Heterogeneous Enantioselective Hydrogenation Of β-keto-esters Using Chirally Modified Supported Ni Nanoparticles

By

Sushma Acharya

Supervisor: Dr. David Watson
Second Supervisor: Dr. Carol Crean

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Faculty of Engineering and Physical Sciences
The University of Surrey
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Abstract

Enantioselective heterogeneous catalysis is an important and rapidly expanding research area. The two most heavily researched examples of this type of catalysis are the enantioselective hydrogenation of α-keto-esters over Pt-based catalysts and the enantioselective hydrogenation of β-keto-esters over Ni-based catalysts. These enantioselective surface reactions are controlled by the presence of adsorbed chiral molecules i.e. tartaric acid on the surface of the metal component of the catalyst. The work presented in this thesis focuses on two parts, the synthesis of pure nickel nanoparticles and enantioselective behavior of the modified nickel nanoparticles.

The works on the synthesis of pure nickel nanoparticles were carried out using two methods, the reverse microemulsion and the reduction method. It was discovered that the reverse microemulsion method produced nickel oxide nanoparticles, whereas the reduction method produced pure nickel nanoparticles.

Chiral modifications of Raney nickel (RNi) and C-supported catalysts were studied. The catalysts were employed in enantioselective hydrogenation of methyl acetoacetate (MAA) to (R) - and (S)-enantiomers of methyl 3-hydroxybutyrate (MHB). The effects of modification and hydrogenation parameters such as concentration of modifier temperature, pressure and solvent on the enantioselectivity of MAA hydrogenation were discussed. For RNi methanol was found to be the best solvent, with tartaric acid concentration 0.2 mol/L for achieving the highest enantiomeric excess under 8 bar at 70 °C.

Characteristic features of the in-situ modification of Raney nickel and C-supported Ni were also evaluated and the results obtained were compared with the conventional (pre-modification) approach. Parameters for the conventional and in-situ methods were optimised in a series of experiments for both types of catalysts. The in-situ modified catalyst was found more active for both RNi and C-supported catalysts with 98 % and 42% enantiomeric excess, respectively.
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<tr>
<td>Ni</td>
<td>Nickel</td>
</tr>
<tr>
<td>RNi</td>
<td>Raney nickel</td>
</tr>
<tr>
<td>MRNi</td>
<td>Modified raney nickel</td>
</tr>
<tr>
<td>TA</td>
<td>Tartaric acid</td>
</tr>
<tr>
<td>MAA</td>
<td>Methyl acetoacetate</td>
</tr>
<tr>
<td>MHB</td>
<td>Methyl-3-hydroxybutyrate</td>
</tr>
<tr>
<td>NiCl₂</td>
<td>Nickel chloride</td>
</tr>
<tr>
<td>CTAB</td>
<td>Cetyltrimethylammonium bromide</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Silicon dioxide</td>
</tr>
<tr>
<td>P-XRD</td>
<td>Powder X-ray diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
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<td>GC</td>
<td>Gas chromatography</td>
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<td>Atomic absorption spectroscopy</td>
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<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>STXM</td>
<td>Scanning transmission X-ray microscopy</td>
</tr>
<tr>
<td>NEXAFS</td>
<td>Near-edge X-ray adsorption fine structure spectroscopy</td>
</tr>
<tr>
<td>ee</td>
<td>Enantiomeric excess</td>
</tr>
<tr>
<td>FWHM</td>
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Chapter 1

1. Introduction

1.1. Importance of Catalysis

Catalysis is an essential phenomenon for the formation and function of living systems as most of the chemical reactions that take place in living organisms are carried out by natural catalysts, known as enzymes. On the other hand, our life style is ruled by catalysis as many products we consume such as food, drinks, chemicals and polymers, amongst others, have been produced using a catalyst at some stage of their manufacture. Today over 90% of all industrial chemicals are produced with the aid of catalysts. [1] Catalysts also contribute a sizable fraction of any nation’s gross domestic product. In 1991 it was estimated that the total value of fuels and chemicals derived from catalysts exceeded $900 billion/year. [1] World catalysts demand grow to $16.3 billion by 2012 according to the Freedonia Group. [1] In 2003 global sales of catalysts exceeded $12 billion which was up from $9.3 billion in 1998. [1] As the global economy is based on catalytic technologies there is a great interest in further study/development of catalytic systems. Moreover, catalysis is a sustainable alternative to control the generation of pollutants, handling and disposal of hazardous materials.

The phenomenon of catalysis was first recognized by Berzelius in 1836. [1] However, some catalytic reactions such as the production of alcoholic beverages by fermentation or the manufacture of vinegar by ethanol oxidation were practiced long before. For example the catalytic production of soap by fat hydrolysis and diethyl ether by dehydration of ethanol were performed in the 16th and 17th centuries. [1] In 1746 in Birmingham, England, nitric oxides (NO/NO₂) were used as catalysts in the lead chamber process for oxidation of SO₂ to give SO₃ in the manufacture of sulphuric acid. [1] There is archaeological evidence that the use of enzymes for fermenting starch during brewing was used in Ancient Egypt since around the 6th millennium BC. [1]
1.2. **Definition of Catalysis/Catalyst**

The International Union of Pure and Applied Chemistry (IUPAC) has defined a catalyst as “a substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction”. [2] The chemical process of increasing the reaction rate is called catalysis, and the catalyst is both a reactant and a product of the reaction, i.e. the catalyst is restored after each catalytic act. Furthermore, the catalyst does not influence the thermodynamic equilibrium composition after the cessation of the reaction. This effect is best seen in the generic reaction energy diagram as below in Figure 1.1. The activation energy (E_a) is shown on a reaction energy profile as the difference in energy between the reactants and the transition state.

![Figure 1.1: An energy diagram demonstrating the effect of a catalyst for the generic exothermic reaction. The catalyst offers an alternative pathway where the rate determining step has a smaller E_a. The relative thermodynamic stabilities remain the same.](image)

1.3. **Properties of a Catalyst**

In addition to the fundamental properties that come from the selection of a catalyst, i.e. activity and selectivity during catalytic performance, industrial applications require that a catalyst be economical, reproducible, mechanically and thermally
stable and possess suitable morphological characteristics. The right balance of all of these standards would allow the best suitable catalyst for a given process.

1.3.1. Catalytic Activity, Selectivity and stability

The activity that a catalyst exhibits for a given chemical transformation can be shown in various ways. It can be described in terms of rate (mole of product per volume unit or mass of catalyst per time unit), in terms of activity per active site (turn over number, TON) or turn over per unit time (turn over frequency, TOF); or simply as a conversion (moles of transformed reactant per moles of initial reactant).

Selectivity can be defined as the amount of desired product obtained while suppressing undesirable competitive and consecutive reactions. Therefore, it can be described as moles of desired product per moles of converted reactant. A catalyst is considered highly selective if it gives high yields of a desired product.

The stability of the catalyst particle, that is, its ability to retain its activity under conditions of long-term use, requires that it be resistant to deactivation. The three most important means of catalyst deactivation are fouling, poisoning and sintering, and all catalysts are susceptible to these to a greater or lesser extent.

The fractional excess of one enantiomer over the other is defined as the enantiomeric excess (ee). It is expressed in Equation 1.1 in terms of the moles (or weights) of the two enantiomers, $\eta_1$ and $\eta_2$ and is equal to the ratio of the observed optical rotation, $\alpha_{obs}$, and to the optical rotation of either pure enantiomer, $\alpha_o$:

$$\text{Enantiomeric excess (ee) of } \eta_1 = \frac{(\eta_1 - \eta_2)}{(\eta_1 + \eta_2)} = \frac{\alpha_{obs}}{\alpha_o} \quad (\text{Equation 1.1})$$

1.4. Types of Catalysis

Catalytic processes can be divided in three main types: homogeneous, heterogeneous and enzymatic processes. In a homogeneous reaction, the catalyst is in the same phase as the reactants (as in the hydrolysis of esters by acid catalysts, all reactants and catalysts are dissolved in water). In a heterogeneous reaction, the catalyst is in a different phase from the reactants. Normally, the catalyst is a solid and reactants are
fluids (liquids or gases). It is characterized by the presence of “active sites” on the catalyst surface. The enzymatic catalysis (biocatalysis) has an intermediate character between homogeneous and heterogeneous processes, because although the enzymes and reactants are in the same phase (solution), they have “active sites” in their structure. In principle, there is no limitation on the phase to be considered; as a matter of fact the first industrial catalysed reaction was the oxidation of SO$_2$ to give SO$_3$ using NO as a homogeneous catalyst, which occurs in the gaseous phase. [1] On the other hand, most of the processes using homogeneous catalysts occur in a liquid phase whereas for the heterogeneous catalyst, the catalyst is usually in a solid form, and the reaction occurs either in liquid or gaseous phase. The fact that the catalyst is in a distinct phase with respect to the reaction medium, leads to some of the major advantages of heterogeneous catalysts over homogenous.

1.4.1. Homogeneous Catalysis

A great variety of homogeneous catalysts are known, ranging from Brönsted and Lewis acids widely used in organic synthesis, metal complexes, metal ions and organometallic complexes. There are many important industrial catalytic processes that use organometallic complexes including: addition, polymerisation and oxidation of olefins; to obtain polybutadiene, polyethylene and polypropylene oxide, respectively. Another application of organometallic complexes is in processes such as hydrogenation of C=C [4-6], C=N [5-7] , C=O [6, 7] bonds; as well as isomerisation, epoxidation, cyclopropanation, addition and sulfoxidation for the production of fine chemicals. Examples of these are shown in Figure 1.2, where TON, TOF and ee refer to turnover number, turnover frequency and enantiomeric excess respectively.

The disadvantages of the homogeneous catalysts as shown in Table 1.1 led to an increased interest in the use of heterogeneous catalysts.
Table 1.1: Comparison of the main advantages/disadvantages of homogeneous vs. heterogeneous catalysts.

<table>
<thead>
<tr>
<th>Property</th>
<th>Homogeneous</th>
<th>Heterogeneous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst recovery</td>
<td>difficult and expensive</td>
<td>easy and affordable</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>Poor</td>
<td>good</td>
</tr>
<tr>
<td>Selectivity</td>
<td>excellent/good-single active site</td>
<td>Good/poor-multiple active sites</td>
</tr>
</tbody>
</table>

A drawback of homogeneous catalysts is the high costs and availability of chiral ligands and metal precursors. Moreover, ligand synthesis, high catalyst loading, isolation of products, recovery and recycling of noble metals, as well as severe problems of corrosion of reactors and tubing when acids are used, are major industrial drawback that need to be resolve.

1.4.2. Heterogeneous Catalysis

A heterogeneous catalytic process is more complex than homogeneous catalysis because the catalyst is not uniformly distributed throughout the reaction medium. Instead it is a distinct two phase system, usually either vapour/solid or liquid/solid,
with the solid phase being the catalyst. In such a system several reaction steps are needed to complete the catalytic cycle:

i. diffusion of reactants

ii. adsorption of reactants

iii. reaction

iv. desorption of product

v. diffusion of products

Heterogeneous catalysts are greatly used in industry, specifically in oil refining and petrochemistry, in processes such as fluid catalytic cracking (FCC), hydrocracking, hydrogenation, dehydrogenation, oxidation and isomerisation.

According to the key properties responsible for their catalytic behaviour, heterogeneous catalysts can be classified in the following subcategories [8]:

i. oxidation-reduction

ii. acid-base

iii. bifunctional

The cooperative behaviour of surface sites with acidic, basic or reduction-oxidation properties is an essential requirement for catalysis on inorganic solids. Hydrogenation and dehydration reactions require acid-base site pairs of intermediate strength because such sites can form stabilize and discard adsorbed intermediates during a catalytic turnover. Deuterium exchange and H-H dissociation reactions also occur on acid-base pairs present in single component or binary oxides and in supported oxide cluster.

1.4.2.1. Oxidation-reduction

The best known catalyst of this category is the three-way catalytic converter, commonly used in motor vehicle exhaust systems. Its task is to reduce the toxic
emissions from an internal combustion engine, according to the following mechanisms [9]:

i. Reduction of nitrogen oxides to nitrogen and oxygen:
   \[ 2\text{NO}_x \rightarrow x\text{O}_2 + \text{N}_2 \]

ii. Oxidation of carbon monoxide to carbon dioxide:
   \[ 2\text{CO (g)} + \text{O}_2 (g) \rightarrow 2\text{CO}_2 (g) \]

iii. Oxidation of unburned hydrocarbons to CO\(_2\) and water:
   \[ \text{C}_x\text{H}_y + (x+y/2) \text{O}_2 (g) \rightarrow x\text{CO}_2 (g) + y/2\text{H}_2\text{O (g)} \]

The active metals are platinum, palladium and rhodium, which are supported on a ceramic honeycomb wash-coated with alumina or silica. [9]

### 1.4.2.2. Acid-base

Acid-base catalysts present acidic and basic sites. According to Brönsted, an acid is a substance which donates a proton, whereas a base accepts it. [8] On the other hand, Lewis acids are those which accept a pair of electrons and Lewis bases those which donate them. Examples of this subcategory are stoichiometric metal oxides such as MgO, Al\(_2\)O\(_3\), CsO and BaO.

### 1.4.2.3. Bifunctional

Bifunctional materials present a combination of the properties of the last two categories: oxidation-reduction and acid-base. The main industrial application of this type of catalyst is on catalytic reforming, which is a process to convert petroleum refinery naphthas with low-octane ratings into reformates or high-octane liquid products, which are components of high-octane gasoline (petrol). Examples of bifunctional catalysts are platinum or rhenium supported on either silica or silica-alumina.

### 1.4.3. Composition and structure of Heterogeneous Catalysts

Heterogeneous catalysts are generally considered to be composed of three distinct, yet complementary and necessary components. These are:

- Active phase
Chapter 1  

- Support  
- Promoter

The function of each of these components and the better understood functions of some specific component materials will be discussed in turn.

- **Active phase**

The active phase is responsible for the primary chemical reaction. The phase can constitute one or more chemical species. Some active components and the reactions which they mediate are given in Table 1.2.

**Table 1.2: Selected active components used in catalysis.**

<table>
<thead>
<tr>
<th>Class</th>
<th>Active components</th>
<th>Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals</td>
<td>Fe, Ni, Pt, Pd, Cu, Co, Ag</td>
<td>- Redox reactions</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Hydrogenation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Hydrogenolysis</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Oxidation</td>
</tr>
<tr>
<td>Oxides and sulfides</td>
<td>NiO, ZnO, CoO, CuO, H₂S</td>
<td>- Redox reactions</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Hydrogenation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Oxidation</td>
</tr>
<tr>
<td>Oxides</td>
<td>MgO, SiO₂, Al₂O₃, Al₂O₃-SiO₂, Zeolites, Pillared Clays</td>
<td>- Carbonium ion reactions</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Cracking</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Dehydration</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Polymerisation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Isomerisation</td>
</tr>
</tbody>
</table>

The active components can be expensive and/or very sensitive to the conditions of the reaction. Therefore, it is often dispersed / stabilised on a support.

- **Support**

The main function of the support is to provide the largest possible surface area for dispersion of the active components. It is essential for the support to have a high melting point to minimise the effects of thermal alteration on its structure. Another important function of the support is to minimise sintering of the active component. However, this ability depends on mobility of the active component, loading of the active component onto the support, interaction between the support and the active component and the reaction temperature. The most commonly used support materials
with the highest surface area and melting points are Al₂O₃, SiO₂ and C. Very often, the support is not just a phase on which the active component is dispersed but also, under certain conditions, it acts as an active component itself. In some other cases, it influences the structure of the active component. The morphology and porosity are other important factors to consider when reactions are dependent on size and shape of the reactant molecules.

- **Promoter**

Promoters are the third component of many catalyst systems, and their addition to the support and active component often results in the enhancement of the activity/stability of catalyst. In general practice, the function of a promoter is determined through trial and error, and the mechanisms behind how promoters work are not well understood.

