH cracking step is found to be energy demanding, shown in free energy plot Figure 5.8 (a.), therefore the coverage of CH* is much greater (>10$^{-2}$) compared to atomic carbon at higher DRM temperatures. Overall it may be considered that Ni$_2$P (0001) catalyst surface with Ni$_3$P$_2$ plane, to be stable towards carbon growth with longer catalyst life span in DRM when compared to traditional Ni surfaces.

5.4. Conclusions

The theoretical analysis performed in this work to examine the potential of Ni$_2$P (0001) surface for DRM provides some interesting insights. The positive feature of the Ni$_2$P surface was found in its ability to be active towards most of the DRM species. Furthermore, Ni-P bridge sites of the Ni$_2$P (0001) surface contributed as co–adsorption sites for DRM reaction mechanisms. DFT and thermodynamic calculations showcased good CH$_4$ and CO$_2$ activation characteristics. Stable catalytic performance was observed in our microkinetic study with a higher degree of carbon tolerance of the Ni$_2$P (0001) surface. Overall, from the theoretical analysis performed, it is concluded that the Ni$_2$P (0001) surface conserves the active characteristics of Ni surfaces, but with increased stability towards carbon formation at high DRM temperatures. Hence, we believe that the Ni$_2$P (0001) surface is a promising catalyst that should be further studied.
Chapter 6: DFT study of CO₂ and CO activation via RWGS on transition metal phosphides (TMPs)

Short abstract: CO₂ and CO activation reactions are integral to many industrial catalytic processes, where the development of active and cost friendly catalysts is of paramount importance. Here we have employed DFT to investigate both activations of CO₂ and CO on two transition metal phosphides (TMPs) which have largely remained unexplored. Our results showcase both MoP (0001) and Ni₃P (0001) surfaces to be possible candidates for the selective CO₂ activation to produce CO and subsequent CO activation. However, the main drawback is elucidated to be the oxygen removal reactions with only Ni₃P (0001) showcasing the reasonable potential for oxygen removal.

6.1 Introduction

Carbon dioxide (CO₂) is considered to be one of the main greenhouse gases, which presents an adverse effect on the Earth’s atmosphere and climate [164]. In the context of CO₂ utilisation a selective conversion of CO₂ to CO in the presence of H₂, commonly known as reverse water gas shift (RWGS, CO₂ + H₂ ⇌ CO + H₂O) is a viable industrial option [165]. Especially this is largely due to the versatile nature of CO, which may be transformed into value-added products or used in the downstream Fischer-Tropsch (FT) or in MeOH synthesis [164, 165]. Recent research has focused on the development of suitable catalysts for the RWGS process, to overcome the challenges mainly due to the endothermic nature of the process which requires higher temperatures to achieve equilibrium CO₂ conversion ranging between 10-50% at (200-500) °C respectively [165]. Therefore to improve the kinetics of the RWGS process, efforts have been made to develop more active catalysts towards CO₂ dissociation to produce a greater yield of CO [165].

In the past decade, both transition metal carbides (TMCs) and phosphides (TMPs) have been investigated for a variety of industrial processes such as the forward water gas shift (WGS) [58, 166] and CO hydrogenation [68, 69, 167]. Among the TMC’s, a major focus has been given to molybdenum (Mo) carbides, which have shown to be successful in transforming CO₂ to CO, methane, methanol and other hydrocarbons [67, 68, 168]. For instance, DFT investigations indicated spontaneous cleavage of C-O bond on metal (Mo) terminated orthorhombic (β-Mo₂C) to transform CO₂ to CO [169]. Further Liu et al. [67] in their
experimental and theoretical investigation, on polycrystalline (α-Mo$_2$C) for RWGS found CO$_2$ conversion to be 16% with CO selectivity (~99%) at 673K, with their theoretical calculations revealing strong binding of CO$_2$, CO and O species on Mo terminated Mo$_2$C (001) facet [67]. The common feature of Mo-carbide catalysts showcased Mo- terminated surfaces to be more active towards CO$_2$ activation [67, 68, 168, 170] with Mo/C ratio of one, usually adsorbing CO$_2$ without breaking the C-O bond of the molecule [68, 169].

In the context of RWGS reaction TMPs have largely remained unexplored with limited experimental and theoretical investigations available to understand the interaction between CO$_2$ and the surface. Among TMPs, Mo phosphide has been investigated in CO hydrogenation reactions [69]. Zaman and Smith using DFT calculations of elementary reaction steps for the conversion of synthesis gas (CO+H$_2$) to methanol on Mo$_6$P$_3$ cluster model, hypothesised the formation of methane to be greater compared to methanol on MoP surface [69]. Additionally, the authors found the formation CHO from CO hydrogenation to be a rate-determining step on MoP [69]. Further, Feng et al. [171], with their in situ Fourier transform infrared (FT-IR) spectroscopy study of CO adsorption on MoP/γ-Al$_2$O$_3$ obtained a similarity in IR bands corresponding to CO adsorption on noble metals (Pt, Pd, Ru) [171]. Strong CO adsorption on MoP (001) was also reported by Liu et al. [172], in their theoretical study. A further experimental investigation conducted by Yao et al. [56], found MoP to be active towards CO$_2$ reforming of methane with better activity and stability compared to Ni/Mo$_2$C [56]. Additionally, strong oxygen to phosphorus interaction on nickel phosphide Ni$_2$P (001) catalyst has shown to facilitate WSGR activity [58].

Therefore, motivated by the findings of effective usability of Mo-carbide catalysts in RWGS and unexplored potential of TMPs for and CO$_2$ hydrogenation reactions, in this chapter using DFT calculations we have focussed on CO$_2$ and CO activation on two TMPs (MoP and Ni$_2$P). Further detailed DFT calculations of the considered reactions on MoP (0001) surface is discussed in this chapter and the comparison between MoP (0001) and Ni$_2$P (0001) surfaces is drawn by using the obtained DFT values on Ni$_2$P (0001) from Chapter 5, for the specific reactions considered here. It is worthwhile to mention that in this chapter the comparison between the considered TMP’s is purely on a qualitative basis and further experimental or theoretical analysis may be required to determine the better catalyst for the considered processes.
6.2 Computational method

Cambridge Sequential Total Energy Package (CASTEP) [117], is used to perform all the DFT calculations in the present work. The exchange-correlation energy was described by generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional [91]. The electron wave functions were expanded in a plane wave basis set with kinetic energy cut off 340 eV for all the calculations, chosen after convergence tests. Further ultra-soft pseudopotentials, introduced by Vanderbilt [99] is considered to describe the ion-electron interaction. Spin polarization is considered for all the calculations. The electron occupancies were determined by the Gaussian smearing method [119], with a smearing value of 0.1 eV. The self-consistency field (SCF) is considered to be converged when the total energy of the system is below the $10^{-6}$ eV/atom. All geometries were optimized using the (BFGS) [150] algorithm, where the geometries converged until the forces between atoms are less than 0.01 eV/Å.

To model the MoP (0001) surface, first, the MoP bulk parameters are calculated with a Monkhorst-Pack [97] k-point grid of 9×9×8. Thereafter the optimized bulk was cleaved in the [0001] direction. Five layers were used to construct the surface slab in a (3×3) surface supercell, corresponding to an adsorbate coverage of 1/9 monolayer (ML), with a vacuum gap of 12 Å to avoid interactions between the slabs, is used to model the MoP (0001) surface. Further, the bottom two layers were constrained to their bulk positions and the top three layers being allowed to relax in all directions. For sampling, the Brillouin zone of MoP (0001) surface a k-point grid of 2×2×1 was found to be suitable after convergence tests. Additionally, tests were performed with a denser k-point grid of (3×3×1) for CO adsorption on MoP (0001), the results did not show an appreciable increase in the adsorption energies value. Therefore, a lower k-point grid was considered in this work to save computational expense.

Adsorption energy ($E_{\text{ads}}$) of the surface adsorbed species is defined by $E_{\text{ads}} = E_{\text{species}+\text{slab}} - E_{\text{slab}} - E_{\text{species}}$, where $E_{\text{species}+\text{slab}}$ represents the total energy of the adsorbed species on the modelled surface, $E_{\text{slab}}$ total energy of the clean surface slab and $E_{\text{species}}$ corresponds to the energy of the gas phase molecules. The charge analysis of the adsorbates and the surface was performed by the Bader charge analysis package [173].

Transition state (TS) searches are performed using the same level of theory for those applied to the reactants and products with the complete linear synchronous transit (LST)/quadratic synchronous transit (QST) method [174] as implemented in CASTEP. The convergence
criterion for the transition state search is set to be 0.05 eV/Å root-mean-square forces on each atom. The uniqueness of the (TS) structures was confirmed using vibrational frequency analysis using the finite displacement method [120].

6.3 Results and discussions

6.3.1 Surface properties of MoP (0001)

To develop the MoP (0001) surface first the bulk parameters were optimised. The obtained lattice parameters for the bulk MoP was found to be a=b=3.246 Å, c=3.21Å, which is in good
agreement with experimental (a=b=3.223 Å, c=3.191 Å) [175] and theoretical (a=b=3.252 Å, c=3.216 Å) [176] findings.

The MoP (0001) surface, shown in Figure 6.1, is developed with (3×3) unit cell consisting of five layers with alternating Mo and P atomic layers Figure 6.1 (b), comprising of 45 atoms (27 Mo and 18P), with 9 atoms per layer. In our calculations, we found Mo terminated MoP (0001) surface to be more stable, with surface formation energy of 7.50 J/m² compared to 11.24 J/m² for P-terminated surface. This result is in line with previous calculation where the Mo-termination of (001) (111) and (100) surfaces of the MoP phase were found to be most stable [177]. Further, Bader charge analysis of the MoP (0001) surface indicated a clear charge transfer between Mo → P (Mo 0.43 and P -0.77). Similar electronegativity of P on MoP surfaces was reported previously [69, 178]. The analysis of the total density of states (DOS) in Figure 6.1 (c) shows the metallic characteristic of MoP (0001) surface. Additionally in the PDOS analysis Figure 6.1 (d), the peak around -10 eV corresponds to the P (s) semi-local states with a region near the Fermi level (E_F) is dominated mainly by Mo (d) and P (p) bonding and anti-bonding states.