### 1.5. Enantioselective Catalysis

#### 1.5.1. Enantioselective Catalysts

The development of enantioselective catalytic routes capable of producing single enantiomer products from a pro-chiral reagent in a catalytic reaction is of the highest beneficial implications for the pharmaceutical and fine chemical industries. It is also an area of fundamental academic interest. One of the major successes of enantioselective catalysis is the Monsanto synthesis of the L-isomer of 3, 4-dihydroxyphenylalanine, otherwise referred to as L-dopa, **Figure 1.3.** [10, 11] This is the first industrial homogenous chiral catalytic process and the product is used in the treatment of Parkinson’s disease. Its importance was reflected by the 2001 Nobel Prize for Chemistry awarded to Knowles and Noyori for their work in enantioselective hydrogenation reactions and Sharpless for his work on enantioselective oxidation reactions. [6, 10, 11]

![Figure 1.3: L-DOPA, a drug used in the treatment of Parkinson's disease.](image-url)
Chirality is a geometric attribute and refers to molecules as a whole rather than to a particular atom. A molecule is either chiral or achiral. The world chiral is derived from the ancient Greek for ‘hand’ and means handedness, reflecting the left and right-handedness of molecules that are chiral in nature. An achiral molecule does not have this property.

Enantiomers are a pair of chiral molecules related as non-superimposable mirror images. Neither enantiomer can be superimposed on the other by translation or rotation. An enantiomer contains a stereogenic centre usually a tetrahedral carbon. The absolute configuration of such chiral centres can be labelled R (for rectus) or S (for sinister) as determined by the Cahn-Ingold-Prelog rules. [12]

From the practical perspective, the importance of molecular chirality comes from the fact that two enantiomers can have the same physical properties such as melting point, boiling point and density but may possess different pharmacological effect. Limonene (4-isopropenyl-1-methyl-1-cyclohexene), for example, is a chiral molecule and exists as a pair of enantiomers as illustrated in Figure 1.4. The two enantiomers of limonene differ greatly. One form smells of lemons but the other of oranges.

Figure 1.4: Two enantiomers of limonene.

The infamous example of the relationship between pharmacology activity and molecular chirality was provided by the horrific tragic administration of thalidomide
to pregnant women in 1960s. [13] The drug was prescribed to counter morning sickness and was administered as a racemix mixture (equimolar concentration of both enantiomers). Tragically, while the \((R)\)-isomer had the desired anti-nausea effects, the \((S)\)-form was a teratogenic and caused foetal abnormalities, such as several underdeveloped limbs. Recent studies suggest that even the distribution of the pure \(R\) - enantiomer of the drug may not have averted the thalidomide tragedy as the drug is known to racemise within the body and the danger that lurks in many other optically active compounds, such as ethambutol and penicillamine, to name but two (Figure 1.5). [13]

There has been an increasing trend towards the application of optically pure compounds for environmental, economic and social reasons. Various methods exist in producing a single enantiomer selectively e.g. separation of enantiomers \textit{via} classical resolution, dynamic kinetic resolution, the chiral pool approach, use of enzymatic and microbial transformations and enantioselective catalysis, among which enantioselective catalysis is the most desirable one. The chiral pool is that collection of available natural products considered cheap enough to use as starting materials for organic synthesis.

For several decades asymmetric catalysis has been extensively studied as it attracts the attention of many areas of chemistry such as synthetic and catalytic chemistry. The pharmaceutical and agrochemical industries use these chiral molecules either as intermediates or final products. The purity of these molecules has increased their importance in medical and veterinary applications. Therefore there is a huge requirement in finding synthetic strategies in order to achieve high yields and enantioselectivity for these molecules which will minimize the need for the purification process.
1.5.1.1 Homogeneous Enantioselective Catalysts

The groups of Noyaki et al. [6, 10, 11, 14], Horner et al. [6, 10, 11, 15] and Knowles and Sabacky [6, 10, 11, 15-17] were the first to report the synthesis of homogeneous chiral metal complexes in 1966 and 1968. They reported a method for catalytic asymmetric hydrogenation employing a soluble rhodium complex catalyst (or more correctly, as a catalyst precursor) which contains optically active tertiary phosphine ligands. The chiral ligand interacts with the prochiral alkene when it coordinates to the complex, fixing the substrate in a particular configuration. As a result, there is only one face of the alkene available for hydrogenation, and a high selectivity toward one enantiomer is observed. Varying the phosphane ligand allowed Knowles to obtain enantiomeric excess of up to 95%. A development of this technique led to the Monsanto synthesis of L-DOPA (Figure 1.3).
Although the homogeneous reactions can be highly stereoselective, there are disadvantages associated with it: namely (1) expense of the catalyst, which is often lost upon work-up of the reaction, (2) the difficult separation of the organic ligands and metal catalyst from the resulting products, and (3) the inability of homogeneous catalysis to provide high stereoselectivity for all substrates and reaction types. [18]

The first two of these difficulties can be partially avoided by immobilizing the homogeneous chiral catalyst on a solid support or by using a heterogeneous chiral catalyst that can either be readily recovered by filtration from a slurry reactor, or can be used in fixed bed reactors. This introduces a different aspect of catalyst usability, namely the stability of the heterogeneous catalyst. Leaching of active components into the solution represents a real significant problem concerning commercialisation. [19] Consequently, emphasis has to be given to the design of stable heterogeneous catalysts that are capable of high enantioselectivity.

1.5.1.2 Heterogeneous Enantioselective Catalysts

Compared to the number of highly selective homogeneous enantioselective catalysts, heterogeneous enantioselective catalysts are still behind as concerns the performance and the mechanistic insight of the reaction. A comparable development as in homogeneous enantioselective catalysis has not (yet) taken place in chiral heterogeneous catalysis due to various reasons, the most important being the difficulty to create well-defined catalytically active and stable sites on a solid surface.

The most obvious strategies for creating heterogeneous enantioselective catalysts are chirally modified metals, chiral polymers and immobilised chiral transition metal complexes. Among these approaches, only modification of the catalytic metal surface by a strongly adsorbing modifier has the synthetic potential. Immobilized chiral metal complexes traditionally belong to the class of homogeneous catalysis and will not be discussed here. Modifiers influence the selectivity and activity of the catalyst when added to the catalyst or to the reaction mixture. These modified catalysts are very specific with respect to the substrate.
In the field of hydrogenation the most important heterogeneous catalytic systems are (i) the nickel catalyst modified with tartaric acid, useful for hydrogenation of β-functionalised ketones, [20-24] (ii) platinum catalysts modified with cinchona alkaloids, for hydrogenation of α-functionalised ketones [24-26] and (iii) supported palladium modified with cinchona alkaloids, for hydrogenation of alkenoic acids (Figure 1.6). [24, 27]

The two most investigated catalytic systems of this family are shown in Figure 1.7. Nickel catalysts modified with α-hydroxy acids (e.g. tartaric acid) and α-amino acids (e.g. alanine or glutamic acid) are useful for the liquid phase hydrogenation of β-functionalised ketones. Secondly, platinum catalysts modified with cinchona alkaloids and related modifiers are successful for the liquid phase hydrogenation of α-functionalised ketones.

![Diagram of hydrogenation reactions](image)

**Figure 1.6:** Heterogeneous enantioselective hydrogenation, R, R’, R” are alkyl or aryl groups or hydrogen and (*) indicates chiral centre.

The discovery of α-ketoester hydrogenation on cinchona-modified Pt by Orito’s group in the late seventies initiated a new wave of interest in chirally modified
metals. The application range of this catalyst system has been extended to several other ketones possessing an electron-withdrawing functional group in α-position, as illustrated with the outstanding examples in Figure 1.8. Continuous improvements made after gathering the knowledge on this catalytic system have been covered in various reviews.

Figure 1.7: (a) Enantioselective hydrogenation of MAA over tartaric acid-modified nickel catalyst. (b) Enantioselective hydrogenation of methyl pyruvate over cinchonidine (CD) or cinchonine (CN)-modified Pt.
Figure 1.8: Hydrogenation of these ketones represents the most selective applications of chirally modified Pt. [24]

1.6. Chiral Metal Surfaces

1.6.1 Adsorption of Chiral Modifier

Noble metals have the ability to adsorb a variety of organic and inorganic molecules on their surface, after which the adsorbed molecule acquires special properties. Heterogeneous catalysis provided such an example, whereby a substrate and a reagent are both adsorbed onto the catalyst surface and, when the two species meet on a surface, a reaction occurs with assistance from the surface metal. The reaction selectivities are governed by both the adsorption step of the substrate and the reaction transition states. The control of reaction selectivity during the adsorption step represents one of the main characteristics of heterogeneous catalysis, and may be due not only to the adsorption rate or constant but also to the geometry of the adsorbed substrate. By applying this unique situation, a coexisting third molecule –
which formally is unreactive with the reagent but may be adsorbed onto the catalyst surface—can affect the adsorption and the reaction of the substrate during the process of catalysis. If the adsorption of the molecule is strong, then the molecule behaves as part of the catalyst. Such a molecule is referred to as a “modifier” and has the potential to regulate, enhance or even to cause a certain catalytic activity. When the modifier is chiral and optically active, the catalyst has the potential to differentiate the enantio-face of the substrate.

1.7. Hydrogenation of β-ketoesters on Nickel

The Ni-catalysed hydrogenations of β-ketoesters and β-diketoesters have been researched very extensively by several prominent research groups in Japan since the late 1950s primarily by Izumi [20], Tai and Harada [30, 31], with tartaric acid as the most often used chiral modifier. Additionally, significant contributions have been made by the groups of Nitta, [27, 32] Sachtler [33, 34] and Webb and Keane [23, 34, 35]. Most works have used Raney nickel and nickel powder as catalysts; however, some have used Ni particles supported on high-surface-area materials such as silica and alumina. [33] These catalysts have demonstrated enantioselectivity for the hydrogenation of methyl acetoacetate to methyl-3-hydroxybutyrate, yielding enantiomeric excesses as high as $ee = 95\%$. [34]

Despite the extensive research carried out by the different groups, the mechanism of this remarkable selectivity control, however, does not seem to be fully understood because of the complexity of the reaction system in the liquid phase, with suspended solid catalysts, under a high pressure of hydrogen. [36, 37] Model surface science studies by Raval and co-workers [38, 39] and Baddeley and co-workers [10, 21, 40] have made significant contributions in understanding the behaviour of these chiral modifiers on achiral single crystal surfaces.

1.7.1 Modification Variables

In order to develop effective enantioselective catalysts for the β-keto-esters system, all the factors that affect the optical yield of enantioselective hydrogenation have to be fully investigated. All the processes of the enantioselective hydrogenation consist of three processes, those are, (i) a catalyst preparation process, (ii) a modification
process and (iii) hydrogenation process. These processes have preparation variables for activated nickel as a base catalyst for modified nickel, modification variables for the activated nickel catalyst and reaction variables for the hydrogenation process, respectively.

The preparation of modified nickel (MNi) catalyst is a simple process, just soaking an activated nickel catalyst in the modification solution. However, a lot of factors determine the selectivity of catalysts. In the case of enantioselective hydrogenation of methyl acetoacetate using nickel catalysts, the nickel source, [41] modification time and temperature, [23, 42-44] modifier concentration, [23, 42-44] co-modifier quantity [23, 43, 44] and modification pH [23, 42-44] can affect enantiomeric excess (ee).

Systematic studies on the heterogeneous enantioselective hydrogenation of carbonyl compounds were carried out by Izumi using Raney nickel with various chiral modifiers, [45] and tartaric acid was found to be the best chiral reagent. The substrates used were β-keto esters, β-keto alcohols and ketones and among these substrates methyl acetoacetate (MAA – simplest reagent) is the best. [46] The hydrogenation of this compound had been investigated extensively using the chirally modified nickel catalyst (Figure 1.7 (a)). The products of this reaction are methyl (R)-3-hydroxybutyrate (R-MHB) and methyl (S)-3 hydroxybutyrate (S-MHB). R-MHB is an important intermediate in the synthesis of a carbonic anhydrase inhibitor MK-0507 used in the treatment of glaucoma. [35]

![Structures of tartaric acid and glutamic acid](image)

**Figure 1.9:** Chiral organic modifier used in the hydrogenation of MAA over Ni catalysts.
Modification with slightly acidic tartaric acid solution, pH adjusted to 3.5 with sodium hydroxide gives optimum enantioselectivities for modified Raney Ni. [34] Below pH 5, tartaric acid corrodes the surface leaching aluminium from the Raney Ni catalyst thus establishing a surface suitable for enantioselectivity. Conversely, above pH 3, tartaric acid adsorbs onto the nickel surface as an appropriate species for enantioselectivity. [30]

Keane found that for Ni/SiO$_2$ catalysts, modification in slightly basic conditions yielded higher levels of enantioselectivity than observed for modification in acidic conditions. [23] Modification process is a corrosive process, characterised by the leaching of Ni into the modifying solution. Extensive research to interpret the causes and effects of nickel leaching during the modification procedure has been carried out. Nitta et al., showed that nickel leaching results in the selective dissolution of small <2 nanometre (nm) particles from the catalyst as determined by electron microscopy and selective chemisorption measurements. [30] This suggests that large nickel particles are preferred for enantioselectivity. [32] Hoek and Sachtler studied the influence of temperature and the nature of the ambient atmosphere during the modification process. [33] They proposed that higher modification temperature gave higher ee because high temperature modification solution would effectively pull Ni atoms out of the Ni lattice to produce Ni-tartrate complexes for making enantioselective site. Using Raney Ni and Ni/SiO$_2$ catalysts, the highest enantioselectivity was achieved at a modification temperature of 100 °C. Hoek and Sachtler also noted that catalysts modified in air had three times larger enantioselectivity than catalysts modified under hydrogen or nitrogen. Kean and co-workers demonstrated that the relation between optical yield and modification temperature depended on the initial TA concentration in the modification solution. [23]

Hoek and Sachtler were also the first to suggest the possibility that tartaric acid interacts with the surface to form a nickel tartrate complex. This complex can either remain on the silica support to form an enantioselective site or diffuse into the modifying solution. [33] Keane and Webb found that under identical conditions, nickel tartrate leached during modification and without any pre-treatment proved both catalytically active and enantioselective. [23]
The extent of tartaric acid adsorption onto the nickel surface is dependent upon both temperature and modification time. In general, with high temperature and concentration less time would be required for tartaric acid to adsorb onto the metal surface. While thirty minutes is sufficient for Raney Ni modification at 100 °C for RNi, a more lengthy treatment required for supported nickel catalysts. [23, 31]

Inorganic salts in the modification solution are known to enhance the enantioselective of unsupported and supported modified Ni catalysts in the MAA hydrogenation. [44] Harada and co-workers reported that sodium salts were effective as secondary modifying reagents. [31] Among those examined, sodium bromide (NaBr) was the best for the hydrogenation of methylacetoacetate, when the catalysts were modified with a solution of an optimum concentration of tartaric acid and NaBr for a longer time, the optical yield increased to 91%. Harada and Izumi [20, 31] proposed that, it could be due to the deactivation of the unmodified (non-enantioselective) site to reduce the production of racemic products, since the ratio of modified (enantioselective) to unmodified sites determines the overall optical yield. As unmodified sites yield a racemic mixture of products, they concluded that sodium bromide is adsorbed onto these sites thereby lowering the hydrogenation activity from these areas and in doing so increasing the overall optical yield. Whilst Bostelaar and co-worker interpret [20, 31] the effects of sodium bromide to alteration of the stereochemistry of the product determining surface complex, whereas Keane and Webb [22-23] suggested that it possibly increases the stability of the nickel tartrate complex in addition to blocking the unmodified sites on the nickel surface.

1.7.2 Reaction Variables
The optical purity of the product and the enantiomeric excess not only depend on the modification method of the catalyst, but also on the reaction conditions. Variables include the pressure of hydrogen, the solvent, the reaction temperature and others.

The enantioselective process has been reported to be both dependent [22, 47] and independent [43] on and of hydrogen pressure, a range of optimum substrate to catalyst ratios have been given, and a variety of selectivity/conversion relationships are illustrated in the literature.
Hydrogenation activities as well as enantioselectivity of the tartaric acid modified Raney nickel catalyst are dependent on the reaction solvent. Hydrogenation of MAA over modified Raney nickel Kukula and Červený have reported that the reaction performed in methanol was five times as fast as in THF, but that the optical yield was significantly lower. [47] On the contrary, Lipgart and co-worker claimed a higher optical yield in MeOH than in THF. [48] Keane also reported higher optical yield for BuOH over Ni/SiO₂. [23] Recently, Hangning Chen and co-worker reported in MeOH the reaction was 7.5 times as fast as in THF, and the optical yield was 3 times as high. [49] There is general agreement that optimum enantioselectivity in the Ni/tartaric acid system is achieved at a hydrogenation temperature of 60-70 °C. This temperature corresponds to dissociation of hydrogen bonding. At higher temperatures, a disruption of the hydrogen bonding between MAA and tartaric acid on the catalyst surface occurs. Transesterification and decomposition of the β-ketoester MAA at higher temperatures has been reported. [23]

### 1.7.3 Summary of Modified Ni Catalyst

Taking an overview of the published data, it is evident that one can only, at best, make qualitative comparisons between results originating from different laboratories. Moreover, the range of experimental conditions that have been considered in each study is too narrow to afford a complete understanding of the underlying principles.

Raney nickel remains a well-used base catalyst due to its high catalytic activity, while tartaric acid is the best chiral modifier for the nickel hydrogenation studied to date. MAA is the smallest β- ketoester, and is still a representation substrate of β-ketoester and their analogues. As tartaric acid is tightly adsorbed onto the catalyst surface and is stable under hydrogenation conditions, the modification catalyst can be used for the recover/reuse process, which is different from the cinchona alkaloid-modified platinum and palladium systems. Modifier pH, temperature, and time are crucial for good catalyst performance. Polar protic solvents, especially methanol give the highest enantiomeric excesses. A reaction temperature of 70 °C and high hydrogen pressures of 90 bar yield good enantioselectivity.
1.8. Surface Science Investigation of Chiral Modifiers Adsorbed onto Metal Surfaces

Trying to understand how a chiral organic molecule bonds to the surface, its molecular orientation and surface structure mode of action of a catalyst is a challenging endeavour. This is particularly true for heterogeneous catalysis and even more for enantioselective catalysis. Industrial processes frequently operate at high temperatures and pressures. The catalysts are in the form of highly dispersed powders, frequently involving transition metals on oxide supports and may include the addition of promoters, which greatly enhance the efficiency of the catalyst. The complexity of a real catalytic system makes it almost impossible to elucidate the local nature of the chiral molecule at the surface; there have been studies on a mimic of a catalytic system by adsorbing pure enantiomers of chiral molecules on defined single crystal metal surfaces. This involves taking flat, usually low Miller index, faces of single crystals of the material of interest and studying the adsorption or co-adsorption of small quantities of atoms and molecules in an Ultra-High Vacuum (UHV) environment.

1.8.1. Adsorption of (R, R)-Tartaric Acid

(R,R)-tartaric acid can exist in three different forms (illustrated in Figure 9), the neutral bi-acid form, the monotertrate form where one of the carboxylic groups has deprotonated and the bitartrate form, in which both acid groups have deprotonated. The carboxylic acid groups are capable of sustaining hydrogen bonds with other acid and alcohol groups, which can lead to a number of intermolecular interactions. [50]

Though the chiral modification step is thought to be crucible in catalysis, there are several key differences between the types of modifiers used in the systems. Firstly, the α-hydroxy and α-amino acids are considerably smaller and mobile than the relatively large alkaloids. Secondly, the hydroxy and amino acids are more likely to interact with neighbouring modifier by H-bonding interactions. Thirdly, the carboxylic acid functions of these modifiers are capable of etching the Ni nanoparticles.
Initial work in this area involved a collaboration between Raval and Baddeley looking at the adsorption behaviour of (R,R)-TA on Cu(110). [50, 51] A series of ordered structures were observed dependent on sample temperature and adsorbate coverage. As these parameters are varied, the adsorbed molecules change between the monitartrate, bitartrate or dimer forms (Figure 1.10). [50] Moreover, these studies revealed the ability for molecules to self-organise on the surface leading to nanostructures with different crystalline architectures (Figure 1.11). [51]

Firstly, it confirms that the adsorption of tartaric acid does not simply create a local chiral environment around the individual adsorbed species, but that the whole surface is covered by an extended chiral array. Secondly, the molecule is bonded to Cu via the two carboxylate groups. This adsorption geometry facilitates intramolecular hydrogen-bonding between the OH groups at the chiral centres and the oxygens of the carboxylic group, leading to an asymmetric distortion in the molecule, which is enantiomeric-specific (the (R,R) enantiomer distorts one way and the (S,S) distorts in a configuration related by a mirror plane). The next level of chiral expression arises from the organisation of individual adsorbates at the surface. Rows of three bitartrate
molecules are formed on the surface. These rows go forward to self-assemble into long chains. This macroscopic surface organisation is therefore chiral. Furthermore, switching adsorbate flips the organisational chirality. In the final level of chiral expression, adsorption stress leads to the creation of vacant, chiral nanochannels. Each longer trimer chain is separated from the adjacent trimer chain by a vacant channel. These nanochannels are also directed along a non-symmetric direction and create therefore chiral spaces on Cu (Figure 1.11).

![Figure 1.11: Schematic illustration of (R,R)-TA and (S, S)-TA on Cu(110) at 77 °C. The short, thick line show extended hydrogen bonding interaction: (a) these interactions dictate the direction of the long chain growth and (b) they “weave together” the three molecular chains. (taken from reference [51])](image)

The nanochannels provide a confined environment within which reacting molecules can dock in preferential orientations forcing hydrogenation to occur at one reactant
face only. Therefore, the active site for these systems is described by groups of modifiers acting cooperatively to confer enantioselectivity to the reactive metal sites. To date, the only reported work investigating the adsorption (R,R)-TA on Ni(111) surfaces is that of Jones and Baddeley. [21, 46] Ni(111) is a more relevant system in the catalytic terms, as copper has not been used in the enantioselective hydrogenation of MAA and has generally found to be a poor hydrogenation catalyst overall. Furthermore, the most thermodynamically stable nanoparticles are truncated octahedral (111) and (100) facets. Therefore, Jones and Baddely studies represent the most realistic model study thus for the chiral modification of nickel nanoparticles.

Their studies show that the chiral adsorbate changes dynamically as temperature and coverage change (illustrated in Figure 1.12), as was in the case of Cu(110) system. They observed two distinct ordered adlayer structures, monotaartrate and bitartrate species that are stabilised by intermolecular hydrogen bonding interaction. These structures were observed for sub-monolayer coverages and were confined to relatively small area of the nickel surface (illustrated in Figure 1.12). [52] This is in contrast to the Cu(111) system. Humblot and co-workers reported no long-range ordered when (R,R)-TA was adsorbed on Ni(111). [52] Moreover, detailed studies have shown that the nickel surface atoms could undergo relaxation or reconstruction upon TA adsorption. The chirality of the reconstructed surface would be retained even if the tartaric acid adsorbate were removed; however no concrete evidence was presented by Humblot and co-worker, to support such theories. [52] TA modification of nickel catalysts is a corrosive process resulting in the leaching of nickel into the modifier solution. The nickel atoms are effectively etched, thereby producing a nickel tartrate species as suggested by Studer and co-worker. [29, 53] Taking the above-mentioned into consideration, it is plausible that a chiral arrangement of metal atoms may result in enantioselectivity.

As the chiral modification of nickel catalysts is carried out in aqueous solutions and in air, studies over oxidised Ni(111) surfaces have been carried out by Jones and Baddely. [10] The interaction of tartrate with pre-oxidised Ni particles may facilitate etching of Ni from the surface. This fact could reveal chiral arrangements of Ni responsible for the enantioselectivity during catalysis. Interestingly, they also found that the adsorption of (R,R)-TA on oxidised nickel surfaces has a decomposition
temperature \( \sim 143 \) °C higher than on clean Ni(111). This suggests that the tartrate species is more thermodynamically stable on oxidised nickel.

**Figure 1.12:** The chemical nature adopted by (R,R)-TA molecules on the Ni(110) surface as a function of temperature and coverage. [54]

### 1.8.2. Understanding the Bonding of the Reactant MAA to Modified Ni

MAA can exist in the diketo- form or as an enol- (illustrated in Figure 1.13). The latter species is stabilised by the possibility of the formation of a six membered ring via hydrogen bonding between the OH group of the enol and the carbonyl group of the ester moiety. To date, the only reported work investigating the adsorption of β-ketoesters on Ni surfaces is that of Jones and Baddeley. [55, 56] MAA was found to adsorb intact on Ni(111) at 27 °C but no ordered structures were observed. MAA is stable on nickel surfaces up to its decomposition temperature of \( \sim 127 \) °C. When MAA is adsorbed (at 27 °C) onto Ni(111) surface that has been pre-covered with a saturated dose of (R,R)-TA displays a low sticking probability. This is of huge importance as it questions the role of ordered modifiers in the nickel system and casts doubt on the application of the template model to this system.
Adsorption of MAA at low coverage of $(R,R)$-TA on Ni(111) is within areas of disordered tartrate species by the displacement of CO from the surface. The presence of CO disrupts the intermolecular bonding between tartrate species and is possibly responsible for the lack of order in the adlayers at low coverage. Two ordered structures were detected upon the co-adsorption of MAA, neither structures were previously observed in the adsorption of $(R,R)$-TA or MAA individually. Jones and Baddeley propose that at lower coverages, MAA rearranges the initially disordered tartrate species into an ordered array held together by intermolecular interactions between the ketone group of MAA and an α-hydroxy group of $(R,R)$-TA. Asymmetry in the MAA related feature, coupled with the fact that the ketone group forms stronger H-bonds than the ester group point to MAA geometry as shown in Figure 1.14(Left). Each MAA in the ordered structure appears to be equivalent. Attack by adsorbed H to the carbonyl bond of MAA would result in the formation of (R)-methyl-3-hydroxybutyrate (R-MHB), which is the preferred product in the heterogeneous catalytic reaction. If this model existed on the nickel nanoparticles, under catalytic conditions, this could explain the observed enantioselectivity. Conversely, the second structure at a higher coverage ((Figure 1.14(Right)) is proposed to contain four bitartrate species sitting in the corners of the unit cell with two MAA molecules fitting in the centre. If the unit cell consists of two MAA molecules of opposite faces, hydrogenation would yield a racemic product. Their data also suggest that at high coverage, the MAA species are adsorbed such that the molecular plane is tilted with respect to the surface, in contrast to the low coverage parallel geometry. If the molecular plane is exactly perpendicular to the surface, hydrogenation would be expected to result in the production of a racemic mixture of S- and R-MHB. This suggest that Ni catalysts being strongly dependent on the relative supply of H₂ and MAA to the catalyst surface.

Figure 1.13: Molecular structure of the diketo and enol tautomer of MAA.
Jones and co-worker investigated the adsorption of \((R,R)\)-TA onto Ni(111) as a function of pH and temperature. [56] They found surfaces from solution results in the formation of nickel tartrate at low pH and nickel and/or sodium tartrate at high pH. Of particular interest is that several mL of nickel tartrate is formed and this is indicative of extensive etching of the nickel surface. After washing (analogous to the modification procedure), the Ni(111) surface contains submonolayer quantities of the adsorbate \((R,R)\)-TA. At 77 °C, the washed/ modified surface displays larger amounts of hydrogen tartrate than at 27 °C. When the aforementioned surfaces are exposed to MAA, the presence of the protonated tartrate species correlates with an enhancement in the diketone- to enol- tautomeric ratio of MAA. Addition of NaBr into the modification/ washing solution resulted in an increase in the diketone- to enol ratio, which suggests that sodium bromide stabilise the diketone- tautomer of MAA. [56] This indicates that the key to optimising enantioselectivity of the catalytic process may lie with control over the tautomeric form present on the surface.
1.8.3. **Summary of Proposed Mechanism**

The precise pathway of the reaction and the mechanism of this enantioselective control have, however, not been yet verified; though several models of the modified surface have been proposed to explain the activity. [55, 57, 58] One possible explanation being a two-point hydrogen-bonding (H-bonding) model in which the protons of the hydroxyl groups of the tartaric acid H-bond to the β-ketoester or β-diketone oxygen atoms. This arrangement sterically favours the adsorption of one β-ketoester conformer over the other, thus resulting in enantioselective hydrogenation (Figure 1.15). [50, 55]

![Diagram of enantioselectivity over TA modified RNi in the hydrogenation of MAA.](image)

**Figure 1.15:** Mode of enantioselectivity over TA modified RNi in the hydrogenation of MAA.

The model shown in Figure 1.15 also explains both of the diastereoisomers formed in the chiral dehydrogenation of acetylacetonate. [59] Furthermore it accounts for the hydrogenation of pro-chiral ketones containing sterically hindered alkyl groups, which can form only one hydrogen bond, with the net result being a very striking reversal of enantioselectivity. The hydrogenation of MAA in this conformation would result in the R-form of MHB. An alternative proposed model involves the formation of 2-dimensional chiral co-crystalline domains on the metal surface formed by the propensity of the chiral adsorbate molecules to self-assemble into
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ordered structures. [21] This template surface model is a reasonable one when used in relation to extended surfaces (for example single crystals or the larger nanoparticles used in this study) but may reach limitations on very small nanoparticles due to limited terrace widths.

All of these admirable attempts to further understand the active site in TA-Ni catalysts for the hydrogenation of MAA have given another dimension to the subject matter but no clear explanation of the catalytic phenomena has been proposed which would bring this into light.

1.9. Aims and Objectives

The main aim of this project is to investigate the effect of the enantioselective hydrogenation of β-keto-esters (methylacetoacetate) over supported and unsupported nickel catalysts in the presence of (R,R)-tartaric acid and sodium bromide co-modifier. These investigations are carried out with the aim of understanding how this catalytic system works mainly the interaction of substrate and chiral modifier at the metal surface, with the goal of extending its applicability to other types of compounds.

The specific aims of the project can thus be summarised as follow(s):

- To examine the relevant literature on enantioselective heterogeneous hydrogenation nickel catalysis.
- To provide a brief overview of the characterisation techniques utilized in this research project.
- To synthesise pure nickel nanoparticles with controllable size and shape.
- To examine the morphology, structure and composition of synthesised Ni materials obtained by Powder X-ray Diffraction (P-XRD), Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM).
- To research the catalytic properties of all of the materials in the hydrogenation of Methyl acetoacetate (MAA).
  ✓ To optimise the variables affecting enantiomeric excess (ee) during chiral modification such as pH, temperature, time and concentration of modifier.
To optimise the variables affecting enantiomeric excess (ee) during hydrogenation such as H₂ pressure, temperature, time and concentration of modifier.

- To analyses the post-hydrogenated solutions to obtain ee values using gas chromatography with flame ionization detector (GC).
- To analyse the post-modifier solutions by atomic absorption spectroscopy (AAS) to determine the extent of TA adsorbed onto and Ni leached from the solids.

Chapter 2 describes the techniques used to characterise the materials. The two synthesis methods, namely microemulsion and reduction for the production of nickel nanoparticles and their results are discussed in Chapter 3 and the use of Raney nickel in the hydrogenation of MAA is explored in Chapter 4. Chapter 5 describes the use of supported and unsupported Ni nanoparticles in hydrogenation of MAA. Finally, conclusions and future work direction are presented in Chapter 6.
Chapter 2

2. Materials and Methods

2.1. Materials

All the chemicals and solvents used in the synthesis of nickel nano-particles were purchased from Sigma-Aldrich (UK) and used without any further purification. They include: nickel chloride (NiCl$_2$) 98 % ( RMM = 129.60, ρ = 3.55 g/ml), hydrazine monohydrate (N$_2$H$_4$H$_2$O) 64-65 % N$_2$H$_4$ (RMM = 50.06, ρ = 1.03 g/ml), sodium-hydroxide (NaOH) ≥ 98 % (RMM = 40.00), acetone (CH$_3$CO) ≥ 99.9 % (RMM = 58.08, ρ = 0.791 g/ml), hydroxyethyl carboxymethyl cellulose (HECMC) (0.06-0.50 mol hydroxyethyl per mol cellulose, 8 wt. % hydroxyethyl, 26 wt. % methoxy, 1.3-2.2 mol methyl per mol cellulose), cetyltrimethylammonium bromide (CTAB) ≥ 98 % ( RMM = 364.45), hexanol (C$_6$H$_{14}$O) ≥ 98 % (RMM = 102.17, ρ = 0.814 g/ml), ammonia solution (NH$_4$OH 28-30 %, NH$_3$) (RMM = 35.05, ρ = 0.9 g/ml), dopamine chloride (C$_8$H$_{12}$C$_1$NO$_2$), powder silicon dioxide (SiO$_2$) (RMM = 60.08, ρ = 2.2-2.6 g/ml), colloidal silica (30 wt. % suspension in H$_2$O) (RMM = 60.08, ρ = 1.22 g/ml), methanol (CH$_3$OH) ≥ 99.5 % (RMM = 32.04, ρ = 0.79 g/ml), propanol (C$_3$H$_6$OH) ≥ 99.5 (RMM = 60.10, ρ = 0.79 g/ml), Toluene ≥ 99 % (RMM = 92.14, ρ = 0.87 g/ml), decane ≥ 99 % (RMM = 142.28, ρ = 0.73 g/ml), tartaric acid (HO$_2$CCH(OH)CH(OH)CO$_2$H) ≥ 99.5 % (RMM = 150.09) (R)-methyl-3-hydroxybutyrate 99 % ( RMM = 118.13, ρ = 1.06 g/ml), (S)-methyl-3-hydroxybutyrate and methyl acetoacetate ≥ 99 % (RMM = 116.12, ρ = 1.08 g/ml).