We have also defined the possible adsorption sites, shown in Figure 6.1 (a), which comprises of the two different hollow sites labelled as H_M and H_P, where H_M is a three-fold hollow site with Mo atoms only and H_P is also a three-fold hollow site with a P atom attached below. The other two sites are a bridge (bri) and Mo top site (top).
6.3.2 Adsorption energetics

6.3.2.1 CO$_2$ adsorption

**Figure 6.2** Front and top view of the stable configurations of the CO$_2$ species on MoP (0001) [a-c] and the most stable configuration on Ni$_2$P (0001) reproduced from Chapter 5 [e]. Cyan spheres represent Mo atoms, Green spheres represent Ni atoms, orange P atoms, grey carbon, red oxygen, and white hydrogen, respectively.

**Table 6.1** Adsorption energies in (eV), bond lengths (Å) and bond angles of CO$_2$ adsorbate on all possible sites on MoP (0001) and for the most stable site on Ni$_2$P (0001) surface. Additionally, the net Bader charges on CO$_2$ adsorbate are provided.

<table>
<thead>
<tr>
<th>Surface</th>
<th>site</th>
<th>$E_{\text{ads}}$ (eV)</th>
<th>Bond lengths (Å)</th>
<th>&lt;OCO angle</th>
<th>Bader charge (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C-O$_1$/C-O$_2$</td>
<td>C-Mo/C-Ni</td>
<td></td>
</tr>
<tr>
<td>MoP (0001)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>bri</td>
<td>-1.89</td>
<td>1.29/1.29</td>
<td>2.26, 2.24</td>
<td>130.0°</td>
</tr>
<tr>
<td></td>
<td>$H_M$</td>
<td>-1.77</td>
<td>1.29/1.35</td>
<td>2.07, 2.42,</td>
<td>129.6°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.29</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HP</td>
<td>-1.84</td>
<td>1.28/1.35</td>
<td>2.03, 2.60</td>
<td>130.3°</td>
</tr>
</tbody>
</table>
Ni$_2$P (0001)

<table>
<thead>
<tr>
<th>MOFA</th>
<th>Site</th>
<th>E (eV)</th>
<th>Bond Length (Å)</th>
<th>Angle (°)</th>
<th>Bader Charge (e$^-$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>Ni ‘3’</td>
<td>-0.05</td>
<td>1.23/1.31</td>
<td>131.1</td>
<td>-0.57</td>
</tr>
<tr>
<td>CO$_2$ <em>gas</em></td>
<td>-</td>
<td>-</td>
<td>1.19/1.19</td>
<td>180.0</td>
<td></td>
</tr>
</tbody>
</table>

To study CO$_2$ activation on both MoP (0001) and Ni$_2$P (0001) surfaces we begin our analysis by first investigating the adsorption characteristics of CO$_2$ on both the surfaces. The stable adsorption configurations of CO$_2$ on MoP (0001) are shown in Figure 6.2 (a-c), whilst Figure 6.2 (d) shows the adsorption configuration on Ni$_2$P (0001) for comparison. Further, the bond length and angles, adsorption energies and Bader charges for CO$_2$ adsorption are described in Table 6.1.

The gas phase CO$_2$ molecule has a linear structure with (O=C=O) bonds at 180°, which, during chemisorption onto a metallic surface, is expected to be changed [67]. This is evident from the CO$_2$ configuration angles obtained from its adsorption on three stable sites (bri, H$_M$ and H$_P$) on the MoP (0001) surface. The <OCO angle of chemisorbed CO$_2$ found on the two hollow sites (H$_M$ and H$_P$) is 129.6° and 130.3° respectively and similarly on the bri site is 130.0°. In comparison, the <OCO angle on the Ni ‘3’ site of Ni$_2$P (0001) is marginally less bent, with a value of 131.1°.

The two C-O bonds of the CO$_2$ molecule namely, C-O$_1$ and C-O$_2$, get elongated during surface adsorption. Here, the C-O$_1$ and C-O$_2$ bonds elongate uniformly from 1.19Å of the gas phase CO$_2$ molecule to 1.29 Å on the bri site of MoP (0001) surface. However, the chemisorbed CO$_2$ configurations on the hollow sites (H$_M$ and H$_P$) of MoP (0001) is different to that on bri, where the elongation of C-O bonds are inequivalent (C-O$_2$ > C-O$_1$). Here, on the H$_M$ site, C-O$_1$ is 1.29Å and 1.35Å on C-O$_2$. Similarly, on the H$_P$ site, C-O$_1$ and C-O$_2$ bond lengths are 1.28Å and 1.35Å respectively. A very similar configuration of chemisorbed CO$_2$ is also obtained on Ni$_2$P (0001) surface, where C-O$_1$ and C-O$_2$ are found to be 1.23Å and 1.31Å respectively.

This bending of CO bonds of the linear CO$_2$ molecule on adsorption with metallic surfaces is attributed to the charge transfer from the surface to CO$_2$ molecule [67]. Therefore, CO$_2$ adsorption greatly depends upon the electronegativity of the metallic surface. Hence we have performed Bader charge [173] analysis for CO$_2$ adsorption on MoP (0001) and Ni$_2$P (0001) surfaces shown in Table 6.1. Our calculations on MoP (0001) show both hollow sites (H$_M$ and H$_P$) to have marginally higher charge transfer with 1.20 e$^-$ and 1.10 e$^-$ compared to the bri site.
0.97 e\textsuperscript{-}. Additionally, the charge transfer to \( \text{CO}_2 \) molecule on all the adsorption sites on MoP (0001) is considerably higher compared to that on Ni\(_2\)P (0001) by 0.57 e\textsuperscript{-}.

From the charge analysis, it is found that the MoP (0001) surface provides greater stability for \( \text{CO}_2 \) adsorbate, which is evidently observed from the calculated adsorption energies (\( E_{\text{ads}} \)) shown in Table 6.1. Interestingly, \( \text{CO}_2 \) adsorption on the bri site on MoP (0001) surface is found to be the most stable adsorption site with \( E_{\text{ads}} \) of -1.89 eV closely followed by the H\(_P\) site with \( E_{\text{ads}} \) of -1.84 eV and on H\(_M\) site \( E_{\text{ads}} \) of -1.77 eV. In comparison, \( \text{CO}_2 \) molecule adsorbs on the Ni\(_2\)P (0001) surface with a low \( E_{\text{ads}} \) of -0.05 eV.

6.3.2.2 Atomic (H) and molecular (H\(_2\)) hydrogen adsorption

![Diagram of hydrogen adsorption configurations](image)

**Figure 6. 3** Front view of the stable configurations of the H and H\(_2\) species on MoP (0001) [a-d] and the most stable configuration on Ni\(_2\)P (0001) reproduced from Chapter 5 [e-f]. Cyan spheres represent Mo atoms, Green spheres represent Ni atoms, orange P atoms, grey carbon, and white hydrogen, respectively.
Table 6.2 Adsorption energies in (eV), bond lengths (Å) and bond angles of H and H₂ adsorbate on all possible sites on MoP (0001) and for the most stable site on Ni₂P (0001) surface. Additionally, net Bader charges of the adsorbates on both considered surfaces are provided.

<table>
<thead>
<tr>
<th>Surface and species</th>
<th>Site</th>
<th>E_{ads} (eV)</th>
<th>Bond lengths (Å)</th>
<th>Bade charge (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H-H</td>
<td>H-Mo/H-Ni</td>
<td></td>
</tr>
<tr>
<td>MoP (0001)</td>
<td>H</td>
<td>-3.24</td>
<td>-</td>
<td>-0.45</td>
</tr>
<tr>
<td></td>
<td>H₉M</td>
<td></td>
<td>2.02, 2.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H₉P</td>
<td>-2.97</td>
<td>-</td>
<td>-0.38</td>
</tr>
<tr>
<td></td>
<td>top</td>
<td>-2.36</td>
<td>-</td>
<td>-0.38</td>
</tr>
<tr>
<td></td>
<td>H₂</td>
<td>-0.73</td>
<td>0.89</td>
<td>-0.12</td>
</tr>
<tr>
<td></td>
<td>top</td>
<td></td>
<td>1.88, 1.89</td>
<td></td>
</tr>
<tr>
<td>Ni₂P (0001)</td>
<td>H</td>
<td>-2.94</td>
<td>-</td>
<td>-0.30</td>
</tr>
<tr>
<td></td>
<td>Ni ‘1’</td>
<td>-0.71</td>
<td>0.91</td>
<td>-0.37</td>
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<tr>
<td></td>
<td>Ni ‘3’</td>
<td></td>
<td>1.59, 1.63</td>
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</tr>
<tr>
<td></td>
<td>H₂₆as</td>
<td></td>
<td>0.74</td>
<td>0</td>
</tr>
</tbody>
</table>

The adsorption configurations of atomic and molecular hydrogen on the possible adsorption sites on MoP (0001) and stable adsorption site is shown in Figure 6.3 (a-d) and on Ni₂P (0001) Figure 6.3 (e-f) and the corresponding adsorption energy details are provided in Table 6.2.

Atomic hydrogen (H) on MoP (0001) strongly binds to the hollow sites H₉M and H₉P, where with an E_{ads} of -3.24 eV on the H₉M site is the strongest. This strong adsorption of H to the H₉M site is in excellent agreement with the previous reported value of -3.23 eV on MoP (001) [179]. Additionally, similar H adsorption energies have been reported for Mo-terminated molybdenum carbide surfaces, β-Mo₂C (0 0 0 1) -3.25 eV [180] and -2.96 eV [181] on α-Mo₂C (0001), which showcases a strong affinity of atomic hydrogen towards Mo containing catalyst surfaces. Further notable H adsorption is also found on the H₉P site with E_{ads} of -2.97 eV and on the top site with -2.36 eV (E_{ads}). Further, H also adsorbs strongly on Ni₂P (0001) with
comparable $E_{\text{ads}}$ of -2.94 eV to that of the $H_p$ site on MoP (0001). Additionally, charge transfer from the metal phosphide surfaces to H is evident with the charges of H on MoP (0001) ranging between (0.45-0.38 e$^-$) and 0.30 e$^-$ on Ni$_2$P (0001).