2.2. Methods

The size distribution, compositions, and properties of metallic nanoparticles can be characterised in a variety of ways. The primary characterisation methods used in this report were Powder X-Ray Diffraction (PXRD), Scanning Electron Microscope (SEM) and Transmission Electron Microscopy (TEM).

To ensure the preparation method chosen produced active catalyst for the hydrogenation of the β-ketoester (methylacetoacetate), Gas Chromatography (GC)
with a Restek Rt-γDEXsa™ chiral column was used to analyze the products produced after the hydrogenation and to separate the different enantiomers.

In this chapter all the instruments used in the characterisation of nickel nanoparticles are explained with the background knowledge of the techniques and the analysis of the reaction mixtures.

2.2.1. Powder X-ray Diffraction

2.2.1.1. Background Theory

Distances between atoms or ions in a solid are typically in the region of angstroms so are comparable to the wavelength of X-rays produced from metals by bombardment with high-energy electrons. Thus the diffraction of X-rays by solids will occur.

Generations of X-Rays

X-rays are a form of electromagnetic radiation with wavelengths in the range of 0.01 to 10 nm, which are located in between gamma rays and ultraviolet rays in the electromagnetic spectrum. The discovery of X-rays radiation was made by a German physicist, Wilhelm Röntgen, in 1895 for which he was awarded the first Noble prize in Physics in 1901. [60]

An electrically heated filament, usually tungsten, emits electrons, which are accelerated by a high potential difference (20-50 kV) and allowed to strike a metal (commonly Cr, Fe, Cu, Mo or Ag) (Figure 2.1(a)). When an electron beam of energy around strikes a metal target, two different processes produce X-rays. In one process, the deceleration of beam electrons from collisions with the target produces a broad continuum of radiation called bremsstrahlung (braking radiation) having a short wavelength limit that arises because the energy of the photon $hc/\lambda$ can be no larger than the kinetic energy of the electron. In the other process, beam electrons knock atomic electrons in the target out of inner shells. When electrons from higher shells fall into the vacant inner shells, a series of discrete X-rays lines characteristic of the target material are emitted as depicted in Figure 2.1(b). [60-62]
The description above has shown that an X-ray source will give a number of wavelengths of X-rays. However, monochromatic radiation (single X-ray wavelength) is required to carry out a diffraction measurement and so it is necessary to “filter out” the other wavelengths. This may be achieved by using a crystal monochromator in which the X-ray beam strikes from a single crystal at a fixed orientation and by adjusting $\theta$ it is therefore possible to select one wavelength from the X-ray spectrum. Normally the most intense $K\alpha$ is used. A second way of selecting only the desired wavelength from the X-ray beam is to use a filter made of a thin metal foil of the element adjacent (Z-1) in the Periodic Table; for example nickel effectively filters out the majority of bremsstrahlung radiation and, more importantly, lines such as $K\beta$ from the copper X-ray spectrum; niobium is used for molybdenum. The X-ray beam emerging from the filter is thus almost monochromatic, consisting mainly of $K\alpha$ radiation. Due to the closeness of the $K\alpha_1$ and $K\alpha_2$ peaks it is not easy to separate them and typically the “monochromatic” X-ray beam will contain both. This does not, however, prove to be a serious problem experimentally.

**Figure 2.1:** (a) Section through an X-ray tube; (b) the X-ray emission spectrum, reproduced from reference. [63]
**Diffraction of X-rays**

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg’s Law. [60, 62]

![Diagram of Bragg's Law](image)

**Figure 2.2: Pictorial view of Bragg’s Law. [60, 62]**

The incident X-ray wave is reflected secularly (mirror-like) as it leaves the crystal planes, but most of the wave energy continues through to subsequent planes where additional reflected waves are produced. Then, as shown in the ray diagram of Figure 2.2 where the plane spacing is denoted d, the path length difference for waves reflected from successive planes is 2d sinθ. Note that the scattering angle (the angle between the original and outgoing rays) is 20.

Constructive interference of the reflected waves occurs when this distance is an integral of the wavelength. The Bragg condition for the angles of the diffraction peaks is thus:

\[ 2d \sin \theta = n\lambda \quad \text{(Equation 1.1)} \]

where n is an integer called the order of diffraction. Note also that the lattice planes, i.e., the crystal, must be properly oriented for the reflection to occur. This aspect of X-ray diffraction is sometimes used to orient single crystals and determine crystal axes.
When \( n=1 \), the reflection are called first order, when \( n=2 \) the reflections are second order and so on. However, the Bragg equation for a second order reflection from a set of planes is:

\[
2\lambda = 2d \sin \theta \quad \text{(Equation 2.2)}
\]

**Equation 2.2** represents a first order reflection from a set of planes with inter-planar spacing \( d/2 \). The set planes with inter-planar spacing \( d/2 \) have Miller indices \( 2h \ 2k \ 2l \). Therefore, the second order reflection from \( hkl \) is indistinguishable from the first order reflection from \( 2h \ 2k \ 2l \), and the Bragg equation may be written more simply as

\[
\lambda = 2d \sin \theta \quad \text{(Equation 2.3)}
\]

**Diffraction of X-rays by Powder**

A finely ground crystalline powder sample contains a very large number of small crystals, known as crystallites, which are oriented randomly to one another. If such a sample is placed in the path of a monochromatic X-ray beam, diffraction will occur from planes in those crystallites which happen to be oriented at the correct angle to fulfill the Bragg condition. The effect of this is that each lattice spacing in the crystal will give rise to a cone of diffraction from a single crystallite within the powder sample. With a large number of crystallite these dots join together to form the cone as shown in **Figure 2.3**. [64]

![Figure 2.3: Cones produced by a powder diffraction experiment.](image)
In order to obtain useful X-ray powder diffraction data the positions of the various diffraction cones need to be determined. This can be done in two ways, by using the Debye-Scherrer photographic film or by using an X-ray sensitive detector. In both cases the idea is to determine the diffraction angle, \(2\theta\), of the various cones. The photographic method makes use of a X-ray camera, which is a very simple way of collecting powder X-ray diffraction data. The other method makes use of a X-ray sensitive detector, such as a scintillation counter, to record the angle and the intensity of the diffracted beams, which are plotted as intensity against \(2\theta\) (Figure 2.4).

![Figure 2.4: X-ray profile of Ni nanoparticles.](image)

**Uses of Powder X-Ray Diffraction**

The most widespread use of X-ray powder diffraction, and the focus here, is for the identification of unknown compounds by their diffraction pattern and crystallite size analysis. Described below are some specific uses that will be covered in this report.

- **Identification of Unknown and Phase purity**

  When the powder diffraction pattern of the sample has been measured and both the d spacing and intensity of the lines recorded, these can be matched against the patterns of known compounds from Inorganic Crystal Structure Database (ICSD) file. The identification of compounds using powder diffraction is useful for quantitative analysis, such as mixtures of small crystals in geological samples. It also gives a
rough check of the purity of a sample; however the powder diffraction does not detect amorphous products or impurities of less than 5%. [60] Powder diffraction can also confirm whether two similar compounds, whether one metal substitute for another for instance, have an isomorphs structure.

- **Crystallite Size**

X-ray diffraction is a convenient method for determining the mean size of single-crystal nanoparticles or crystallites in nanocrystalline bulk materials. The first scientist to investigate the effect of limited particle size on X-ray diffraction patterns was Paul Scherrer, who published his results in a paper that included what became known as the Scherrer equation. [65, 66] Scherrer derived his equation for the ideal condition of a perfectly parallel, infinitely narrow and monochromatic X-ray beam incident on a monodisperse powder of cube-shaped crystallites. The equation is

\[
D = \frac{K \lambda}{B \cos \theta}
\]  

*(Equation 2.4)*

where \( D_{hkl} \) is the crystallite size in the direction perpendicular to the lattice planes, \( hkl \) are the Miller indices of the planes being analysed, \( K \) is a numerical factor frequently referred to as the crystallite-shape factor, [66] \( \lambda \) is the wavelength of the X-rays, and \( B \) is the line broadening in radians which is calculated by the Warren's formula:

\[
B^2 = (B_m^2 - B_s^2)
\]  

*(Equation 2.5)*

where \( B_m \) is the full width at half maxium of the sample and \( B_s \) is the full width half maxium of a standard quartz sample with a gain size of around 2 µm. In addition to depending on the crystallite shape, the numerical factor \( K \) also depends on the definitions of the average crystallite size. The structure of the formula is not affected by these definitions, but the numerical value of \( K \) may change appreciably. Using the above definition of \( D \), and in the absence of detailed shape information, \( K=0.9 \) is a good approximation. [65]

It is important to note that Scherrer’s equation can only be applied for average sizes
up to about 100–200 nm (depending on the instrument, sample and signal-to-noise ratio), because diffraction-peak broadening decreases with increasing crystallite size and it becomes difficult to separate the peak broadening due to crystallite size from the broadening due to other factors.

It is also important to note that the size determined by diffraction methods corresponds to the magnitude of the coherent crystal regions, that is, to regions where the periodic arrangement of the atoms is perfect and continuous. Therefore, the size obtained by diffraction cannot always be simply compared to the sizes determined by other techniques.

- **Following Reaction and Phase Diagrams**

  Powder X-ray diffraction is also a useful method for following the progress of a solid state reaction and determining mechanisms, and for determining phase diagrams. By collecting the x-ray pattern at regular intervals as the sample is heated on a special stage in the diffractometer, evolving phases can be seen as new lines which appear in the pattern, with a corresponding decrease in the lines due to the starting material(s). A careful comparison of the intensities of particular lines using standards, not only enable the different phases be identified but also the proportions of different phases to be determined so that a phase diagram can be constructed.

**2.2.1.2. Experimental and Sample preparation**

The phases present in the products were identified from their powder X-ray diffraction (PXRD) patterns, which were collected on a Bruker D8 Diffractometer using Ni filtered Cu Kα radiation (λ = 1.540598 Å) operated at a voltage of 40 kV and a current of 30 mV.

The measurements were carried out with a step scan mode: step size = 0.02 [20], time per step = 18.87 sec, in the range of 50-140 2θ and total run time of 2 h. The goniometer was calibrated with a cubic α-quartz standard (a = 5.4309 Å). Corrections for systematic deviation in 2θ were applied. Profiles were compared with the Joint Committee for Powder Diffraction Standards (JCPDS) from the International Centre for Diffraction Data (ICDD) database. From the full-width at
half-maximum of the Ni (111) peak, the mean crystallite size of the Ni particles was calculated using Scherrer’s equation.

2.2.2. Scanning Electron Microscopy (SEM)

2.2.2.1. Background Theory

An electron microscope operates on the same basic principles as the optical/light microscope but uses electrons instead of light. What can be seen with an optical microscope is limited by the wavelength of light. Electron microscopies use electrons as "light source" and their much lower wavelength makes it possible to get a resolution a thousand times better than with an optical microscope. The electron beam is produced by heating a tungsten filament, and focused by magnetic fields in a high vacuum where the vacuum prevents interaction of the beam with any extraneous particles in the atmosphere. The sample is placed within a sample chamber mounted on a platform at a set height, in order for the electron beam to be in line with the detector.

When the electrons strikes the sample, a variety of signals are generated, and it is the detection of specific signals which produces an image or a sample’s element compositions. The three signals which provide the greatest amount of information in SEM are the secondary electron, backscattered electrons, and X-rays.

The secondary electrons are emitted from the atoms occupying the top surface and produce a readily interpretable image of the surface. The contrast in the image is determined by the sample morphology.

Backscatter electrons are primary beam electrons which are reflected from the atoms in the solid. The contrast in the image produced is determined by the atomic number of the elements in the sample.

The interaction of the primary beam with atoms in the sample causes shell transitions which result in the emission of an x-rays. The emitted x-ray has an energy characteristic of the parent element. Detection and measurement of the energy permits elemental analysis (Energy Dispersive X-ray Spectroscopy or EDS). X-rays
can also be used to form maps or line profiles, showing the elemental distribution in a sample surface.

Figure 2.5: Schematic diagram of the SEM process.[67]

2.2.2.2. Experimental and Sample Preparation
Nickel nanoparticles were characterised for their shape and elemental compositions with a Scanning Electron Microscope (JEOL JSM-7100F). The microscope is fitted with a Thermo Scientific triple analysis system, featuring an UltraDry EDS detector, a MagnaRay parallel beam WDS spectrometer and a QuasOr system for electron backscattered diffraction (EBSD). All three analytical functions are integrated into a single Noran System 7 data system to allow integration between three complementary techniques. All samples were coated to a depth of 6 nm with a thin film of gold on their surface using a sputtering device.

2.2.3. Transmission Electron Microscopy (TEM)
2.2.3.1. Background Theory
A TEM works in a similar way to the previously mentioned SEM instrument. In TEM, a focused, high energy electron beam is transmitted through an ultra-thin sample to provide important information about morphology, crystallography, particle
size, and distribution and atomic-resolution lattice images. The dark field (DF) and a bright field (BF) give images in nanoscale.

An "electron gun" at the top of the microscope emits the electrons that travel through vacuum in the column of the microscope. Instead of glass lenses focusing the light in the light microscope, the TEM uses electromagnetic lenses to focus the electrons into a very thin beam. The electron beam then travels through the specimen and depending on the density of the material present, some of the electrons are scattered and disappear from the beam. The image is formed when the electron beam strikes a phosphor screen or charge coupled device (CCD) camera, with its different parts displayed in varied darkness according to their density.

![Image of TEM instrument with schematic diagram](image_url)

**Figure 2.6:** The image of the TEM instrument on the left hand side with a schematic diagram on the right. [68]

### 2.2.3.2. Experimental and Sample Preparation

The Philips CM200 transmission electron microscope (TEM) operating at up to 200 kV is a very versatile microscope. The computer controlled eucentric sample holder can tilt from -45º to +45º along the X axis and -30º to +30º along the Y axis making it ideal for diffraction work. The CM200 can also achieve a line resolution of 0.14nm with the same holder, good as a dedicated High-resolution transmission electron
microscopy (HRTEM). Furthermore the attached ultra-thin window Energy-dispersive X-ray spectroscopy (EDX) detector and Electron Energy Loss Spectrometer (EELS) make the CM200 a true analytical microscope.

In order to measure the particle size and morphology of the Ni nano-particles using TEM the sample need to be dispersed before deposition onto carbon coated Cu grids. First, few milligram of each sample was added into acetone, then it was sonicatated (Branson Sonifier W-450D, ½ inch tip, 70% amplitude, 10 s pulse, 1 s pause) for 5 minutes in an ice bath. Then a tiny drop of the resulting sample suspension was placed onto a carbon coated Cu grid and allowed to dry in air. After solvent was evaporated, the sample was transferred into the TEM sample holder for TEM measurement.

2.2.4. Scanning Transmission X-ray Microscopy (STMX)

2.2.4.1. Background Theory

A simplified view of STXM is shown in Figure 2.7. It generates microscopic images of a thin section of specimen by monitoring the X-ray signal transmitted through the specimen as it is raster-scanned at the focused X-ray beam. The flux of transmitted X-rays is measured to obtain the image intensity. This technique has been developed and applied to the life sciences. [69] X-ray absorption spectra can be obtained from microscopic features on the sectioned sample. In materials science X-ray absorption spectra can be characteristic of the chemical state of atomic species and the structure of crystalline materials. [69]

![Diagram of STXM process](image)

*Figure 2.7: Schematic diagram of the STXM process. [70]*
The STXM at the PolLux beamline (X07DA) of the Swiss Light Source (SLS), Paul Scherrer Institut, Villigen, Switzerland, which can record images with better than 40 nm spatial resolution, and NEXAFS spectra from 250 - 1600 eV with an energy resolution (E/ΔE) of about 3000.

**NEXAFS: Near-Edge x-ray absorption fine structure**

As an X-ray phases through matter, it is absorbed to an extent which depends on the nature of the substance, the thickness of the sample and the density of the sample. The absorbed photons cause excitation of the inner shell electrons of atoms in the substances. These excited inner shell (core) electrons can be promoted to unoccupied energy levels to form a short lived excited state or they can be removed completely to form an ionized state. Traditionally, X-ray absorption spectroscopy was described in terms of absorption edges which are the one sets of inner-shell ionization. There is an edge associated with each inner shell energy level of an atom, such that all elements have X-ray absorption edge in the soft X-ray energy range (250-1600 eV). The amount of a particular element can be determined quantitively from the difference in the X-ray absorption just above and just below its absorption edge.

### 2.2.4.2. Experimental and Sample Preparation

The PolLux microscope operates in transmission geometry with a zone plate (outer zone width of 35 nm) used to focus monochromatic X-rays from the beamline (bending magnet beamline with monochromator and higher order suppressor [3X]) onto the sample. The excellent spatial resolution afforded by the PolLux STXM beamline of the Swiss Light Source to locate individual nanoparticles and subsequently measure the Ni L$_{2,3}$-edge NEXAFS spectra as well as the C K-edge NEXAFS spectra of the adsorbed tartaric acid molecules.

Ni nanoparticles for STXM analysis were prepared using the chemical reduction route. It was prepared by adding methyl 2-hydroxyethylcellulose (0.2 wt.%) to 1.2 M aqueous NiCl$_2$ solution at 90 °C. NaOH solution (20 wt.%) was added drop-wise until a pH of 11 was achieved. Prior to the addition of the 6.2 M N$_2$H$_4$·H$_2$O (the reduction step) silicon nitride windows were immersed into the reaction mixture until the reduction of the metal salt was complete. Two types of window were used: either ‘clean’ Si$_3$N$_4$ window (Silson Ltd, UK) or Si$_3$N$_4$ windows that had previously been
modified with 10 nm of alumina applied from an aluminium evaporator source located in a vacuum system with an O₂ partial pressure of ~1 × 10⁻⁶ mbar. The alumina coated windows were further heated in air for 12 hrs to ensure that the aluminium was fully oxidised and also to relieve lattice strain that could damage the membrane, the ‘clean’ windows were used without further treatment.

Finally, the product was washed with distilled water and ethanol several times to remove impurities, and then dried at room temperature. Tartaric acid was adsorbed onto the samples, when required, from aqueous solution. A single droplet of 0.5 M (R,R)-tartaric acid (pH=1.8, T=298 K) was placed onto the sample window. The solution was allowed to sit for 3 min and then the window was washed three times in clean Milli-Q water before drying followed by insertion into the vacuum chamber and placing the sample in to the STXM chamber.

2.2.5. Gas Chromatography (GC)

2.2.5.1. Background Theory

The main components to consider with GC are; carrier gas, flow control, sample inlet and devices, columns, temperature controlled areas and detectors. Figure 2.9 shows a basic schematic of GC with a detector. This technique has become extremely popular because of the rapidity and ease with which complex mixtures can be analyzed, and the very small sample required and also because of the flexibility, reliability and relative low cost of the instrumentation required.

![Figure 2.9: Sample on Si₃N₄ window.](image)

![Figure 2.10: Schematic diagram of GC. [71]](image)
The sample solution is injected into the GC inlet where it is vaporized and swept onto a chromatographic column by the carrier gas (helium). As carrier gas sweeps the analyte molecules through the column, this motion is inhibited by the adsorption of the analyte molecules either onto the column walls or onto packing materials in the column. There are two types of column used in GC: packed and capillary. The main difference between them relies in their internal diameters.

The rate which the molecules progress along the column depends on the strength of adsorption, which in turn depends on the type of molecule and on the stationary phase materials. Since each type of molecule has a different rate of progression, the various component of the analyte mixture are separated as they progress along the column and reach the end of the column at different times (retention time). A detector is used to monitor the outlet stream from the column; thus, the time at which each component reaches the outlet and the amount of that component can be determined.

Generally, substances are identified (qualitatively) by the order in which they elute from the column and by the retention time of the analyte in the column. The most common detectors are flame ionization detectors (FID) and thermal conductivity detectors (TCD). [72] TCD detects components with different thermal conductivity to the carrier gas. TCD is a non-destructive method, whereas FID is a destructive method. For most organic molecules, the sensitivity of the TCD is lower compared to the FID. [72]

Chromatographic data is presented as a chromatogram, which provides a spectrum of peaks for a sample representing the analytes present in a sample eluting from the column at different times. Retention time can be used to identify analytes if the method conditions are constant. The area under the peak is proportional to the amount of analyte present in the chromatogram. By integration, the concentration of an analyte in the original sample can be determined. Concentration can be calculated using a calibration curve created by finding the response for a series of concentrations of analyte, or by determining the relative response factor of an analyte. The relative response factor is the expected ratio of an analyte to an internal standard (or external standard) and is calculated by finding the response of a known
amount of analyte and a constant amount of internal standard (a chemical added to
the sample at a constant concentration, with a distinct retention time to the analyte).

2.2.5.2. Experimental and Sample Preparation
All the hydrogenated solution were analysed using the Agilent technologies gas
chromatograph instrument equipped with a FID detector and the Chiral Rt-YDex,TM
Column 30 m, 0.32 mm, ID 0.25 μm. The oven temperature was programmed from
90°C to 140°C ramping at 3 °C/minute, holding at the initial temperature (90°C) for
5 minutes. Conditions used in GC:

- Split ration ratio 100:1
- Injector 200°C
- Detector 200°C
- Flow rate 1 ml/min
- Velocity 22 cm/sec
- Dichloromethane (DCM) was run between each sample to ensure that the
column was clean for each sample

Whenever new samples were analysed, a gas chromatograph was always recorded
for a calibration solution that was made up of known concentration of MAA, R-
MHB and Decane (internal standard).

2.2.6. Flame Atomic Absorption Spectroscopy (FAAS)

2.2.6.1. Background Theory
Optical spectroscopy has origins back with Sir Isaac Newton with his observation of
sunlight through a prism resulting in coloured light. [73] Since then technology has
enabled scientists to observe specific range of absorption bands, which act like a
fingerprint for the element. In flame atomic absorption spectroscopy a liquid sample
is aspirated and mixed as an aerosol with combustible gasses (acetylene and air). The
mixture is ignited in a flame of temperature ranging from 2100 to 2800 °C. During
combustion, atoms of the element of interest in the sample are reduced to free,
unexcited ground state atoms, which absorb light at characteristic wavelengths. The
characteristic wavelengths are element specific. The wavelength, therefore, can be measured in order to determine which element has adsorbed the wavelength.

2.2.6.2. Experimental and Sample Preparation

Measurements of Ni leached out from the solid during chiral modification was carried out by AAS using PerkinElmer Analyst 400 atomic absorption spectrometer equipped with a Ni cathode lamp at $\lambda = 58$ nm. Calibration standards across a range of 1-10 ppm were prepared using Ni-solution containing 1000 ppm Ni. Hydrogenated solutions were decanted from the solid catalyst and diluted according to linear calibration and detection limits.
3. **Synthesis of Nanoparticles**

Nickel nanoparticle powders with uniform size and shape have attracted increasing synthetic attention due to their potential technological applications such as chemical catalysts, conducting paints, rechargeable batteries, microwave absorbing materials and magnetic recording media. [74-78]

The first stage of synthesis was to reproduce methodologies from selected literature, which claimed to have produced pure Ni nanoparticles. A number of methods have been used for the production of Ni nanoparticles. [79-84] Recently, several popular methods including coprecipitation, microemulsion, thermal decomposition, solvothermal synthesis and sol gel synthesis have been employed in the production of nanoparticles. [85-89] The conventional methodologies tested were microemulsion-based technology and reduction.

The aim of this part of the work is producing nickel using a microemulsion and reduction route. For the microemulsion method both the ‘two-step microemulsion’ and ‘one-step microemulsion’ methods were employed to synthesise the nickel nanoparticles for method comparison.

3.1. **Microemulsion method**

3.1.1. **Introduction**

The term microemulsion was first introduced as early as the 1940s by Hoar and Schulman who generated a clear single-phase solution by titrating a milky emulsion with hexanol. [82] They prepared the first microemulsion by dispersing oil in an aqueous surfactants solution and adding an alcohol as a co-surfactant, leading to a transparent stable formulation. In 1959 Schulman and co-workers subsequently coined the term microemulsion [82] and since then, microemulsions have found a wide range of applications, from oil recovery to synthesis of nanoparticles, as reported by Chhabra *et al.* in their review articles from 1997. [82]
Chapter 3

The idea of using microemulsion systems for catalyst preparation was first suggested by Gault in collaboration with Friberg. [89] Due to the specific structure of a microemulsion, it was expected to be a suitable environment for producing small metal nanoparticles of narrow size distribution as well as bimetallic particles of controlled composition. Since the first report on the use of microemulsions in the preparation of noble-metal catalysts in the early 1980s by Boutonnet et al. [82], the microemulsion technique has been widely used to prepare nanoparticles of numerous materials, including metals, metal sulfides and selenides, metal oxides and hydroxides and organic polymers. [82]

3.1.2. Microemulsion: Definition

A microemulsion is defined as a system of at least three components; an oily phase, an aqueous phase and a surface active species, so called surfactants. Sometimes a fourth component a co-surfactant can/must be present. Depending on the concentrations of the components the microstructure of the emulsion can vary from very tiny water droplets dispersed in oil phase (define as water/oil microemulsion) to oil droplets dispersed in a water phase (define as oil/water microemulsion). At high concentration of water, the internal structure of the microemulsion consists of small droplets in a continuous water phase (micelles). With increased oil concentration, a bicontinuous phase without any clearly defined shape is formed. At high concentration, the biocontinuous phase is transformed into a structure of small water droplets in a continuous oil phase (reverse micelles). The weight percent compositions at the end points of all these mixing are then plotted on a triangular coordinate to create a pseudo-ternary phase diagram, which illustrates different regions in it representing microemulsions and other types of entities as shown in Figure 3.1.

Surfactants are amphiphilic molecules that contain a nonpolar segment, commonly called “the tail” and a polar segment called “the head”. These properties place the surfactant molecules at the interface between two phases separating the polar and the non-polar domains producing a stabilised system. The concentration of the surfactant within the system is critical, if there is too little surfactant, the interface becomes unstable and a number of physical changes to the system are observed. They are;
1. flocculation: hydrolysed particles stick together;
2. sedimentation: flocculated particle fall out of suspension;
3. creaming: two liquids of different densities separate;
4. coalescence: phase separation.

At the point where micelles begin to form, the concentration of monomers will have reached a maximum in the solution. Any further increase in the total concentration of the surfactant will result in an increase in the number of micelles, but no significant change in the individual surfactant molecules that are in the system but are not part of a micelle.

The micelles not only act as microreactors for the processing reactions but also inhibit the excess aggregates of particles. As a result, the particles obtained in such medium are generally very fine and monodispersed.

![Figure 3.1: A comprehensive ternary phase diagram depicting various structure.](image)

3.1.3. Preparation of nanoparticles

From a nanoparticle-preparation point of view, the microemulsion system with an internal structure consisting of small droplets is the most interesting. The w/o microemulsion is of particular interest since it can be considered as tiny compartments made up of the hydrophilic moiety of the surfactant filled with water. In the hydrophilic interior of these droplets, a certain amount of water-soluble
material can be dissolved; for example, transition metal salts that then serve as precursor(s) for the final metal particles. As stated previously, this system is very sensitive to temperature due to the physical and chemical properties of its constituents. Therefore, it is of importance in the case of nanoparticle preparation to choose microemulsion systems which are stable at room temperature or at higher temperatures.

There are two main routes of preparation in order to obtain nanoparticles from w/o microemulsions are illustrated in Figure 3.2.

**Figure 3.2:** Modes of particle preparation from microemulsion: (a) two-step microemulsions: mixing of two microemulsions; (b) one-step microemulsion direct addition of precipitating (reducing) agent to the microemulsion. [82]

(a) **Two-step microemulsion:** by mixing two microemulsions, one is containing the precursor and the other precipitating agent.
(b) One-step microemulsion: by adding the precipitating agent directly to the microemulsion containing the metal precursor.

3.1.4. Experimental

Two-step microemulsion
For two-step microemulsion two separate microemulsion solutions were prepared; one microemulsion containing 18 ml of solubilizing aqueous NiCl\(_2\) (0.05 M) into a 27 ml CTAB and 55 ml n-hexanol mixture and another containing 0.5 ml N\(_2\)H\(_4\).H\(_2\)O (1.0 M) solution with the same component ratio of CTAB/n-hexanol as the NiCl\(_2\). After continuous stirring for 20 min, a homogenous and transparent solution was obtained. The pH of the microemulsion containing aqueous N\(_2\)H\(_4\).H\(_2\)O was adjusted to 12-13 with ammonium hydroxide. The preparation of nanoparticles was achieved by mixing the two microemulsion solutions at 73 °C and then stirred for 1 hour before adding the 0.175g SiO\(_2\) support. Once the support was added the mixed solution was heated and stirred for further hour at the same temperature to ensure the reaction had gone to completion. Finally, the metal nanoparticles were repeatedly washed with acetone, followed by drying overnight at room temperature. The crude product is a light purple powder.

One-step microemulsion
NiCl\(_2\) aqueous solution (0.05 M) was prepared by dissolving 0.116 g of NiCl\(_2\) in 18 ml de-ionised water, which was then slowly added into the mixture of 27 ml of CTAB and 55 ml n-hexanol under magnetic stirring, in which CTAB and n-hexanol were used as the surfactant and oil respectively. After continuous stirring for 20 min, a homogenous and transparent solution was obtained. The pH of the mixture was adjusted to 12-13 with ammonium hydroxide. Aqueous hydrazine monohydrate (1.0 M) was directly added to the microemulsion system. This allows the reduction of the metallic precursors to give metallic particles. The mixed solution was heated and stirred for 1 hour at 73 °C in an oil bath before adding the 0.175 g SiO\(_2\). Once the support was added the mixed solution was heated and stirred further for 1 hour at the same temperature to take the reaction to completion. Finally, the metal nanoparticles were repeatedly washed 3 times with 20 ml acetone, followed by drying overnight at room temperature in a desiccator. The crude product is a light purple powder.
3.1.5. Results and Discussion

In order to demonstrate the successful synthesis of pure nickel nanoparticles, samples were characterised initially with the powder X-ray diffraction for rapid conformation of the phases present and crystallite size analysis. The single phase samples were analysed for particle shape and size determination using scanning electron microscope (SEM) and transmission electron microscope (TEM).

3.1.5.1. Characterisation of Materials

The powder X-ray diffraction (P-XRD) pattern for pure cubic nickel (ICSD No. 00-004-0850) is shown in Figure 3.3. This represents the reference pattern to which all the other X-ray diffraction patterns were compared. The presence of any peaks not observed in the Nickel nanoparticles pattern could indicate impurities in the sample. A significantly different pattern would indicate the presence of a different phase which had been formed preferentially, for example, a sample containing nickel oxides (NiO, Ni₂O₃) or nickel hydroxides (Ni(OH)₂). The broadening of the diffraction peaks would indicate the reduced size of the particles.

In order to reveal the crystal structure of the commercially available nickel nanoparticles, X-ray diffraction was conducted and presented in Figure 3.4 (a). It can be seen that the XRD pattern exhibits three well-resolved peaks at 2θ = 44.5°, 51.8°, 76.4°, 92.9° and 98.3° were indexed as the (111), (200), (220), (311) and (222) planes of the face centred- cubic (fcc) nickel, respectively, according to a standard Nickel (ICSD No. 00-004-0850). No impurity diffraction peaks, such as nickel oxides or nickel hydroxides, were detected, indicating that phase was pure nickel metal. The crystallite size of the nickel nanoparticles can be calculated from the major diffraction peak (111) using the Scherrer's equation (Chapter 2 / Section 2.1.1). The grain size of the nickel nanoparticles is calculated to be 43 nm according to Equation 2.4, which agrees well with the SEM image shown in the Figure 3.4 (b).
Table 3.1: Peaks list for the reference pattern of pure nickel (ICSD No. 00-004-0850).