To study the stability of molecular hydrogen (H$_2$) on MoP (0001), the H$_2$ molecule is adsorbed horizontally to the surface shown in Figure 6.3 (d) and was found to adsorb on the top site with an adsorption energy of -0.73 eV ($E_{\text{ads}}$). Comparatively slightly higher than that found on Ni$_2$P (0001) -0.71 eV. Further dissociative adsorption of H$_2$ is observed on the hollow sites ($H_M$ and $H_P$), which was also found to occur on Ni$_2$P (0001) surface.

### 6.3.2.3 Adsorption of CO

![Figure 6.4](image.png)

**Figure 6.4** Front view of the stable configurations of the CO species on MoP (0001) [a-d] and the most stable configuration on Ni$_2$P (0001) [e]. Cyan spheres represent Mo atoms, Green spheres represent Ni atoms, orange P atoms, grey carbon, red oxygen and white hydrogen, respectively.
Table 6.3 Adsorption energies in (eV), bond lengths (Å) and bond angles of CO adsorbate on all possible sites on MoP (0001) and for the most stable site on Ni2P (0001) surface. Additionally, net Bader charges of the adsorbate on both considered surfaces are provided.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Site</th>
<th>E_{ads} (eV)</th>
<th>Bond Lengths</th>
<th>Bader charge (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C-O</td>
<td>C-Mo/C-Ni'</td>
<td></td>
</tr>
<tr>
<td>MoP (0001)</td>
<td>CO top</td>
<td>-2.22</td>
<td>1.19</td>
<td>2.02</td>
</tr>
<tr>
<td></td>
<td>bri</td>
<td>-2.07</td>
<td>1.23</td>
<td>2.15, 2.15</td>
</tr>
<tr>
<td></td>
<td>Hp</td>
<td>-2.27</td>
<td>1.25</td>
<td>2.21, 2.22, 2.22</td>
</tr>
<tr>
<td></td>
<td>H_M</td>
<td>-2.42</td>
<td>1.25</td>
<td>2.21, 2.22, 2.22</td>
</tr>
<tr>
<td>Ni2P (0001)</td>
<td>CO Ni ‘1’</td>
<td>-1.97</td>
<td>1.20</td>
<td>2.02, 2.02, 2.03</td>
</tr>
<tr>
<td></td>
<td>CO gas phase molecule</td>
<td>-</td>
<td>-</td>
<td>1.15</td>
</tr>
</tbody>
</table>

The stable adsorption geometries of CO on all the possible adsorption sites on MoP (0001) is shown in Figure 6.4 (a-d) and the most stable site on Ni2P (0001) is shown in Figure 6.4 (e). Further their corresponding energetics, bond lengths and charge analysis are given in Table 6.3.

From our calculation on the MoP (0001) surface, CO is found to be stable and strongly bonded to all the possible adsorption sites on the MoP (0001) in Figure 6.4 (a-d). This effective bonding of CO to Mo-terminated MoP (0001) plane has been observed previously by Feng et al.[171] in their Fourier transform infrared spectroscopic and DFT investigation [171]. In our calculations, CO is found to prefer the H_M site the most, with E_{ads} of -2.42 eV. Also the H_p, top and bri sites with E_{ads} -2.27 eV, -2.22 eV and -2.07 eV respectively. The adsorption energy obtained from our calculation of CO on the top site of MoP (0001) matches closely with the value of -2.18 eV reported previously [171]. However, Feng et al. found the top site on MoP (0001) plane to be the most preferable adsorption site for CO [171], and an adsorption energy
difference of (~0.68 eV) is found between the calculated values in this work for CO adsorption on the hollow (H\textsubscript{M} and H\textsubscript{P}) and bri sites compared to theirs. One reason for this higher CO adsorption value of ours may be due to monolayer (ML) coverage of the MoP (0001) plane in our DFT calculations. For instance Feng \textit{et al.} performed their DFT calculations on a (1×1) unit cell of MoP (0001) which corresponds to 1 ML coverage. In comparison, our calculation was performed at a much lower ML coverage of 1/9 ML corresponding to (3×3) MoP (0001) plane. Therefore it may be considered that CO adsorption on MoP (0001) may be coverage dependent. Again, in a recent DFT study by Liu \textit{et al.} \cite{67} on (1×1) Mo-terminated, \textit{\alpha}-Mo\textsubscript{2}C (001) found CO to binding strongly onto similar hollow sites with adsorption energies ranging between (2.42-2.67 eV) \cite{67}.

Also, from Table 6.3, the C-O bond is found to elongate from 1.15 Å in its gas phase configuration to 1.19 Å on the top, 1.23 Å on bri and 1.25 Å on both H\textsubscript{M} and H\textsubscript{P} sites respectively of MoP (0001). Further, the calculated C-Mo bond distances on the surfaces sites on adsorption vary from 2.02 Å on the top, with uniform C-Mo bond distance of 2.15 Å found on bri and similar bond lengths of 2.21-2.22 Å on H\textsubscript{M} and H\textsubscript{P} sites. Additionally, the charge analysis shows the most charge transfer occurring from MoP (0001) hollow sites (0.83-0.85\textit{e}\textsuperscript{-}) with the 0.69 \textit{e}\textsuperscript{-} on the bri site and slightly less on the top site 0.45 \textit{e}\textsuperscript{-}.

In comparison from the value obtained on the most stable site (H\textsubscript{M}) for CO adsorption on MoP (0001), the \textit{E\textsubscript{ads}} of CO on Ni\textsubscript{2}P (0001) is less by -1.97 eV with lower charge transfer by 0.42 \textit{e}\textsuperscript{-}. The later indicates that CO binds strongly to MoP (0001) surface compared to Ni\textsubscript{2}P (0001).
6.3.2.4 Adsorption of carboxyl (COOH)

Figure 6.5 Top and front view of the stable configurations of the COOH species on MoP (0001) [a-b] and the most stable configuration on Ni$_2$P (0001) [c]. Cyan spheres represent Mo atoms, Green spheres represent Ni atoms, orange P atoms, grey carbon, red oxygen and white hydrogen, respectively.

Table 6.4 Adsorption energies in (eV), bond lengths (Å) and bond angles of COOH adsorbate on all possible sites on MoP (0001) and for the most stable site on Ni$_2$P (0001) surface. Additionally, net Bader charges of the adsorbate on both considered surfaces are provided.

<table>
<thead>
<tr>
<th>Surface</th>
<th>site</th>
<th>$E_{ads}$ (eV)</th>
<th>Bond lengths (Å)</th>
<th>Bader charge $(e)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C-O$_1$/C-O$_2$/ O-H</td>
<td>C-Mo/O-Mo/ C-Ni / O-Ni</td>
</tr>
<tr>
<td>MoP (0001)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COOH</td>
<td>$H_M$</td>
<td>-3.63</td>
<td>1.37/1.38/1.01</td>
<td>2.12, 2.5 / 2.23, 2.24</td>
</tr>
<tr>
<td></td>
<td>$H_P$</td>
<td>-3.79</td>
<td>1.36/1.37/1.01</td>
<td>2.12 / 2.22, 2.23</td>
</tr>
<tr>
<td>Ni$_2$P (0001)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COOH</td>
<td>Ni ‘3’</td>
<td>-2.27</td>
<td>1.22/1.44/1.02</td>
<td>1.92 / 2.10</td>
</tr>
</tbody>
</table>
COOH adsorption on the possible adsorption sites on MoP (0001) is shown in Figure 6.5 (a-b) and the most stable site on Ni$_2$P (0001) is shown in Figure 6.5 (c). Further their corresponding energetics, bond lengths and charge analysis are given in Table 6.4.

Notably from Figures 6.4 (a-b) and (c), it may be observed that COOH adsorbs in two different configurations on MoP (0001) and Ni$_2$P (0001) respectively. Here by two different configurations, we refer to cis-COOH and trans-COOH configurations, which are distinguished by their OH group directions. In our calculations we found only the trans-COOH configuration to be stable on MoP (0001), where the H$_M$ and H$_P$ sites were the preferred adsorption sites for COOH. On both H$_M$ and H$_P$ sites trans-COOH interacts via the Mo-C and Mo-O bonds. Further COOH adsorption on both the hollow sites obtains similar adsorption energies of -3.63 eV and -3.79 eV on H$_M$ and H$_P$ respectively. Additionally, the charge acquired by COOH from the surface on adsorbing on the mentioned sites is between (0.80-0.86 e$^-$).

In comparison, the cis-COOH configuration is found to be stable on Ni$_2$P (0001) which similarly interacts with the surface with C-Ni and O-Ni bonds. Compared to MoP (0001) the adsorption of COOH is weaker on Ni$_2$P (0001) by -2.27 eV with a lower net charge of 0.34 e$^-$ on COOH.

### 6.3.2.4 Adsorption of OH and H$_2$O

![Images of adsorption configurations](image-url)

**Figure 6.6** Top and front view of the stable configurations of the OH and H$_2$O species on MoP (0001) [a-d] and the most stable configuration on Ni$_2$P (0001) [e-f]. Cyan spheres represent Mo atoms, Green spheres represent Ni atoms, orange P atoms, grey carbon, red oxygen and white hydrogen, respectively.
Table 6.5 Adsorption energies in (eV), bond lengths (Å) and bond angles of OH and H$_2$O adsorbates on possible sites on MoP (0001) and for the most stable sites on Ni$_2$P (0001) surface. Additionally, net Bader charges of the adsorbates on both considered surfaces are provided.

<table>
<thead>
<tr>
<th>Surface and species</th>
<th>Site</th>
<th>$E_{ads}$ (eV)</th>
<th>Bond length (Å)</th>
<th>Bader charge ($e$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoP (0001)</td>
<td>OH</td>
<td>-4.27</td>
<td>O-H 1.0</td>
<td>O-Mo/O-Ni 2.25, 2.26, 2.26</td>
</tr>
<tr>
<td></td>
<td>HP</td>
<td>-4.43</td>
<td>O-H 1.0</td>
<td>O-Mo/O-Ni 2.26, 2.27</td>
</tr>
<tr>
<td></td>
<td>top</td>
<td>-3.87</td>
<td>O-H 1.0</td>
<td>Ni ‘1’ 1.94</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td>-0.87</td>
<td>O-H 1.02, 1.02</td>
<td>O-Mo/O-Ni 2.28</td>
</tr>
<tr>
<td>Ni$_2$P (0001)</td>
<td>OH</td>
<td>-3.63</td>
<td>O-H 1.0</td>
<td>Ni ‘1’ 2.04</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td>-0.50</td>
<td>O-H 1.01, 1.01</td>
<td>Ni ‘3’ 2.13</td>
</tr>
</tbody>
</table>

Figures 6.6 (a-c) represent the adsorption of OH on H$_M$, H$_P$ and top sites on MoP (0001). Also, H$_2$O adsorption on MoP (0001) shown in Figure 6.6 (d) with Figures 6.6 (e-f) representing the most stable configurations of OH and H$_2$O respectively on Ni$_2$P (0001) surface. Additionally, the details about the adsorption characteristics of OH and H$_2$O are provided in Table 6.5 for both the metal phosphide surfaces.

From Figures 6.6 (a-c) it is observed that OH molecule interacts with the MoP (0001) surface through the O-Mo bond, which is also common on Ni$_2$P (0001) shown in Figure 6.6 (e). On
MoP (0001) OH prefers most the H_M and H_P sites with E_{ads} of -4.27 eV and -4.43 eV respectively. Additionally, H also adsorbs on the bri site with a trans-OH configuration shown in Figure 6.6 (c), but with slightly lower E_{ads} of -3.87 eV. Further, the O-Mo bond distances on H_M and H_P sites are similar ranging between (2.24-2.27 Å) with O-Mo bond distance on the top site is found to be closer by 1.94 Å. Moreover, the charge on OH adsorbate on MoP (0001) sites is found to range between (0.44-0.61 e^-), with major charge transfer occurring at the H_P site. Also, comparable charge gain of OH is observed on Ni_2P (0001) surface by 0.55e^- with the adsorption energy being lower compared to the most stable OH adsorption site on MoP (0001).

H_2O adsorption Figure 6.6 (d) on MoP (0001) occurs only on the top site of MoP (0001) surface. Here again, H_2O molecule interacts with the surface via the O atom with a O-Mo distance of 2.28 Å and equivalent O-H bonds of 1.02 Å each. The adsorption is less exothermic by -0.87 eV and positive net charge (0.002 e) on the H_2O adsorbate. Similar positive charge (0.09 e) of H_2O is observed on Ni_2P (0001) surface with E_{ads} of -0.50 eV.

6.3.2.5 Adsorption of CHO

Figure 6. 7 Top and front view of the stable configurations of the CHO species on MoP (0001) [a-c] and the most stable configuration on Ni_2P (0001) [d]. Cyan spheres represent Mo atoms, Green spheres represents Ni atoms, orange P atoms, grey carbon, red oxygen and white hydrogen, respectively.
Table 6.6 Adsorption energies in (eV), bond lengths (Å) and bond angles of CHO adsorbate on possible sites on MoP (0001) and for the most stable site on Ni$_2$P (0001) surface. Additionally, net Bader charges of the adsorbates on both considered surfaces are provided.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Site</th>
<th>E$_{ads}$ (eV)</th>
<th>Bond Length (Å)</th>
<th>Bader charge (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C-H/C-O</td>
<td>C-Mo/C-Ni$^-$</td>
<td></td>
</tr>
<tr>
<td>MoP (0001)</td>
<td>CHO</td>
<td>H$_M$</td>
<td>1.21 / 1.36</td>
<td>2.16, 2.24, 2.25</td>
</tr>
<tr>
<td></td>
<td>CHO</td>
<td>H$_P$</td>
<td>1.20 / 1.37</td>
<td>2.18, 2.24, 2.27</td>
</tr>
<tr>
<td></td>
<td>CHO</td>
<td>bri</td>
<td>1.26 / 1.29</td>
<td>1.98, 2.26</td>
</tr>
<tr>
<td>Ni$_2$P (0001)</td>
<td>CHO</td>
<td>Ni ‘1’</td>
<td>1.12 / 1.31</td>
<td>2.0, 2.0, 2.63</td>
</tr>
<tr>
<td>CHO gas phase molecule</td>
<td>-</td>
<td>-</td>
<td>1.14 / 1.19</td>
<td>-</td>
</tr>
</tbody>
</table>

The CHO intermediate species which forms due to the hydrogenation of CO is found to absorb on the H$_M$, H$_P$ and bri sites on MoP (0001). Further in all the three sites CHO molecule bonds to the surface with C-Mo, O-Mo and H-Mo bonds Figure 6.7 (a-c). Also on adsorption, the C-H and C-O bonds of CHO molecule increases compared to its gas phase structure shown in Table 6.6. The adsorption energy is found to be similar on all the stable sites with a very minor difference in energies. Additionally the highest E$_{ads}$ of -3.77 eV is obtained for the H$_P$ site, which is lower compared to the reported value of -4.09 eV or -94.32 kcal by Zaman and Smith [69]. Further highest charge on the CHO adsorbate is obtained on the H$_M$ site 1.01 e$^-$ followed by the H$_P$ and bri sites. Additionally, the charge transfer is considerably lower on the Ni$_2$P (0001) surface by 0.47 e$^-$ with E$_{ads}$ of -2.66 eV.
6.3.2.6 Adsorption of atomic carbon (C) and oxygen (O)

Figure 6.8 Front views of the stable configurations of the C and O species on MoP (0001) [a-b, d-f] and the most stable configuration on Ni2P (0001) [c, g]. Cyan spheres represent Mo atoms, Green spheres represent Ni atoms, orange P atoms, grey carbon, red oxygen and white hydrogen, respectively.

Table 6.7 Adsorption energies in (eV), bond lengths (Å) and bond angles of C and O adsorbates on possible sites on MoP (0001) and for the most stable site on Ni2P (0001) surface. Additionally, net Bader charges of the adsorbates on both considered surfaces are provided.

<table>
<thead>
<tr>
<th>Surface and species</th>
<th>Site</th>
<th>E_{ads} (eV)</th>
<th>Bond length (Å)</th>
<th>Bader charge (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoP (0001)</td>
<td>C H_M</td>
<td>-8.08</td>
<td>2.03, 2.03, 2.04</td>
<td>-1.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H_P</td>
<td>-7.98</td>
<td>2.05, 2.05, 2.06</td>
<td>-1.03</td>
</tr>
<tr>
<td></td>
<td>O H_M</td>
<td>-7.18</td>
<td>- 2.09, 2.11, 2.11</td>
<td>-1.03</td>
</tr>
</tbody>
</table>
Atomic carbon (C) is found to be stable on the H$_M$ and H$_P$ site of the MoP (0001), as shown in Figure 6.8 (a-b), with high adsorption energies. The adsorption energy obtained for C on the H$_M$ site is -8.08 eV closely followed by the H$_P$ site by -7.98 eV. This strong carbon binding has also been observed on Mo (110) surface with reported adsorption energy value of -7.65 eV for 1/9 (ML) surface coverage [182]. Additionally in our calculations the charge on the C atom is found to be similarly high on both sites, with 1.08 e$^-$ on H$_M$ and 1.03 e$^-$ on H$_P$ sites respectively.

Atomic oxygen (O) is found to adsorb on the H$_M$, H$_P$ and top sites of the MoP (0001) surface as shown in Figure 6.8 (d-f). Similar to C, high adsorption energies of O is observed on all the stable sites with H$_P$ being the most stable site, with E$_{ads}$ of -7.29 eV, followed by -7.18 eV on H$_M$ and relatively lower on the top site -6.48 eV. The net charge on the O atom varies between (0.80-1.03) from top to H$_M$ site. Atomic oxygen has been found to be very stable on Mo (110) surface facet with adsorption energy reported to be -7.22 eV for 1/9 (ML) surface coverage.

Comparatively the adsorption of C and O on Ni$_2$P (0001) is lower by -6.53 eV and -6.00 eV, however, from the adsorption energy analysis, it is found that C and O are the most stable species on both Ni$_2$P (0001) and MoP (0001) surfaces.
6.3.3 Reaction mechanisms

In the previous section, the adsorption characteristics of the CO$_2$ and CO activation species on both the MoP (0001) and Ni$_2$P (0001) surfaces was discussed. In this section, insights into the activity of the mentioned catalysts is developed using the reaction mechanism scheme shown in Figure 6.9.

An ideal RWGS catalyst should perform both C-O bond scission as well as hydrogen activation and subsequent hydrogenation [165]. Therefore, to understand the mechanistic of TMPs, we have used the mechanism scheme shown in Figure 6.9. The scheme is broadly divided into three categories where we first look into the CO$_2$ activation routes to understand the potentiality of selective CO generation from CO$_2$, using two considered routes (i) direct dissociation of CO$_2$ (CO$_2$* → CO* + O*) and (ii) H assisted CO$_2$ activation ( CO* + H* → COOH*, COOH* → CO* + H*). We have also studied the oxygen (O) removal routes via O and OH hydrogenation forming OH* and H$_2$O* respectively, which is an important measure for oxygen poisoning of the surface during RWGS [170]. Finally, the activation of the CO generated from the RWGS process is analyzed through the direct and hydrogenated routes. Additionally, the
dissociation reaction of H₂, which produces the main reducing agent during the hydrogenation process is also studied on both MoP (0001) and Ni₃P (0001) surfaces. It is to be noted here that calculations of the above-mentioned mechanisms on Ni₃P (0001) are reproduced from Chapter 5 and is shown in Table 6.8.