<table>
<thead>
<tr>
<th>Lattice indices</th>
<th>d[A]</th>
<th>2θ [deg]</th>
<th>Intensity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H    K   L</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 1 1</td>
<td>2.0</td>
<td>45</td>
<td>100</td>
</tr>
<tr>
<td>2 0 0</td>
<td>1.8</td>
<td>52</td>
<td>42</td>
</tr>
<tr>
<td>2 2 0</td>
<td>1.3</td>
<td>77</td>
<td>21</td>
</tr>
<tr>
<td>3 1 1</td>
<td>1.1</td>
<td>93</td>
<td>20</td>
</tr>
<tr>
<td>2 2 2</td>
<td>1.0</td>
<td>98</td>
<td>7</td>
</tr>
<tr>
<td>4 0 0</td>
<td>0.9</td>
<td>122</td>
<td>4</td>
</tr>
<tr>
<td>3 3 1</td>
<td>0.8</td>
<td>145</td>
<td>14</td>
</tr>
<tr>
<td>4 2 0</td>
<td>0.8</td>
<td>156</td>
<td>15</td>
</tr>
</tbody>
</table>

Figure 3.3: Reference XRD pattern of pure nickel (ICSD No. 00-004-0850).
3.1.5.2. XRD Characterisation

The microemulsion method was intended to produce pure nickel nanoparticles with SiO$_2$ support from the selected microemulsion compositions within the water/CTAB/n-hexanol as described in **Section 3.1.4**. The first few attempts at repeating the microemulsion method carried out by Chen and Wu [90], gave a very low yield that was insufficient to perform XRD. By changing the reactions time from 1 hour to 2 hours under reflux conditions a higher yield was produced. Addition of an inert support (SiO$_2$) made the sample sufficient to do all the required analysis.

**Figure 3.4:** (a) The P-XRD pattern (b) SEM of the commercially available nickel nanoparticles with grain size 43.03 nm
Figure 3.5: The P-XRD pattern of the samples prepared in the two-step microemulsion method with a proportion of: \([\text{NiCl}_2] = 0.05 \text{ M}\); \([\text{N}_2\text{H}_4\text{H}_2\text{O}] = 1.0 \text{ M}\); water/CTAB/n-hexanol = 18/27/55 (weight %); \(T = 73 \degree\text{C}\) (as produced).

Figure 3.5 shows the P-XRD pattern of the samples prepared in the two-step microemulsion method. There is complete lack of real peak except one from SiO₂, broad peak at 21° 2theta value. This suggests the catalyst prepared using the microemulsion method is covered with organic residues and has an amorphous structure. This was expected as surfactant molecules bind very strongly to metallic nanoparticles; the simple washing method using organic solvent wouldn’t remove the surfactants. As these organic residues reduce the activity of a catalyst, a commonly used method for cleaning a catalyst surface was introduced, namely calcination. The samples were dried at room temperature in a desiccator and then placed in a furnace at 180, 250, 300, 350 and 450 °C respectively ramped at 10 °C/minute, holding at the final temperature for 4 hrs under static air atmosphere then allowed to cool back to room temperature before doing the XRD analysis.

Figures 3.6 shows the effect of temperature on the removal of all the organic residues and crystallinity of the Ni nanoparticles material. The P-XRD diffractogram
confirms that longer times and/or higher temperatures during the calcination processes help to remove all the organic residues present in the catalyst surface and improve the crystallinity of the materials.

![XRD profile](image)

**Figure 3.6**: P-XRD studies over nickel nanoparticles prepared in the 'two-step microemulsion' method with a proportion of: \([\text{NiCl}_2] = 0.05 \text{ M}; [\text{N}_2\text{H}_4\text{H}_2\text{O}] = 1.0 \text{ M}; \text{water/CTAB/n-hexanol} = 18/27/55 \text{ (weight %)}; T = 73 ^\circ\text{C}.\) From bottom to top: as prepared, calcined at 180 ^\circ\text{C}, 250 ^\circ\text{C}, 350 ^\circ\text{C} and 450 ^\circ\text{C} for 4 hrs; (*) denotes peaks associated with the nickel phase.

Profiles were compared visually, as well as utilising the profile recorded by the International Centre for Diffraction Data (ICDD), for the confirmation of the right product and for crystallite size calculation (Table 3.2). The diffractrogram also confirmed the presence of NiO (ICDD No. 03-065-5745).
Table 3.2: Crystalline size the nickel nanoparticles prepared in the ‘one-step microemulsion’ method.

<table>
<thead>
<tr>
<th>Microemulsion composition (wt %)</th>
<th>2θ / deg</th>
<th>full-width at half-maximum ( \beta_{hl} / \text{deg} )</th>
<th>line broadening B / radian</th>
<th>crystallite size ( D_{hkl} / \text{nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water/CTAB/n-hexanol 18/27/55 (SiO(_2))</td>
<td>37.241</td>
<td>0.2293</td>
<td>0.00385</td>
<td>38</td>
</tr>
</tbody>
</table>

Figure 3.7: The P-XRD patterns of commercially available Nickel powder and samples prepared in the microemulsion (‘one and two-step microemulsions’) with a proportion of: \([\text{NiCl}_2]\) = 0.05 M; \([\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}]\) = 1.0 M; water/CTAB/n-hexanol = 18/27/55 (weight %); \( T = 73^\circ \text{C} \) (calcined at 450 °C).

Figure 3.7 shows the P-XRD patterns of ‘one-step’ and ‘two-step’ microemulsion synthesised nickel nanoparticles (calcined at 450 °C). The spectrum of the SiO\(_2\) support powder and commercial nickel nanoparticles are shown for comparison. The P-XRD spectrum of the synthesised Ni-nanoparticles shows low intensity but sharp peaks indicating that the samples were in crystalline form. On the other hand, P-XRD spectrum of the commercial nickel showed very sharp and intense peaks indicating high crystallinity and the presence of bigger crystallite size. The
diffraction peaks of the samples produced using both methods shifted toward lower 2θ values on the diffractogram in comparison to the nickel diffraction peaks. These peaks appearing at 2θ = 37.2°, 43.29°, 62.83°, 75.43° and 79.36° were indexed as the (111), (200), (220), (311) and (222) planes of the fcc nickel oxides, respectively.

3.2. Reduction Method

3.2.1. Introduction
A chemical reduction method usually involves the reduction of metal ions into free metal in the form of nanoparticles. In this chemical reduction method, hydrazine or alkali metal borohydride have been generally used as an external reducing agent. But in the case of alkali metal borohydride, borohydride ions are known to reduce metal cations to metal borides, particularly in aqueous systems. [91] On the other hand, hydrazine has more widely been used as reducing agent for the preparation of metal nanoparticles because of the pH and temperature dependent reducing ability of hydrazine, which allow controllable reduction rates.

3.2.2. Preparation of nanoparticles
The solution reduction route for the preparation of metal nanoparticles is of particular interest because of its simplicity, precise size control and low cost compared with other methods. [91] A high number of studies have been performed on the synthesis of nickel nanoparticles using hydrazine as a reducing agent in liquid phase processes, [92, 93] however, relatively few exist on its synthesis with controlled size by solution reduction method. Syukri et al. prepared Ni fine powder with the size range from 200 nm to 700 nm by sol-gel process using Ni(OAc)₂·4H₂O and methyl hydrazine as additive and reducing agent. [92] Abdel-Aal et al. have reported the synthesis of Ni particles in the range of 55-250 nm by solvothermal reduction method. [93] Chen and Wu reported Ni nanoparticles with the mean size of 4.2 nm by the reverse micelle technique. [90] Chen and Wu studied the effect of nickel chloride and hydrazine concentrations on particle size and produced Ni particles with controlled size of 9-12 nm. [94]

Ni nanoparticles were prepared by reduction process in aqueous solution using inexpensive metallic salt resources and hydrazine monohydrate as a reducing agent
at 60-90 °C. Methyl 2-hydroxyethyl cellulose was used as a surface modified and stabilising reagent to prevent the nanoparticles from coalescing.

### 3.2.3. Experimental

Ni nanoparticles were prepared by adding methyl 2-hydroxyethyl cellulose (0.2 wt. %) in 10 ml aqueous solution containing 0.8-0.075 M NiCl₂ while vigorously stirring. NaOH solution (20 wt. %) was added drop-wise until a pH of 11 was achieved. The resulting solution became cloudy green with a precipitate forming as soon as the pH reached \( \approx 7 \) and then solution thickened as more NaOH added to the solution mixture. From this point two different procedures were carried out depending on the intended use of the resulting nanoparticles. A) For Ni catalysts to be used for XRD analysis and high-pressure hydrogenation reactions: 6.2 M \( \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \) was added directly to the solution either with or without simultaneous addition of sufficient \( \alpha\)-\( \text{Al}_2\text{O}_3 \) to result in a 50% metal loading. B) For Ni catalysts to be used for STXM analysis different procedure is used, described in chapter 2, section 2.3.2. As the reduction reaction proceeded in both procedures, the green precipitate nickel chloride solution turned into blue, blue violet and then black, indicating the formation of metallic nickel. The mixture was kept in the thermostatic bath at 65-90 °C until black power precipitated completely. The solution was then allowed to cool in ambient conditions at room temperature. After cooling, the resulting black fluffy product floating on the solution was collected using a magnetic bar. Then it was washed 3 times thoroughly with 1:1 mixture of deionized water and ethanol under centrifuge at the speed of 4000 rpm for removal of reaction residues, such as NaCl and unreacted hydrazine or NaOH. Finally, the nanoparticles were dried in vacuum and collected for further studies. The schematic representing the above process is summarised in Figure 3.8.

**Figure 3.8:** Schematic representation of the synthesis procedure of nickel nanoparticles.
The reaction equation between nickel chloride and sodium hydroxide in aqueous medium can be written as follows:

\[
\text{NiCl}_2 (\text{aq}) + \text{NaOH} (\text{aq}) \rightarrow \text{Ni(OH)}_2 (\text{s}) + 2\text{NaCl(}\text{aq})
\] (Equation 3.1)

Hydrazine is added to the solution containing nickel oxide at elevated temperature to enhance the reaction rate. The reaction equation between nickel and hydrazine is:

\[
2\text{Ni}^{2+} + \text{N}_2\text{H}_4 + 4\text{OH}^- \rightarrow 2\text{Ni} + \text{N}_2\uparrow + 4\text{H}_2\text{O}
\] (Equation 3.2)

3.2.4. Results and Discussion

3.2.4.1. Characterisation of Materials

P-XRD was used to confirm the formation of pure Ni (rather than the more thermodynamically favourable NiO) nanoparticles without the need for further calcination/reduction steps. Figure 3.9 compares the P-XRD pattern of the produced Ni nanoparticles with that of commercially available Ni powder (<100 nm) between 5 and 110 degrees 2θ. In both samples one can observe characteristic peaks at 44.5°, 51.8°, 76.4°, 92.9° and 98.3°, 20 corresponding to the Miller indices (111), (200), (220), (311) and (222) planes of Ni respectively and does not contain any impurity, although the ratios of the peaks intensities show small differences. Peak broadening observed in the P-XRD pattern of synthesised Ni nanoparticles is indicative of a reduction of particle size. Energy dispersive analyses X-ray (EDX) analysis on various regions confirmed that the particles are pure nickel, with energy band centred on 7.5 and 8.3 keV (K lines) and 0.8 keV (L lines) (Figure 3.10 and Table 3.4). The oxygen detected could be attributed to partial oxidation of the nanoparticles during the handling of the sample or to the presence of some residual solvent. This is however not seen in P-XRD which might be due the formation of a very thin surface oxide layer that not crystalline. With the presence of pure nickel nanoparticles confirmed, samples were prepared as described in the characterisation techniques section to be examined using SEM, TEM and STXM. The crystallite size of the nickel nanoparticles can be calculated from the major diffraction peak (111) using Scherrer's equation shown in Equation 2.5.
Table 3.3: Crystalline size of a sample by the reduction method.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>2Theta, 2θ / deg</th>
<th>full-width at half-maximum β_{hkl} / deg</th>
<th>line broadening B / radian</th>
<th>crystallite size D_{hkl} / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Ni-nanoparticles</td>
<td>44.5325</td>
<td>0.5770</td>
<td>0.0100</td>
<td>15</td>
</tr>
</tbody>
</table>

Figure 3.9: (a) The P-XRD pattern of a sample prepared by the reduction method with a proportion of: [NiCl₂] = 0.6 M; [N₂H₄.H₂O] = 6.2 M; HECMC = 0.022 g weight percentage of NiCl₂; pH = 11; T = 65 °C and (b) commercially available nickel nanoparticles.
As can be seen for the SEM image Figure 3.11 (a), the size of nanoparticles was quiet large due to the formation of large aggregates in the process of centrifugation and drying. It shows that particles aggregates together to form somewhat flower shape structures in the range 400 to 800 nm. A closer examination using low resolution TEM Figure 3.11 (b) also showed self-assembled flower shape. Interestingly, high resolution TEM Figure 3.11 (c) revealed unique morphological features of the particles. It appears that the particles were self-assemblies of smaller particles with diameters ranging from 15-20 nm, which is close to the crystallite size calculated using the Scherrer’s equation 15 nm. It is known that nickel is magnetic and at the same time nano-sized particles are known to have very large surface areas, hence these synthesized nano-particles will also have very high surface energy. Consequently these fine nickel crystals will be attracted towards each other and very quickly form aggregated nickel particles in order to reduce their surface energies. Hence, low resolution SEM is not indicative of the particle size, thus would only be used for the morphology analysis. The calculated particle size using Scherrer’s equation is approximately in agreement with the TEM observation. It can be
speculated that the size enlargement could be due to the formation of crystal aggregates upon drying. Therefore, from here onwards Scherrer’s equation would be used to calculate the particle size.

Figure 3.11: (a) SEM, (b) low resolution and (c) high resolution TEM images of as-synthesized nickel nanoparticles by the reduction method.

A representative 1 × 1 μm STXM image of Ni nanoparticles deposited on a clean Si₃N₄ window at photon energy of 854.5 eV is shown in Figure 3.12. The image shows the presence of four pure nickel nanoparticles of ~90–140 nm in diameter. The red line shown in Figure 3.12 indicates the trajectory of a typical line scan used for near-edge X-ray absorption fine structure spectroscopy (NEXAFS) acquisition. Further analysis of this sample will be discussed in chapter 5.
Figure 3.12: Scanning transmission X-ray microspectroscopy image of Ni nanoparticles. Image size = 1 × 1 μm, photon energy = 850 eV, step size = 10 nm. Red line indicates typical line profile (line length=1 μm) used for NEXAFS acquisition and covers both nanoparticle and background region used for normalization.

3.2.5. Parameters effecting size and shape of the nanoparticles

3.2.5.1. The effect of NiCl$_2$ concentration on the obtained particles

The effects of nickel chloride concentration on the formation of nickel nanoparticles were investigated. The reduction reactions were carried out with 6.2 M constant concentration of N$_2$H$_4$.H$_2$O and pH 11, while the concentration of NiCl$_2$ varied from 0.075 M, 0.15 M, 0.30 M and 0.6 M at 65 °C.

Figure 3.13 shows the P-XRD diffractograms of the nickel nanoparticles obtained from different concentrations of NiCl$_2$. In all the samples only five characteristic peaks of fcc nickel (2θ = 44.5°, 51.8°, 76.4°, 92.9° and 98.3°), corresponding to Miller indices (111), (200), (220), (311) and (222) respectively, appeared in the diffractogram which indicated that all these products are pure fcc structured metallic nickel without any other impurity. The SEM images of these samples are shown in Figure 3.14. The samples prepared in all four concentrations had spherical shape morphology and flower shape structure.
Figure 3.13: The P-XRD patterns of samples prepared by the reduction method with different concentration of NiCl₂ and a proportion of: \([N_2H_4.H_2O] = 6.2 \text{ M}; \text{HECMC} = 0.2 \text{ % weight percentage of NiCl₂}; pH = 11; T = 65 ^\circ C\), (*) denotes peaks associated with the pure nickel.