Table 6. 8 Elementary reactions for the considered reaction scheme on MoP (0001) and Ni₃P (0001) surfaces with an activation energy of the forward (ΔEₐₜ) and reaction energy (ΔHᵣ). Additionally, bond lengths for bond forming or breaking reactions for the transition state geometries on MoP (0001) are given.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Ni₃P (0001)</th>
<th>MoP (0001)</th>
<th>Bond distances at the transition state</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔEₐₜ (ΔHᵣ)</td>
<td>ΔEₐₜ (ΔHᵣ)</td>
<td>Bond</td>
</tr>
<tr>
<td>R1</td>
<td>CO₂* → CO* + O*</td>
<td>0.96 (-0.61)</td>
<td>0.95 (-1.51)</td>
</tr>
<tr>
<td>R2</td>
<td>CO₂* + H* → COOH*</td>
<td>1.19 (-0.11)</td>
<td>1.92 (0.96)</td>
</tr>
<tr>
<td>R3</td>
<td>COOH* → CO* + H*</td>
<td>0.23 (-0.51)</td>
<td>1.02 (-1.30)</td>
</tr>
<tr>
<td>R4</td>
<td>H₂* → H* + H*</td>
<td>0.14 (-0.22)</td>
<td>0.22 (-0.60)</td>
</tr>
<tr>
<td>R5</td>
<td>O* + H* → OH* + *</td>
<td>1.55 (0.89)</td>
<td>1.58 (1.03)</td>
</tr>
<tr>
<td>R6</td>
<td>OH* + H* → H₂O* + *</td>
<td>0.98 (-0.06)</td>
<td>1.64 (1.11)</td>
</tr>
<tr>
<td>R7</td>
<td>CO* + H* → CHO* + *</td>
<td>0.82 (0.27)</td>
<td>0.99 (0.77)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R8</td>
<td>CO* + * → C* + O*</td>
<td>3.44 (2.26)</td>
<td>0.94 (-0.31)</td>
</tr>
</tbody>
</table>
6.3.3.1 CO$_2$ activation routes

![Diagram of CO$_2$ activation reactions on MoP (0001) surface showing (R1) CO$_2^*$ → CO* + O* transition state configurations including (IS) initial state (TS) transition state (FS) final state for CO$_2$ activation reaction. Black dashed line indicates C-O bond breaking distances. Cyan spheres represent Mo atoms, orange P atoms, grey carbon, and red oxygen respectively.](image)

**Figure 6.10** Front views of CO$_2$ activation reactions on MoP (0001) surface showing, (R1) CO$_2^*$ → CO* + O*. Transition state configurations including (IS) initial state (TS) transition state (FS) final state for CO$_2$ activation reaction. Black dashed line indicates C-O bond breaking distances. Cyan spheres represent Mo atoms, orange P atoms, grey carbon, and red oxygen respectively.

In this section, we first determine the direct CO$_2$ dissociation step into CO. From the adsorption energies calculation, we found CO$_2$ to bind strongly on the H$_M$, H$_P$ sites with the bri site having the strongest binding on the MoP (0001) surface. Therefore we have considered the CO$_2$ adsorbed on the bri site as the (IS) configuration, as shown in Figure 6.10 (R1). In the (FS) configuration CO and O are placed initially on opposite H$_P$ sites separated by a distance of 3.28 Å. During the transition state calculation, the C-O bond of the adsorbed CO$_2$ molecule elongates from 1.29 Å found in the (IS) to 1.77 Å in (TS) resulting in the C-O bond scission. The reaction is found to be highly exothermic by -1.51 eV (ΔH$_r$) with energy barrier obtained for the reaction found to be 0.95 eV (ΔE$_{a,f}$).
Figure 6.11  Front views of CO\textsubscript{2} activation reactions by H* on MoP (0001) surface showing, (R2) CO\textsubscript{2}* + H*→COOH* and (R3) COOH* →CO* + H*. Transition state configurations including (IS) initial state (TS) transition state (FS) final state for CO\textsubscript{2} activation reaction. Black dashed line indicates C-O and O-H bond breaking or forming distances. Cyan spheres represent Mo atoms, orange P atoms, grey carbon, and red oxygen, white hydrogen, respectively.* denotes surface adsorbate.

Figure 6.11(R1-R2), represents the CO\textsubscript{2} hydrogenation routes (R2-R3) where on hydrogenation CO\textsubscript{2} first forms the carboxyl (COOH) intermediate and thereafter it subsequently dissociates to form CO and OH species on the MoP (0001) surface.

Figure 6.11 (R2), the (IS) of CO\textsubscript{2} with co-adsorbed H occupying the bri and opposite H\textsubscript{M} sites with the O-H bond separated by a distance of 2.70 Å. Which in the (TS) geometry decreases to 1.31 Å to form the O-H bond of trans- COOH configuration shown in the (FS) with an O-H bond of 1.01 Å. The activation energy barrier for the reaction is high by 1.92 eV (\(\Delta E_{a,f}\)) with reaction energy being endothermic by 0.96 eV (\(\Delta H_{r}\)).

The dissociation of COOH intermediate on MoP (0001) occurs with the cleavage of the C-O bond of COOH. In the (IS) geometry, COOH is considered to be on the H\textsubscript{P} site with C-O bond of 1.37 Å which in the TS configuration stretches to 1.73 Å and eventually forms CO and OH, as shown in Figure 6.11 (R3). The reaction is found to be highly exothermic by -1.30 (\(\Delta H_{r}\)) with the forward activation of 1.02 eV (\(\Delta E_{a,f}\))
Figure 6.12 Potential energy surfaces (PES) for the comparison of (a) R1 direct CO$_2$ dissociation (b) R2-R3 H assisted CO$_2$ activation mechanisms between MoP (0001) and Ni$_2$P (0001) surfaces.

Figure 6.12 (a) represents the potential energy surfaces (PES) for direct CO$_2$ activation (R1) on MoP (0001) and Ni$_2$P (0001). In the PES Figure 6.12(a), CO$_2$ adsorption from the gas phase onto the respective catalyst surfaces are considered to be the initial state for the CO$_2$ activation. Here CO$_2$ adsorbs strongly on the MoP (0001) surface compared to Ni$_2$P (0001), however, the corresponding CO$_2$ dissociation energy barrier is comparable with 0.95 eV on MoP (0001) and 0.96 eV on Ni$_2$P (0001). This may be due to the strong bonding of the CO$_2$ molecule onto the
MoP (0001) surface, not allowing for easier C-O bond cleavage with lower energy barriers. Similar theoretical observations of CO$_2$ activation have been reported for different surface terminations of $\alpha$-Mo$_2$C [67]. Further, from the PES, it is also evident that both the surfaces are active towards breaking of the C-O bond for selective production of CO with MoP (0001) being slightly favourable compared to Ni$_2$P (0001). From the PES in Figure 6.12 (b), it may be seen that CO$_2$ activation via CO$_2$ hydrogenation is unfavourable on MoP (0001) with high energy barrier for the formation of the COOH$^+$ intermediate. Comparatively both COOH$^+$ formation and subsequent decomposition energy barrier is much lower on Ni$_2$P (0001), however, the direct CO$_2$ dissociation route is preferred on Ni$_2$P (0001) for selective CO production. Additionally, the direct CO$_2$ dissociation route has been found to be favourable on Mo-terminated $\alpha$-Mo$_2$C (0001) [67], on monometallic Ni (111) surfaces [36] with CO$_2$ hydrogenation route has been found to be favourable on plane surfaces of Pd and Pt [36].

6.3.3.2 H$_2$ dissociation

![Diagrams showing H$_2$ dissociation on MoP (0001) surface.](image)

**Figure 6.13** Front views of H$_2$ dissociation reaction on MoP (0001) surface showing, (R4) H$_2^*$ $\rightarrow$H$^*$ +H *. Transition state configurations including (IS) initial state (TS) transition state (FS) final state for H$_2$ dissociation reaction. Black dashed line indicates H-H bond breaking distances. Cyan spheres represent Mo atoms, orange P atoms and white H atoms respectively.

In our calculations, we found hydrogen to either adsorb in the molecular form (H$_2$) onto the top site or dissociate onto the hollow (H$_M$ and H$_P$) sites of the MoP (0001) surface. Therefore to calculate the activation energy barrier for H$_2$ dissociation the molecular hydrogen configuration on the top site was considered to be the (IS) for the reaction. Here in the (IS) H-H bond distance was calculated to be 0.89 Å which in the (TS) geometry increased to 1.45 Å before occupying
the adjacent H_p sites in the (FS) configuration. The reaction occurs easily on the MoP (0001) surface with a low forward activation energy barrier of 0.22 eV (ΔE_a,f) with good exothermicity by -0.61 eV (ΔH_r).

**Figure 6.14** Potential energy surfaces (PES) for the comparison of (R4) H_2 dissociation between MoP (0001) and Ni_2P (0001) surfaces.

From the PES shown in Figure 6.14, it is observed that H_2 activation is an exothermic reaction with very low energy barriers on both the metal phosphide surfaces.

### 6.3.3.3 Oxygen (O) removal routes

During RWGS reaction the atomic oxygen (O) is generated on the MoP (0001) surface from initial C-O bond cleavage (R1), where in the reaction, atomic O forms on the catalyst surface in conjunction with CO intermediate. The removal of this atomic O from the catalyst surface is important to restrict catalyst surface poising by O [170]. Therefore we have investigated the stepwise hydrogenation of O by H to form either OH or H_2O.

Figure 6.15 shows O removal reactions on MoP (0001) surface. From Figure 6.15 (R5), in the (IS) configuration of O and H are occupying opposite H_p and H_m sites respectively with O-H.
distance of 2.26 Å. During the (TS) geometry the O-H decreases to 1.22 Å which in the (FS) is found to be 1.0 Å representing the OH adsorbate. The energy barrier obtained for the reaction is high at 1.58 eV (ΔE_{a,f}) and even thermodynamically the reaction is endothermic at 1.03 eV (ΔH_r).

![Figure 6.15 Front views of O removal reactions on MoP (0001) surface showing, (R5) O* + H* → OH* and (R6) H* + OH* → H_2O*. Transition state configurations including (IS) initial state (TS) transition state (FS) final state for CO_2 activation reaction. Black dashed line indicates O-H bond breaking or forming distances. Cyan spheres represent Mo atoms, orange P atoms, red oxygen and white hydrogen, respectively.* denotes surface adsorbate.](image)

From Figure 6.15 (R6), the considered route for H_2O on MoP (0001) occurs from the combination of OH and H (IS) occupying the H_M and H_P sites respectively separated by a 3.67 Å (O-H) distance. Both OH and H moves to the top of Mo atom during the (TS) configuration with (O-H) distance decreasing 1.42 Å, which eventually forms H_2O in the (FS), with an O-H bond distance of 1.02 Å. Again the reaction is found to be endothermic by 1.11 eV (ΔH_r) with a high energy barrier 1.64 eV (ΔE_{a,f}).

From the above reactions, it is evident that oxygen removal from the MoP (0001) is both kinetically and thermodynamically difficult. One reason may be due to the high binding energy of oxygen with the MoP (0001). This has also been found to occur on transition metal carbide
surfaces TiC (111) and Mo₂C (0001) in a previous study [170]. Further, we have compared the oxygen removal reactions of MoP (0001) with Ni₂P (0001) shown in Figure 6.16(a-b).

![Potential energy surfaces (PES) for the comparison of (a) R5 direct OH formation (b) R6 H₂O formation mechanisms between MoP (0001) and Ni₂P (0001) surfaces.](image)

**Figure 6.16** Potential energy surfaces (PES) for the comparison of (a) R5 direct OH formation (b) R6 H₂O formation mechanisms between MoP (0001) and Ni₂P (0001) surfaces.

From Figure 6.16 (a), (R5) is similarly endothermic and accounts for high energy barriers, with the barrier on the Ni₂P (0001) being marginally lower (~0.3 eV). Interestingly H₂O (R6) formation is favoured both kinetically and thermodynamically on Ni₂P (0001) compared to MoP (0001) with the energy barrier difference being (~0.66 eV).

Overall from the above comparison, it may be considered that O removal from MoP (0001) may be rate determining whereas on Ni₂P (0001) it may occur through the hydrogenation of OH to H₂O formation route.
6.3.3.4 CO activation routes

**Figure 6.17** Front views of CO activation reactions on MoP (0001) surface showing, (R7) CO\(^*\) →C\(^*\) + O\(^*\) direct dissociation and (R8) CO\(^*\) + H\(^*\) →CHO\(^*\). Transition state configurations including (IS) initial state (TS) transition state (FS) final state for CO activation reaction. Black dashed line indicates C-O and C-H bond breaking or forming distances. Cyan spheres represent Mo atoms, orange P atoms, red oxygen, grey carbon and white hydrogen, respectively.* denotes surface adsorbate.

From RWGS, CO formation on the MoP (0001) surface occurs through the direct CO\(_2\) activation route shown in (R1). Further, the activation of C-O bond, either directly via CO dissociation or H assisted hydrogenation, is a point of great interest as it is a key step in the initiation of Fisher Tropsch synthesis [165]. Therefore we have investigated the CO activation pathways on MoP (0001) and have used PES to discuss the behaviour of CO activation on the considered TMPs.

Figure 6.17 (R7) shows the direct C-O bond cleavage reaction for CO dissociation on MoP (0001). The stable configuration of CO adsorbed on the H\(_M\) site is considered to be the (IS), where the C-O bond is found to be 1.25 Å. During the (TS) the oxygen atom of CO moves to the opposite H\(_P\) site, with the C-O bond stretching to 1.73 Å. The reaction is found to be exothermic with ΔH\(_r\) = -0.31 eV and the activation energy barrier is found to be ΔE\(_{a,f}\) = 0.94 eV. Tian *et al.* [183] in their theoretical study, found the energy barriers for CO dissociation on
Mo (100) to be independent of surface coverage. Additionally, they reported a low energy barrier of 0.58 eV at 1/9 ML coverage for CO dissociation [183]. Further low energy barriers of 0.89 eV for CO dissociation on β-Mo2C (0001) was also reported previously [184].

Figure 6.17 (R8) showcases CO activation through hydrogenation, forming the CHO* intermediate. In the (IS) geometry co-adsorbed species of CO and H is occupying H_M sites with C-H distance of 2.97 Å which during the (TS) decreases as the H atom moves to the top site forming C-H bond distance of 1.51 Å. The reaction is found to be endothermic by 0.77 eV (ΔH_r) with an energy barrier for the reaction is slightly higher 0.99 eV (ΔE_a,f) compared a direct CO dissociation reaction step. Further, the energy barrier obtained is found to be considerably lower compared to the value of 1.79 eV reported by Zaman and Smith [69], where they found the CO hydrogenation step to be rate limiting in synthesis gas conversion to methane or methanol [69]. This difference may be due to different models used to perform the calculation; for instance, Zaman and Smith performed their calculations on Mo6P3 cluster compared to the plane surface MoP (0001) used in the present case.
Figure 6.18 Potential energy surfaces (PES) for the comparison of (a) R7 direct CO activation (b) R8 CO hydrogenation mechanisms between MoP (0001) and Ni$_2$P (0001) surfaces.

Figure 6.18 (a-b) shows the PES for CO activation reactions (R7-R8) on MoP (0001) and Ni$_2$P (0001) surfaces. Interestingly in Figure 6.18 (a) it may be observed, that direct CO dissociation is not possible on Ni$_2$P (0001), as the energy barrier (3.44 eV) is much higher than the adsorption energy of CO (-1.97 eV) which showcases that CO will prefer to desorb from Ni$_2$P (0001) surface than dissociate. Comparatively direct CO dissociation is preferred on the MoP (0001) surface. Therefore on MoP (0001) the intermediates C* formed from direct activation may be further hydrogenated to form carbene (CH$_2$*) leading to further polymerization for higher chained hydrocarbons [185]. However further analysis may be required to ascertain the hypothesis which is not the main focus here. Further Figure 6.18 (b) shows CO hydrogenation to formyl (CHO) intermediate to be favourable on Ni$_2$P (0001) surface compared to MoP (0001).

It may be observed from the above analysis that overall CO activation is more favourable on both MoP (0001) and Ni$_2$P (0001) surfaces with different activation routes (direct or indirect) and may be considered to be good candidates for CO activation process.
6.4 Conclusions

Systematic DFT study was performed to analyse two TMPs MoP (0001) and Ni2P (0001) for crucial CO₂ and CO activation reactions with implications in the relevant process such as the RWGS and the Fischer-Tropsch synthesis. The results obtained from this study showcase both the TMPs may be considered good candidates to direct CO₂ dissociation to selective CO production. However, oxygen removal may be an issue on the MoP (0001) surface with both the O and OH hydrogenation paths showcasing high activation energy barriers. In the case of Ni₂P (0001) O removal by the OH hydrogenation is a viable process. Additionally, both CO activation routes were found to have comparable energy barriers with direct CO dissociation on Ni₂P (0001) being unfavourable with only CO hydrogenation to CHO possible route for CO activation. Overall both catalyst surfaces are found to be good candidates towards CO₂ and CO activation reactions.
Chapter 7: Conclusions and future research outlook

7.1 Conclusions

Predicting catalytic trends using computational methods, leading to the development of advanced noble-metal free catalysts for gas phase CO₂ utilisation reactions is the main cornerstone of this thesis work. Essentially one of the major focus of this work has been devoted towards increasing the stability of nickel catalysts towards carbon formation in DRM, by exploring bimetallic (NiSn) and interstitial (Ni₂P) catalyst options. Also, the final part of the thesis concentrates on DFT analysis of CO₂ interaction and hydrogenation reactions on two metal phosphides (Ni₂P, MoP) surfaces. The theoretical findings achieved from this thesis work will guide catalyst design in DRM and CO₂ hydrogenation chemical process and may be used to corroborate with experimental investigations. The main findings are summarised below;

In Chapter 3, the investigation was started with DFT and microkinetic analysis of DRM on Ni (111) close-packed surface. The adsorption studies of the DRM species on Ni (111) highlighted the stability of the DRM gas phase reactants (CH₄ and CO₂), which were only able to physisorb with very low energies. Additionally, chemisorption of CO₂ gas phase linear molecule on Ni (111) will only be achieved via a bent structure. Further, from the adsorption studies, it became evident that atomic carbon has strong binding with the Ni (111) facet of nickel crystal, showcasing high carbon stability. This was further confirmed with carbon diffusion between stable sites on Ni (111) occurring relatively easily with low activation energy barriers compared to that witnessed on noble metals such as Pt. Information gained from the free energy analysis and microkinetic studies showed, CH₄ activation on Ni (111) requires a higher temperature to occurs compared to CO₂ activation and, mainly this reaction determines the DRM reaction rate. An important insight towards the CO formation route was observed, where CH-O route being kinetically favourable compared to the C-O route for CO formation on Ni (111) surface. Also, microkinetic analysis also revealed the coverage of carbon to be higher than oxygen, indicating carbon nucleation to occur during the reaction. Reflecting on the analysis performed in this chapter, one key insight that was gained is that the main source of carbon formation in DRM comes from the CH* cracking step (CH* + *→C* + H*) in sequential CH₄ dissociation. Therefore if the occurrence of these steps becomes thermodynamically and kinetically difficult then the tendency of carbon formation on Ni (111) may be deterred. Building onto this
observation (tin) Sn to was used to modify the Ni (111) surface and its effect was studied in Chapter 4.

In Chapter 4, DFT analysis ascertained the thermodynamic stability of Sn on the outermost layer of the Ni (111) surface. This insight led to the development of two Ni/Sn surfaces, one with a high Sn concentration (2/9 ML) and the other with low concentration (1/9 ML) corresponding to NiSn$_2$ and NiSn$_1$ respectively. The positive effect of Sn addition was first observed in the potential energy surface (PES) analysis of CH$_4$ sequential dissociation in the CH* cracking where the activation energy barrier for this step had the following sequence NiSn$_2$ $>$ NiSn$_1$ $>$ Ni (111). This shows the difficulty of atomic carbon formation with higher Sn concentration of the Ni (111) surface at least from CH$_4$ dissociation. This positive effect of Sn is mainly attributed to the “ensemble effect”, which causes the reduction in active sites for atomic carbon to form. However, it was also found Sn concentration plays a critical role in determining the CH$_4$ activation step (CH$_4^*$ + $*$→CH$_3^*$ + H*) where lower energy barriers are expected to achieve a good CH$_4$ activation. This activation step had the following sequence of energy barrier Ni (111) $<$ NiSn$_1$ $<$ NiSn$_2$. From this analysis, it became clear that a low concentration of Sn (NiSn$_1$) leads to a good compromise between activity and carbon resistance. Continuing the theoretical calculations for CO$_2$ activation, CO and H$_2$ formation reactions on NiSn$_1$ surface, the promoting effect of Sn on alloying with Ni was also observed. CO* formation from both C* and CH* oxidation reactions were marginally favourable on NiSn$_1$ compared to Ni (111) surface. From the insights gained in the theoretical calculations one key point that should be stressed for Ni-Sn catalyst design for DRM, is that optimisation of Sn loading is a key factor since relatively high amounts of Sn will impact negatively towards the catalytic activity. Following this work, the main focus was given towards studying unexplored alternative Ni-based catalyst materials for DRM, where the potentiality of an interstitial catalyst compound nickel phosphide (Ni$_2$P) was explored. This catalyst has previously shown to have performed very well in the hydro-treating process. However, due to the lack of experimental findings of DRM reaction on Ni$_2$P, the focus was given in understanding the catalytic activity of Ni$_2$P in DRM using DFT based microkinetic analysis. This work was carried out in Chapter 5.