Table 3.5 shows that the average particle size stays more or a less the same for 0.60-0.15 M concentration of NiCl₂, however there is an increase in the particle size with 0.075M concentration of NiCl₂. The reason for the observed effect of the concentration can be explained by the reaction rate on the nucleation. Fast nucleation results in smaller particles, so that, at a higher concentration, nucleation is expected to speed up, resulting in smaller particles, as observed in Figure 3.14 and Table 3.5. It is known that the average particle size decreases with an increase in the nuclei concentration in the solution due to the suppression of the growth of particles by the formation of many nuclei in the course of nucleation [79]. Additionally, when most nuclei are formed at the same time and grow at the same rate, the size distribution of the resulting particles will be in the narrow range. In these cases, the formation of a smaller number of nuclei in the lower concentration, such as \([\text{NiCl₂}] = 0.075 \text{ M}\) would induce growth of particles and broad size distribution, Table 3.5.
Chapter 3  
Synthesis of Nanoparticles

Figure 3.14: The SEM images of samples prepared by the reduction method with different concentration of NiCl$_2$ and a proportion of: [$N_2H_4.H_2O$] = 6.2 M; HECMC = 0.2 weight percentage of NiCl$_2$; pH = 11; T = 65°.

Table 3.5: Crystalline size of as synthesised nanoparticles with different concentration of NiCl$_2$.

<table>
<thead>
<tr>
<th>NiCl$_2$ / M</th>
<th>20 / deg</th>
<th>full-width at half-maximum $\beta_{hkl}$/ deg</th>
<th>line broading B / radian</th>
<th>crystallite size $D_{hkl}$/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.60</td>
<td>44.5339</td>
<td>0.5773</td>
<td>0.0100</td>
<td>15</td>
</tr>
<tr>
<td>0.30</td>
<td>44.4878</td>
<td>0.5512</td>
<td>0.0096</td>
<td>16</td>
</tr>
<tr>
<td>0.15</td>
<td>44.5070</td>
<td>0.5484</td>
<td>0.0095</td>
<td>16</td>
</tr>
<tr>
<td>0.075</td>
<td>44.4634</td>
<td>0.3402</td>
<td>0.0058</td>
<td>26</td>
</tr>
</tbody>
</table>

3.2.5.2. The effect of cellulose concentration

The effects of cellulose concentrations on the formation of nickel nanoparticles were investigated. The reduction reactions were carried out with constant concentration of
NiCl₂, N₂H₄·H₂O and pH, while the weight percentage of cellulose varied from 0.1, 0.2, and 0.40 wt. % with respect to NiCl₂ at 65 °C.

**Figure 3.15**: The P-XRD patterns of samples prepared by the reduction method with different wt. % of cellulose and a proportion of: [NiCl₂] = 0.6 M; [N₂H₄·H₂O] = 6.2 M; pH = 11; T = 65 °C, (*) denotes peaks associated with the pure nickel.

**Figure 3.15** shows the P-XRD diffractograms of the nickel nanoparticles using different amount of cellulose. The diffractrogram confirmed the presence of Ni (ICDD No. 03-065-2865) with characteristic peaks of fcc nickel (2θ = 44.5°, 51.8°, 76.4°, 92.9° and 98.3°). Intensities of the peaks are almost the same; therefore changes in the cellulose wt. % have very little, if any, effect on the size of the nanoparticles. Calculated crystallite size using the Scherrer’s equation also directs towards the same finding.
Table 3.6: Crystalline size calculation using Scherrer's equation.

<table>
<thead>
<tr>
<th>Cellulose / wt. %</th>
<th>2Theta, 2θ / deg</th>
<th>full-width at half-maximum $\beta_{hkl}$ / deg</th>
<th>line broading B / radian</th>
<th>crystallite size $D_{hkl}$ /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>44.5864</td>
<td>0.4664</td>
<td>0.0081</td>
<td>19</td>
</tr>
<tr>
<td>0.2</td>
<td>44.5517</td>
<td>0.4874</td>
<td>0.0084</td>
<td>18</td>
</tr>
<tr>
<td>0.4</td>
<td>44.6337</td>
<td>0.4733</td>
<td>0.0082</td>
<td>18</td>
</tr>
</tbody>
</table>

3.2.5.3. The effect of temperature

Temperature is another parameter that affects the rate of nucleation, thus the particle size. Three samples were synthesized to investigate the effects of temperature on the formation of nickel nanoparticles. These samples were synthesized similarly to those described in 3.2.3, with constant concentration of 0.78 g of NiCl$_2$, 3 ml of N$_2$H$_4$.H$_2$O, pH of 11 and the 0.2 wt. % of cellulose at different temperature.

Shown in the Figure 3.16 is the P-XRD diffractogram pattern of as synthesized nickel nanoparticles at different reaction temperatures. It can be seen that the XRD pattern of the samples produced at 65 and 85 °C exhibits five well-resolved peaks at 2θ = 44.5°, 51.8°, 76.4°, 92.9° and 98.3° which were indexed as the (111), (200), (220), (311) and (222) planes of the fcc nickel, respectively. No impurity diffraction peaks were detected. However, evidence of Ni(OH)$_2$ diffraction peaks were found at 45 °C reaction temperature. There was no indication of reaction at 25 °C even after several weeks. This suggests that the synthesis reaction needs to be carried out temperatures at or above 65 °C to obtain pure nickel nanoparticles.
Figure 3.16: The P-XRD patterns of samples prepared by the reduction method with different temperature and a proportion of: $[\text{NiCl}_2] = 0.6 \, M$; $[\text{N}_2\text{H}_4\text{H}_2\text{O}] = 6.2 \, M$; $pH = 11$. (*) Denotes peaks associated with the pure nickel and (#) denotes peaks associated with the nickel hydroxide.

Shown in the Figure 3.16 is the P-XRD diffractogram pattern of as synthesized nickel nanoparticles at different reaction temperature. It can be seen that the XRD pattern of the samples produced at 65 and 85 °C exhibits five well-resolved peaks at $2\theta = 44.5^\circ$, $51.8^\circ$, $76.4^\circ$, $92.9^\circ$ and $98.3^\circ$ were indexed as the (111), (200), (220), (311) and (222) planes of the face centred- cubic (fcc) nickel, respectively. No impurity diffraction peaks were detected. However, at 45 °C temperature, the sample mixed with some nickel hydroxide. No sign of reaction at 25 °C even after several weeks of stirring. This indicates that the synthesis reaction needs to be carried out temperatures at or above 65 °C to obtain pure nickel nanoparticles.
3.2.5.4. The effect of pH

The effect of pH on synthesis of nickel nanoparticles was investigated to study the effect on the reduction of Ni\(^{2+}\) ions, particles size distribution and morphology. The corresponding P-XRD diffractograms of the precipitates at pH of 7.0, 7.5, 8.5, 10.5, 11, 11.5, 12.5, 13.0 and 13.5 are shown in Figure 3.18 respectively. The five characteristic peaks that were observed for the products at 20 = 44.5°, 51.8°, 76.4°, 92.9° and 98.3°, corresponding to the lattice planes (111), (200), (220), (311) and (222) respectively of fcc Ni (ICSD 64989 (PDF 01-087-0712)).
At pH ≥ 8.5, the P-XRD spectrum shows a peak at of Ni(OH)$_2$ and a few unknown peaks which are most probably related to Ni-hydrazine complexes. This formation might be due to incomplete reaction.

![P-XRD Patterns](image)

**Figure 3.18:** The P-XRD patterns of samples prepared by the reduction method with different pH and a proportion of: [NiCl$_2$] = 0.6 M; [N$_2$H$_4$.H$_2$O] = 6.2 M; pH = 11 at 65 °C. (*) Denotes peaks associated with the pure nickel, (#) denotes peaks associated with the nickel hydroxide and (▪) denotes unknown peaks.

Shown in Table 3.7 is the crystallite size of the nanoparticles at different pH, which shows between 7.5-12.5 pH there is little or no significant change on the size of the particles. However pH>12.5 the crystallite size almost. This suggests the best pH for 15-16 nm nickel nanoparticles lays in-between pH 8.5-12.5. SEM results of as-synthesised nanoparticles at different pH are shown below in Figure 3.19.
Table 3.8: Crystalline size of as-synthesised nanoparticles at different pH.

<table>
<thead>
<tr>
<th>pH value</th>
<th>2Theta, θ / deg</th>
<th>full-width at half-maximum βhkl / deg</th>
<th>line broading B / radian</th>
<th>crystallite size D_{hkl} /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0</td>
<td>44.5052</td>
<td>0.4605</td>
<td>0.0066</td>
<td>23</td>
</tr>
<tr>
<td>7.5</td>
<td>44.4911</td>
<td>0.5465</td>
<td>0.0095</td>
<td>16</td>
</tr>
<tr>
<td>8.5</td>
<td>44.5535</td>
<td>0.5450</td>
<td>0.0094</td>
<td>16</td>
</tr>
<tr>
<td>10.5</td>
<td>44.6215</td>
<td>0.5933</td>
<td>0.0103</td>
<td>15</td>
</tr>
<tr>
<td>11.0</td>
<td>44.5663</td>
<td>0.5452</td>
<td>0.0095</td>
<td>16</td>
</tr>
<tr>
<td>11.5</td>
<td>44.4993</td>
<td>0.5503</td>
<td>0.0095</td>
<td>16</td>
</tr>
<tr>
<td>12.5</td>
<td>44.5556</td>
<td>0.5193</td>
<td>0.0090</td>
<td>17</td>
</tr>
<tr>
<td>13.0</td>
<td>44.5092</td>
<td>0.2444</td>
<td>0.0041</td>
<td>36</td>
</tr>
<tr>
<td>13.5</td>
<td>44.5903</td>
<td>0.2813</td>
<td>0.0048</td>
<td>31</td>
</tr>
</tbody>
</table>

Figure 3.19: The SEM images of samples prepared by the reduction method with different pH and a proportion of: [NiCl₂] = 0.6 M; [N₂H₄.H₂O] = 6.2 M at 65 °C.
3.2.5.5. The effect of using different supports

The particle size of the conventionally prepared supported metal catalyst often depends on the nature and the surface area of the support. For example, two catalysts made via the same synthetic procedure on SiO$_2$ supports having different surface areas would likely exhibit different metal particle size distribution. Furthermore, optimal synthetic protocols are often not transferable between various oxide supports of similar surface area. To test this hypothesis, four 50 wt % Ni catalyst were prepared from the same NiCl$_2$ precursor on different commercial supports: low surface area $\gamma$-Al$_2$O$_3$, higher surface area C, colloidal SiO$_2$ and SiO$_2$. These supports were chosen because they cover wide range surface areas. The catalysts were synthesized under the exact conditions described in section 3.2.3, with the exception being that the catalyst was supported by means of the addition of SiO$_2$, Al$_2$O$_3$, C and colloidal SiO$_2$ without the addition of cellulose (Figure 3.20 (a-d)).
The corresponding P-XRD spectrum of the nickel nanoparticles supported in Al₂O₃, carbon and colloidal SiO₂ have the five characteristic peaks at 2θ = 44.5°, 51.8°, 76.4°, 92.9° and 98.3°, corresponding to the fcc Ni. However, catalyst supported with powder SiO₂ have very broad and small peaks at 2θ = 33.4, 38.3 and 59.3, all indicating presence of Ni(OH)₂ rather than the expected pure nickel nanoparticles. This suggests either the powder SiO₂ was not dry or the reaction time was not colloquial to form pure nickel nanoparticles.

As expected, the size and the intensity of the P-XRD peaks varied with different support, suggesting the production of different size distributions of nickel nanoparticles. For example the colloidal silica supported nanoparticle P-XRD has much shaper peaks in comparison to other supports, hence the smaller nanoparticles. The calculated crystallite size of the nickel nanoparticles according to Equation 2.5 and the SEM imagwas notes in Figure 3.21 shows the same finding. Colloidal SiO₂
and carbon supported nanoparticles produced nearly identical nanoparticle average size of 14-15 nm distribution. **Equation 2.5** allows estimation of the nickel particle sizes on various supports. This data is given in **Table 3.8**:

**Table 3.9: Crystalline size of samples prepared by the reduction method with different supports.**

<table>
<thead>
<tr>
<th>Different Support</th>
<th>2Theta, θ / deg</th>
<th>full-width at half-maximum β&lt;sub&gt;hkl&lt;/sub&gt; / deg</th>
<th>line brooding B / radian</th>
<th>crystallite size D&lt;sub&gt;hkl&lt;/sub&gt; / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder SiO₂</td>
<td>38.2620</td>
<td>1.4360</td>
<td>0.0250</td>
<td>6</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>44.4242</td>
<td>0.6720</td>
<td>0.0117</td>
<td>13</td>
</tr>
<tr>
<td>Carbon</td>
<td>44.4573</td>
<td>0.6110</td>
<td>0.0106</td>
<td>14</td>
</tr>
<tr>
<td>Colloidal SiO₂</td>
<td>44.4821</td>
<td>0.5656</td>
<td>0.0098</td>
<td>15</td>
</tr>
</tbody>
</table>

**Figure 3.21:** The SEM images of the 50 wt % nano-particles that were deposited on different supports.
3.3. Conclusions

The original synthetic methodologies used were designed around selected journal articles describing the formation of pure nickel nanoparticles using a microemulsion method. Chen and Wu [80] showed the production of nickel nanoparticles in the cationic w/o microemulsion of water/CTAB/n-hexanol by reduction of nickel chloride with hydrazine at 73 °C. The report does not indicate that calcination was used to remove the organic residue. However, the diffraction peaks of the samples produced using both methods showed the evidence of organic residues and the associated amorphous structure. After the calcination processes all the organic residues present in the catalyst surface were removed and the crystallinity in the materials improved. The diffraction peaks of the samples after calcination process shifted toward lower 2θ values on the diffractogram in comparison to the nickel diffraction peaks, indicating presence of nickel oxide rather than the expected pure nickel nanoparticles.

A synthetic route without any other protective agent or inert atmosphere protection has been successfully developed for the preparation of metallic nickel nanoparticles by hydrazine reduction. P-XRD spectrum shows that the resultant product is pure fcc structured metallic nickel. The method is simple, easy to operate and relatively cheap. For the formation of monodispersed nickel nanoparticles, the initial concentration of Ni²⁺ can determine the particle number and size of the resulting product.

Ni nanostructures with sizes range of 14-36 nm have successfully been prepared by the reduction method. The synthesis was tailored by changing the Ni²⁺/OH⁻, pH and temperature. Temperatures below 45 °C were unsuccessful to produce pure Ni nanoparticles which identify temperature were crucial to enhance the reaction rate thus forming difference size at difference temperature. Increasing the concentration of Ni²⁺ decreased the size of nano-particles. SEM revealed formation of flower-like nanostructures having a diameter ranging from 400 to 800 nm due to self-assembly of smaller nanoparticles of the size approximately 14-36 nm. Meanwhile, P-XRD revealed all as-synthesized Ni nanoparticles were present as face-centred cubic structures. The reduction of Ni²⁺ to metallic Ni nanoparticles can be simply shown in
the following equation: $2\text{Ni}^{2+} + \text{N}_2\text{H}_4 + 4\text{OH}^- \rightarrow 2\text{Ni} + \text{N}_2 + 4\text{H}_2\text{O}$. The solution pH influences the synthesis of the nickel nanoparticle. Produced materials were kept in sealed bottles under atmospheric conditions for several months and were still found in same phase solid state.
4. **Hydrogenation of MAA over TA-RNi Catalyst**

Raney nickel was discovered by Murray Raney in 1927 and is the most widely used unsupported Ni catalyst for liquid-phase reactions. [95] It serves as a versatile hydrogenation catalyst in the production of fine chemicals and also in the hydrogenation of D-glucose to sorbitol, which is used in the cosmetic, food and drinks industries and building materials in the manufacture of ascorbic acid.

Metal catalysts can adopt various new properties by simple chemical treatment. These catalysts with new properties are called modified catalysts. Among the modified catalysts, Raney nickel (RNi) modified with optically active compounds has the longest history of investigation and has been the most systematically studied catalyst [20, 22, 29, 36, 42, 44]. By modification with optically active compounds, RNi is capable of the new function of enantioselective differentiation in addition to the function of hydrogenation. For instance, RNi modified with an optically active amino acid or hydroxyl acid hydrogenates methyl acetoacetate (MAA) to produce optically active methyl 3-hydroxybutyrate (MHB).