In Chapter 5, First the electronic analysis of the Ni$_3$P$_2$ – terminated plane of Ni$_2$P (0001) surface was performed, where the surface atoms indicate a small charge transfer occurring from Ni → P, making P slightly electro- negative. This is popularly known as “ligand effect”. Eight possible adsorption sites on the Ni$_3$P$_2$ surface plane comprising mainly of Ni and Ni-P hybrid
sites was recognized. Interesting findings were revealed from the adsorption studies of the DRM species on Ni$_2$P (0001). Notably, adsorption of CH$_4$ and CO$_2$ gas phase molecules showed similar features to that on Ni (111) surface (Chapter 3). Further, the majority of the DRM species preferred to adsorb on the nickel hollow site with the Ni-P hybrid sites being additional adsorption sites for (O*, OH*, H*) with C* preferring only nickel hollow sites. The free energy analysis of the reaction mechanisms indicates that CO$_2$ activation will occur before CH$_4$, via a direct dissociation route. Further CO formation occurs through the CH-O oxidation route. Interestingly, free energy analysis also indicated reverse water gas shift (RWGS) to be possible on the surface. This was evident in our microkinetic analysis where, the H$_2$/CO ratio was found to be less at lower temperatures, indicating CO production to be higher at a lower temperature (below 1000 K), typical conditions for RWGS to occur. Further H$_2$ gas production mainly occurs (above 1000 K), which indicates optimal reactions temperatures for DRM to produce syngas on Ni$_2$P (0001) will be high. The most interesting aspect on Ni$_2$P (0001) was found to be higher oxygen coverage compared to carbon, quite an opposite trend to what was observed on Ni (111) surface in Chapter 3. This observation was supported by the calculations of the activation energy barriers for C* diffusion between two stable sites on Ni$_2$P (0001) surface are nearly four times more compared to that found on Ni (111). This indicates that mobility of carbon atoms which is important for carbon nucleation is restricted to a greater extent on Ni$_2$P (0001). From the systematic theoretical observations it was hypothesised, that Ni$_2$P (0001) surface acts as an oxygen sink, due to its stability on most of the (Ni and Ni-P) sites. This drives the point that at high DRM temperatures (above 1000 K) carbon will be prone to oxidation rather than nucleation.

Following the observation from the interaction of CO$_2$ with Ni$_2$P (0001) surface, where RWGS was found to play a major role in CO generation, therefore focus was given to study the interaction of both CO$_2$ and CO on two metal phosphide surfaces Ni$_2$P (0001) and MoP (0001) in Chapter 6. Here first a detailed DFT analysis of the MoP (0001) surface was performed, where the Mo-terminated MoP (0001) was found to be more stable than P terminated one. Further, similar to Ni$_2$P (0001) charge transfer between (Mo $\rightarrow$ P) was observed here. One notable observation from the adsorption energy calculations of the species (CO$_2$, CO, H$_2$O, H$_2$, H, OH, COOH, CHO, O and C), were found to bind to MoP (0001) surface, with higher adsorption energies and charge transfer compared to that found on Ni$_2$P (0001). Strong adsorption was observed on MoP (0001) with high chemisorption energy, while on Ni$_2$P (0001) it encounters physisorption. This is primarily due to the higher charge transfer occurring from
the surface to the CO₂ moiety. Moving onto the reaction mechanisms was studied to analyse the trends on these catalyst surfaces by primarily using three groups of reactions RWGS, oxygen removal and CO activation. Some interesting findings came out from the PES analysis of the considered reactions. The positive effects of these surfaces were found in the direct dissociation of CO₂ to CO, occurring with activation similar energy barriers. This shows the potentiality of these catalysts for application in the RWGS process. However CO₂ hydrogenation to CO, is not favourable on MoP (0001), with reasonable favourability on Ni₂P (0001) surface. This shows that Ni₂P (0001) may be a more favoured catalyst in RWGS, as this step apart from generating CO* also is a reaction for OH* formation, necessary towards oxygen removal from the catalyst surfaces. Due to the strong binding of oxygen found on both the metal phosphides its removal from the surface as H₂O is important during the RWGS process to restrict oxygen poisoning. The calculated reactions for this mechanism showed O removal may be considered to be an issue on MoP (0001) while water formation is thermodynamically favourable on Ni₂P (0001). Further activation of CO on MoP (0001) will occur via direct dissociation, with the hydrogenation path for formation of CHO intermediate also favourable. CO activation on Ni₂P (0001) may only happen via the CO hydrogenation route. Finally, H₂ gas activation on both the metal phosphides is very favourable showcasing the hydro-treating characteristics of these catalysts.

7.2 Novel findings

In this section the novel findings obtained from the theoretical investigations performed in the present thesis work is summarized below;

- The CO production route on plane Ni (111) surface has been shown to occur either from CH-O or C-O pathways. In the present study using DFT based MKM study, it was ascertained that the CH-O pathway is more dominant compared to the C-O pathway for CO production on Ni (111) surface.

- DFT and MKM study showcased that Sn forms stable surface alloys with Ni which restricts carbon formation on the catalyst surface thereby increasing the stability of the Ni-Sn catalyst in DRM without sacrificing the activity of the catalyst. However, DFT
calculations also showed that the concentration of Sn on the Ni surface is very important, with higher Sn concentration may severely deter catalytic activity.

- Combined DFT and MKM study ascertained the potentiality of Ni$_2$P (0001) catalyst, especially the Ni$_3$P$_2$ termination to be active towards DRM. Among the notable findings, adsorption energy calculations indicated the stability of the DRM species on Ni$_2$P (0001) surface. Free energy analysis calculations showcased CO formation to occur via CH-O route with microkinetic calculations indicating CO formation to be higher below 1000 K with H$_2$ gas production requiring a higher temperature above 1000 K. Further MKM study indicates higher oxygen coverage on the Ni$_2$P surface compared to carbon. Also, the ‘ensemble effect’, a characteristic feature of the Ni$_2$P (0001) surface, the carbon diffusion on the surface is greatly restricted, thereby increasing the stability of the Ni$_2$P (0001) for applications in DRM reaction conditions.

- In the study of TMP’s potentiality for RWGS, most of the intermediate species adsorbed strongly on the MoP (0001) surface with greater charge transfer from the surface compared to Ni$_2$P (0001). Further, DFT calculations ascertained the active nature of the considered TMP’s towards RWGS reaction. Also, the calculations indicated oxygen removal from the MoP (0001) surface to be a key issue compared to Ni$_2$P (0001) surface during RWGS reaction conditions. Another key finding was the favourability of the MoP (0001) surface towards CO activation reactions compared to Ni$_2$P (0001).

### 7.3 Future research outlook

In this section, the future research possibilities based on the work conducted in this thesis is summarised below.

- From Chapters (3-4), some interesting findings was achieved from DFT and MKM investigations which established the positive interaction of Sn with Ni in a surface alloy formulation especially towards carbon stability. This work can be further expanded into a multi-facet theoretical study, for example, consideration of DRM reaction
mechanisms and adsorbate interactions on Sn alloyed Ni (100), (110) and (221) facets. As in a real heterogeneous catalyst scenario, these facets contribute towards determining overall catalytic activity and stability. Further the study of structure sensitive effects of Ni-Sn alloy catalyst surfaces in DRM may provide more detailed insights towards the carbon formation mechanism on the closed and open Ni alloyed facets. Therefore it will be worthwhile to investigate these facets with Sn addition. Further microkinetic calculations of a multi-facet Ni-Sn alloyed system may corroborate better with experimental observations.

- From chapter 5, we have explored only the Ni_2P_2 – plane of Ni_2P (0001) surface with key insights obtained in regards to DRM reaction. However the stability of the alternate plane of Ni_2P (0001), Ni_3P, which has comparable thermodynamic stability with Ni_2P_2. Therefore this termination can also be used to investigate at least the adsorption characteristics of the DRM species and form scaling relations [186] between the two planes, to identify suitable descriptors for DRM reaction mechanism on Ni_2P (0001) surface. Further calculation of the DRM reaction mechanism may be extended to a P-covered Ni_3P_2 plane, which has been recently reported in theoretical studies [187]. These studies will allow to again greater understanding about the Ni_2P surface behaviour under DRM reaction conditions.

- Finally from Chapter 6, MoP (0001) surface comprises of alternating Mo and P layers, where the DFT investigations were performed for CO_2 and CO interaction with Mo terminated MoP (0001) surface. The data obtained from the DFT analysis may be further used to perform microkinetic calculations to ascertain the kinetics of RWGS reaction on the MoP (0001) surface. Also further DFT calculations may also be performed on the P terminated MoP (0001) termination to draw a comparison between the two MoP terminations in RWGS scenario.
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Appendix A: Vibrational frequencies of intermediates of DRM reaction on Ni (111), NiSn$_1$ and NiSn$_2$

A1. Vibrational frequencies of intermediates and transition states on Ni (111)

<table>
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<th>Vibrational modes (cm$^{-1}$)</th>
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<td>C</td>
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</tr>
<tr>
<td>O</td>
<td>386, 387, 488</td>
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<tr>
<td>H</td>
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<tr>
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<tr>
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</tr>
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</tr>
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</tr>
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<td>CH-H</td>
<td>171, 411, 417, 601, 645, 902, 1935, 3072, (-679.77)</td>
</tr>
<tr>
<td>C-H</td>
<td>203, 513, 530, 550, 1842, (-725.24)</td>
</tr>
<tr>
<td>H-H</td>
<td>118, 246, 1820, 1925, (-995)</td>
</tr>
<tr>
<td>CO-O</td>
<td>117, 247, 568, 1917, (-395.74)</td>
</tr>
<tr>
<td>C-O</td>
<td>269, 364, 528, 565, (-432.23)</td>
</tr>
<tr>
<td>CH-O</td>
<td>179, 357, 402, 505, 568, 779, 3278, (-450.53)</td>
</tr>
<tr>
<td>Species</td>
<td>Vibrational modes (cm(^{-1}))</td>
</tr>
<tr>
<td>---------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>C</td>
<td>503, 544, 582</td>
</tr>
<tr>
<td>O</td>
<td>355, 404, 487</td>
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<tr>
<td>H</td>
<td>826, 967, 1143</td>
</tr>
<tr>
<td>H(_2)</td>
<td>173, 211, 844, 1714, 2218</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>38, 44 , 89, 117, 1248, 1268, 1273, 1478, 1481, 2969, 3074, 3084, 3105</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>188, 251, 353, 434, 484, 498, 1165, 1281, 1295, 2776, 2831, 2868</td>
</tr>
<tr>
<td>CH(_2)</td>
<td>274, 338, 359, 518, 649, 695, 1469, 2276, 3037</td>
</tr>
<tr>
<td>CH</td>
<td>385, 445, 614, 654, 703, 3043</td>
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<tr>
<td>CO(_2)</td>
<td>44, 90, 127, 184, 277, 485, 639, 1135, 1756</td>
</tr>
<tr>
<td>CO</td>
<td>133, 160, 260, 313, 367, 1770</td>
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<tr>
<td>CHO</td>
<td>153, 159, 254, 316, 469, 625, 1163, 1314, 2927</td>
</tr>
<tr>
<td>CH(_3)-H</td>
<td>67, 161, 288, 302, 410, 786, 843, 1211, 1373, 1387, 1860, 2768, 2.870, 3006, (-937.11)</td>
</tr>
<tr>
<td>CH(_2)-H</td>
<td>120, 193, 291, 427, 508, 604, 765, 1301., 1757, 2416, 2999, (-299.92)</td>
</tr>
<tr>
<td>CH-H</td>
<td>312, 381, 453, 586, 709, 937, 2064, 2882, (-880.92)</td>
</tr>
<tr>
<td>C-H</td>
<td>413, 477, 520, 569, 1748, (-753.20)</td>
</tr>
<tr>
<td>H-H</td>
<td>179, 266, 1921, 2082, (-981.12)</td>
</tr>
<tr>
<td>CO-O</td>
<td>58, 178, 226, 274, 401, 524, 1725, (-557.677)</td>
</tr>
</tbody>
</table>

#The imaginary frequency in negative, confirming a transition state is denoted in bold

**A2. Vibrational frequencies of intermediates and transition states on NiSn\(_1\)**
### A3. Vibrational frequencies of intermediates and transition states on NiSn₂

<table>
<thead>
<tr>
<th>Species</th>
<th>Vibrational modes (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>533, 577</td>
</tr>
<tr>
<td>H</td>
<td>736, 1120, 1157</td>
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<tr>
<td>CH₄</td>
<td>1256, 1274, 1282, 1489, 1491, 2980, 3089, 3098, 3110</td>
</tr>
<tr>
<td>CH₃</td>
<td>613, 1100, 1319, 1354, 2889, 2941, 3062</td>
</tr>
<tr>
<td>CH₂</td>
<td>613, 748, 1412, 2344, 3039</td>
</tr>
<tr>
<td>CH</td>
<td>608, 699, 736, 3051</td>
</tr>
<tr>
<td>CH₃-H</td>
<td>509, 702, 1343, 1370, 1617, 2926, 3106, 3113, (-480.00)</td>
</tr>
<tr>
<td>CH₂-H</td>
<td>532, 590, 792, 1352, 1766, 2583, 3084, (-618.05)</td>
</tr>
<tr>
<td>CH-H</td>
<td>603, 615, 733, 910, 1572, 3073, (-849.52)</td>
</tr>
<tr>
<td>C-H</td>
<td>561, 572, 1751, (-642.40)</td>
</tr>
</tbody>
</table>

# The imaginary frequency, in negative, confirming a transition state is denoted in bold
Appendix B :  Vibrational frequencies of intermediates od DRM reaction on Ni$_2$P (0001)

B1. Vibrational frequencies of intermediates and transition states on Ni$_2$P (0001)

<table>
<thead>
<tr>
<th>Species</th>
<th>Vibrational modes (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>603, 620, 1160</td>
</tr>
<tr>
<td>H-H</td>
<td>384, 581, 1439, 1858, (-516.03)</td>
</tr>
<tr>
<td>H$_2$</td>
<td>202, 290, 312, 964, 1586, 2448</td>
</tr>
<tr>
<td>C</td>
<td>491, 495, 576</td>
</tr>
<tr>
<td>C-H</td>
<td>283, 444, 518, 539, 2000, (-909.96)</td>
</tr>
<tr>
<td>C-O</td>
<td>263, 310, 439, 469, 554, (-538.54)</td>
</tr>
<tr>
<td>C-OH</td>
<td>296, 354, 400, 505, 531, 788, 3279, (-300.90)</td>
</tr>
<tr>
<td>CH</td>
<td>374, 378, 603, 676, 678, 2998</td>
</tr>
<tr>
<td>CH-H</td>
<td>308, 393, 555, 615, 657, 949, 1878, 2946, (-825.51)</td>
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<tr>
<td>CH-O</td>
<td>247, 265, 401, 459, 555, 658, 1013, 3037, (-603.84)</td>
</tr>
<tr>
<td>CH$_2$</td>
<td>257, 288, 392, 508, 579, 682, 1393, 2447, 2998</td>
</tr>
<tr>
<td>CH$_2$-H</td>
<td>101, 268, 360, 396, 532, 663, 830, 1316, 1905, 2796, 3067, (-624.37)</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>209, 213, 331, 350, 416, 416, 1125, 1284, 1287, 2825, 2886, 2888</td>
</tr>
<tr>
<td>Chemical</td>
<td>Frequencies (cm⁻¹)</td>
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<tr>
<td>----------</td>
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<tr>
<td>CH₄</td>
<td>70, 162, 173, 196, 1250, 1264, 1268, 1472, 1474, 2927, 3043, 3048, 3054</td>
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<tr>
<td>CHO</td>
<td>157, 201, 229, 326, 516, 695, 1175, 1316, 2887</td>
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<tr>
<td>CO</td>
<td>124, 128, 244, 251, 331, 1688</td>
</tr>
<tr>
<td>CO-H</td>
<td>130, 163, 271, 316, 405, 524, 1172, 1497, (-1620.72)</td>
</tr>
<tr>
<td>CO-O</td>
<td>14, 82, 261, 295, 347, 359, 472, 1878, (-198.83)</td>
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<tr>
<td>CO₂</td>
<td>3, 39, 140, 194, 290, 443, 657, 1089, 1646</td>
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<tr>
<td>COH</td>
<td>131, 160, 378, 401, 430, 1078, 1291, 3191</td>
</tr>
<tr>
<td>COO-H</td>
<td>78, 132, 158, 267, 463, 593, 623, 859, 1163, 1638, (-1301.12)</td>
</tr>
<tr>
<td>COOH</td>
<td>27, 93, 151, 248, 270, 326, 490, 606, 903, 1106, 1633, 3096</td>
</tr>
<tr>
<td>H-CO</td>
<td>130, 160, 270, 335, 558, 1091, 1420, 2210, (-382.06)</td>
</tr>
<tr>
<td>H-OH</td>
<td>116, 369, 441, 624, 740, 1366, 3164, (-1016.42)</td>
</tr>
<tr>
<td>H₂O</td>
<td>48, 79, 260, 469, 523, 1510, 3149, 3236</td>
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<tr>
<td>O</td>
<td>313, 314, 462</td>
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<tr>
<td>O-H</td>
<td>261, 297, 352, 446, 1788, (-1061.36)</td>
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<tr>
<td>OC-OH</td>
<td>50, 90, 146, 210, 241, 319, 364, 447, 736, 1790, 3310, (-101.81)</td>
</tr>
<tr>
<td>OH</td>
<td>259, 262, 403, 610, 614, 3273</td>
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<tr>
<td>CH₄</td>
<td>1261, 1262, 1262, 1482, 1484, 2942, 3060, 3061, 3062</td>
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<tr>
<td>CO</td>
<td>1973</td>
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<tr>
<td>CO₂</td>
<td>625, 630, 1272, 2229</td>
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<tr>
<td>H₂</td>
<td>4117</td>
</tr>
<tr>
<td>H₂O</td>
<td>3405, 3295, 1556</td>
</tr>
</tbody>
</table>

#The imaginary frequency, in negative, confirming a transition state is denoted in bold
Appendix C: Vibrational frequencies of intermediates CO$_2$ and CO activation reactions on MoP (0001)

C1. Vibrational frequencies of intermediates and transition states on MoP (0001)

<table>
<thead>
<tr>
<th>Species</th>
<th>Vibrational modes (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>564, 408, 407</td>
</tr>
<tr>
<td>O</td>
<td>479, 352, 350</td>
</tr>
<tr>
<td>OH</td>
<td>479, 352, 350</td>
</tr>
<tr>
<td>H$_2$</td>
<td>2495, 1578, 293, 272, 107</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>3132, 3055, 1456, 495, 464, 325, 101, 97</td>
</tr>
<tr>
<td>CO</td>
<td>1493, 334, 290, 276, 90.9, 84</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1537, 1154, 716, 379, 364, 349, 137, 123, 97</td>
</tr>
<tr>
<td>COOH</td>
<td>3185, 1270, 1220, 1067, 680, 542, 426, 365, 294, 228, 175</td>
</tr>
<tr>
<td>C-O</td>
<td>497, 419, 360, 282, 259</td>
</tr>
<tr>
<td>CO-O</td>
<td>1657, 713, 422, 408, 229, 125, (540.66)</td>
</tr>
<tr>
<td>COO-H</td>
<td>1476, 1339, 1137, 719, 590, 345, 264, 244, 143, 73, (433.49)</td>
</tr>
<tr>
<td>H-H</td>
<td>1652, 1529, 218, 197, (792.03)</td>
</tr>
<tr>
<td>H-OH</td>
<td>3192, 1271, 698, 558, 426, 178, 120, (992.60)</td>
</tr>
</tbody>
</table>
O-H  1403, 619, 430, 332, (-990.42)

CO-H  3179, 1426, 804, 521, 502, 363, 278, 241, 152, 61, (-593.64)

#The imaginary frequency, in negative, confirming a transition state is denoted in bold