### 4.1. Preparation of the catalysts

Commercial Raney nickel was used for the preparation of the modified catalysts. When a nickel-aluminium alloy such as Raney nickel is used as a starting material for the preparation of the modified nickel catalyst, aluminium cannot be removed from the catalyst by simply washing off with distilled water and the residual aluminium decreases the optical yield. Furthermore, it is unavoidable that the residual alkaline solution used for the development of the nickel-aluminium alloy affects the modification procedure. This is due to a small portion of the alkaline ions remaining on the RNi catalysts even after thorough washing of the RNi with distilled water. Therefore, the following method was used for the preparation of the *ex-situ* modified catalysts that were used for the hydrogenation.

The catalyst (3 g) was first washed three times with 20 ml of de-ionised water and then introduced to a so-called pre-modification step, during which it was washed by
10 ml of 1% \((R,R)-(+)\)-tartaric acid solution. Pre-modification was carried out under stirring with a magnetic stirrer for a period of 10 min. Then, the catalyst was again washed with 20 ml of di-ionised water and was introduced to the modifying solution (100 ml, c TA = 0.2 mol/l). In the case of modifying with a co-modifier, 3 g of sodium bromide were introduced to the modifying solution. The pH of the modifying solution was adjusted to 5.1 with 20 wt % solution of sodium hydroxide. Suspension of the catalyst and the modifying solution was stirred in round bottom flask under reflux conditions with a magnetic stirrer at a constant temperature of 100 °C for a period of 60 mins. During modification, the pH of the suspension was monitored using the pH meter. After decanting, the modifying solution was removed and the catalyst was gradually washed with 20 ml of de-ionised water, methanol and a portion of a reaction solvent. Chirally modified catalysts were used immediately after the preparation to achieve the optimal activity and enatioselectivity. It is known that, nickel has an inherent drawback since its metallic surface is liable to be oxidized upon exposure to air which reduces its activity. Therefore to minimise nickel exposure to air, samples were kept immersed in water prior to the characterisation experiments.

### 4.2. Hydrogenation Reactor Studies

The use of reactors allows the progress of reactions to be monitored under carefully controlled conditions. A Radleys Carousel reactor Figure 4.1 was used for the preliminary experiments to ensure that the preparation method chosen produced active catalyst. Three high pressure reaction vessels were used for all the hydrogenation reactions studies (Figure 4.2).

The advantage of the carousel reactor is its ease of use, capability to run twelve reactions at a time at elevated temperature and the possibility of running reactions with small samples of catalyst. As such, it was chosen to run small number of the preliminary experiments. The reactions were run at 70 °C under reflux. The reaction mixture consisted of 0.50 g of catalyst, 5 g of methanol and 43.1 mmol of methyl acetoacetate (MAA) and was stirred rapidly. The hydrogen gas, present in the balloons (Figure 4.1) was filled depending upon uptake. The results showed the catalysts were active; however the pressure in the balloon was not sufficient enough
to accelerate the reaction to a satisfactory rate. Hence, once it was established that hydrogenation occurred, the reactions were transferred to high pressure reaction vessels.

*Figure 4.1: The carousel reactor with significant components labelled.*

The Autoclave high-pressure reactors are shown in *Figure 4.2*, with the significant components labelled. The high pressure reactor consists of three separate controlled stirred reactors. The specialised design allows for hydrogenation reactions to be undertaken at pressures up to 200 bar and temperature of 200 °C.

A typical procedure for hydrogenation using the Autoclave high pressure reactor is as follows. The hydrogenation experiment was performed in 100 ml batch autoclave reactors using a maximum working pressure of 8 bar and temperature of 100 °C. The reactor was first purged with H₂ at room temperature. For all the hydrogenation reactions, 0.5 g of wet catalyst and 43.1 mmol (12.5 ml) of reactant were introduced with the solvent. When the preset temperature was reached, the hydrogen pressure was set to the desired pressure and stirring of the mixture was started. After 24 hours reaction time, the catalyst was recovered from the solution by decanting and the
products of the reaction was analysed using chiral GC with FID detector (described in Chapter 2 Section 2.2.5) to determine the hydrogenation yield, $ee$ and selectivity respectively.

![Figure 4.2: The autoclave reactors with significant components labelled.](image)

### 4.3. Results and Discussion

The chiral GC was used extensively in the analyses of the hydrogenated samples so it was calibrated to ensure that the results obtained were correct and representative, see Appendix 8.1.1 for the calibration. It showed a very good calibration for MAA, R-MHB and S-MHB with $R^2$ values of ~0.99. In each sample decane was added as an internal standard before the GC was performed. 5 µl was added to each sample this meant that all peak areas could be standardised. Having calibrated the GC and the internal standard in the GC there is a minimal amount error from this area of the experiment.

For comparison, a mixture of commercially available pure MAA, decane S-MHB and R-MHB were analysed under the same conditions as for the hydrogenated
solutions. A significant difference in retention time peaks would indicate the presence of different products.

**Table 4.1**: Elution times of compounds from the Rt- γDEX<sub>sa</sub><sup>TM</sup> column 30 m, 0.32 mm ID, 0.25 µm.

<table>
<thead>
<tr>
<th>Retention time / mins</th>
<th>Identity</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.34</td>
<td>Decane (internal standard)</td>
</tr>
<tr>
<td>14.28</td>
<td>S – MHB</td>
</tr>
<tr>
<td>14.59</td>
<td>R – MHB</td>
</tr>
<tr>
<td>18.24</td>
<td>MAA</td>
</tr>
</tbody>
</table>

### 4.3.1. Hydrogenation

The hydrogenation of MAA on a bare or unmodified nickel surface generates a racemic product. As discussed in Chapter 1 section 1.7.1, there are many factors that affect the optical yield of enantioselective hydrogenation, from the catalyst preparation process and modification process to the hydrogenation process parameters. These processes have preparation and reaction variables for the hydrogenation process. For example pH, temperature, pressure and time are crucial for a good catalyst performance. Polar protic solvents, especially methanol give the highest enantiomeric excesses. A reaction temperature of 70 °C and high hydrogen pressures of 90 bar yield good enantioselectivity. Due to a variety of reasons the experiments were performed at a lower pressure, 8 bar or below.

Taking an overview of the published data, it is evident that one can only make qualitative comparisons as the results originating from different laboratories are not reproducible. Furthermore, the range of experimental conditions that have been considered in each study is too narrow to afford a complete understanding of the underlying principles. Therefore, the initial experiments using the high pressure reactors were performed to optimise the reaction conditions for hydrogenation of methyl acetoacetate using Raney Nickel (RNi).

#### 4.3.1.1. The effect of the amount of TA

Hydrogenation reactions using the ex-*situ* modified catalysts were carried out using 43.1 mmol (12.5 ml) of MAA, 0.5 g of RNi and 25 mL of methanol solvent. All
reactions were carried out at 70 °C at a pressure of 8 bar hydrogen for 24 hours with a stirring rate of 750 RPM.

A number of experiments were carried out using the *ex-situ* modified RNi, modification process is described on Section 4.1, in the absence of a NaBr co-modifier. Effects of the different concentrations of TA on the enantioselective hydrogenations were tested. The results are shown in Figure 4.3. It shows that increasing the concentration of TA increases the enantiomeric excess until it reaches 50 % wt/wt RNi of TA then it remains constant. This suggests that the modification with >50 % wt/wt RNi of TA would cover the RNi surface that is available. Less than 50 % wt/wt RNi would not be sufficient enough to cover the surface of the RNi providing the non-enantioselective sites for hydrogenation. Hence, the formation of racemic product and the enantioselectivity decreases with a decrease in the TA adsorption. With this in mind we would predict that excess TA on the catalyst surface would also decrease the enantioselective hydrogenation because it would block the smooth progress of the hydrogenation of methyl acetoacetate to the optically active methyl 3-hydroxybutyrate over the TA-adsorbed area. However, in our work this is not the case. The enantioselectivity for the catalysts stays almost the same with >50% wt/wt RNi of TA. This suggests that the excess TA was washed off during our washing step in the *ex-situ* modification process.
Chapter 4 Hydrogenation of MAA over TA-RNi Catalyst

Figure 4.3: The relationship between the amount of TA (% wt/wt RNi) for ex-situ modification and enantiomeric excess of R-MHB after hydrogenating the MAA under 8 bar at 70 °C for 24 hrs.

Few of the above reactions at 20, 50 and 100 °C were repeated to calculate the error bars. There were negligible, therefore not included in the Figure 4.3.

4.3.1.2. The influence of solvent

Hydrogenation activities as well as enantioselective ability of the tartaric acid modified RNi catalyst are clearly dependent on the reaction solvent. Although currently it is generally agreed that higher optical yields can be obtained when a reprotic semi-polar solvents such as THF are used. However, there is disagreement from Kukula and Červený [47]. They reported that the reaction performed in methanol was 4.5 times as fast as in THF, but that the optical yield was significantly lower. When methanol was used as the reaction medium, the highest optical yield of 37.3% was attained. On the contrary, Lipgart et al. claimed higher optical yield in MeOH than in THF over modified Raney nickel [48]. Keane also reported higher optical yield for BuOH over Ni/SiO₂ [23]. However, their attained optical yields were 19 and 27%, respectively [23] [48]. This indicated that it was necessary to further investigate the influence of solvent types on hydrogenation.
The effect of the selected solvent on the hydrogenation activity and enantioselective ability is shown in Table 4. The solvent polarity was increased in the order, Toluene < PrOH < MeOH. In MeOH (dielectric constant, ε=33), the ee was 4.6 times higher than in Toluene (ε=2.3). The reason may be that the higher the medium polarity is the more quickly the hydrogen is dissolved into the reaction medium, and the higher the amount of the dissolved hydrogen is probably adsorbed on the catalyst surface, which results in the higher ee. These results agree with Kukula and Červený results [47].

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric constant ε</th>
<th>ee / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>2.3</td>
<td>5.90</td>
</tr>
<tr>
<td>Propanol</td>
<td>20</td>
<td>25.97</td>
</tr>
<tr>
<td>Methanol</td>
<td>33</td>
<td>27.30</td>
</tr>
</tbody>
</table>

Modifying conditions: $C_{TA} = 0.2 \text{ mol/L, pH } 5.1, T = 100 \degree \text{C, } t = 24 \text{ hrs; reaction conditions: solvent (25 mL), MAA (12.5 mL), catalyst (0.5 g), H}_2 \text{ (8 bar) at 30}^\circ \text{C.}$

4.3.1.3. The influence of reaction temperature

Figure 4.4 shows the effect of the hydrogenation temperature on the enantioselectivity under 8 bar hydrogen pressure. The highest enantioselectivity of 73% was achieved at 70 °C and above and below this temperature enantioselectivity decreases. This may be due to the disruption of the hydrogen bonding interaction between methyl acetoacetate and tartaric acid, which are responsible for a stereospecific reaction course. Or this may simply be due to the catalyst switching in the preferred enantiomeric product with different temperature as described by Jones and Baddeley [10]. They have studied the influence of temperature on the adsorption of chiral modifier, (S)-glutamic acid, on Ni (111) using Reflection Absorption Infrared Spectroscopy (RAIRS) and Scanning Tunnelling Microscopy (STM) and found that the modification at 27 °C results in an excess of the (R)-product while modification at 77 °C and above causes a slight preference for the (S)-product. Our results showed that the preferred enantioselectivity of the modified catalyst switches above 70 °C.
4.3.1.4. The influence of hydrogen pressure

The influence of hydrogen pressure on the enantioselectivity is examined. As shown in Figure 4.5, the enantioselectivity of R-MHB remained almost constant at different hydrogen pressure. This indicates that the hydrogen pressure in the range of 2-8 bar plays no role to the enantioselectivity.
4.3.1.5. Durability of chirally modified catalysts

One of the several important factors in applying a heterogeneous catalyst to practical hydrogenation reaction is the durability or shelf life of the catalyst activity and selectivity. Even though Ni is much less expensive than platinum or palladium, it has an inherent drawback that its metallic surface is liable to be oxidised upon exposure to air. Therefore, the chirally modified nickel catalyst should be used immediately after the preparation to achieve the optimal activity and enantioselectivity. Little is known about the shelf life of TA-modified catalyst. Tai et al. reported that TA-modified nickel embedded in a silicon polymer can be stored in the air for 6 months without decreasing the enantioselectivity upon hydrogenation. [96] However, the silicone polymer easily swells to absorb part of the reaction mixture under the hydrogenation conditions. This suggests a more straightforward method to prepare a durable catalyst of long shelf life is highly desired.

In order to investigate the durability of MRNi with TA, the modified catalyst was stored for a given period under the wet condition. The modifying solution was removed by decantation and the catalyst was washed with 20 ml of de-ionised water,
methanol and a portion of a reaction solvent and stored in a sealed bottle in a minimum amount of de-ionized water. The effect of storage period after modification on the hydrogenation activity of the catalyst is shown in Figure 4.6.

![Figure 4.6](image)

**Figure 4.6:** Effects of the storage period on the enantioselective ability of the modified catalyst. Modifying conditions: $C_{TA} = 0.2 \text{ mol/L}$, pH 5.1, $t = 24 \text{ hrs}$; reaction conditions: solvent (25 mL), MAA (12.5 mL), catalyst (0.5 g) and $H_2$ (8 bar) at 70°C.

As can be seen from Figure 4.6, there is steady drop in enantioselective ability as the storage period increase. Enantioselective ability dropped from 73% to 66% just after 3 days, then to 63% after 9 days.

### 4.3.1.6. *In-situ* modification

One of the important factors leading to low hydrogenation activity is the modifying method. In the traditional modification method, the catalyst is prepared by soaking a catalyst in an aqueous solution of modifier as described in this chapter Section 4.1. By using the *ex-situ* method, corrosion of the surface of the nickel catalyst occurred. Therefore, both the adsorption of the modifier on the nickel surface and the change in the nickel surface affects the hydrogenation. Tsutomu Osawa *et al.* reported an alternative modification method called the *in-situ* modification method [42]. The *in-situ* modification procedure is to add simple tartaric acid to the reaction media and then the mixture of the substrates is subjected to hydrogenation. By this method, the
adsorption of the modifier is carried out in the reactor during the initial stage of the hydrogenation without corrosion of the nickel surface by the modification solution. Therefore, the in-situ modification is suitable for comparing the enantioselectivity and nickel leached over the hydrogenation of MAA using ex-situ modified catalyst.

**Table 4.3:** GC results for the hydrogenation of MAA using the in-situ modified catalyst with different amount of TA (% wt/wt RNi) under 8 bar at 70 °C for 24 hrs.

<table>
<thead>
<tr>
<th>TA (% wt/wt RNi)</th>
<th>Identity</th>
<th>Retention time / Mins</th>
<th>Peak Area / A. u</th>
</tr>
</thead>
<tbody>
<tr>
<td>0a</td>
<td>Unknown 1</td>
<td>6.06</td>
<td>50.50</td>
</tr>
<tr>
<td></td>
<td>Decane</td>
<td>7.28</td>
<td>342.10</td>
</tr>
<tr>
<td></td>
<td>Unknown 2</td>
<td>12.82</td>
<td>92.90</td>
</tr>
<tr>
<td></td>
<td>R-MHB</td>
<td>14.37</td>
<td>2718.80</td>
</tr>
<tr>
<td></td>
<td>S-MHB</td>
<td>14.06</td>
<td>2152.70</td>
</tr>
<tr>
<td></td>
<td>MAA</td>
<td>19.38</td>
<td>4395.76</td>
</tr>
<tr>
<td>1</td>
<td>Unknown 1</td>
<td>6.07</td>
<td>49.80</td>
</tr>
<tr>
<td></td>
<td>Decane</td>
<td>7.29</td>
<td>358.50</td>
</tr>
<tr>
<td></td>
<td>Unknown 2</td>
<td>12.81</td>
<td>302.30</td>
</tr>
<tr>
<td></td>
<td>R-MHB</td>
<td>14.37</td>
<td>3027.70</td>
</tr>
<tr>
<td></td>
<td>S-MHB</td>
<td>14.09</td>
<td>1473.80</td>
</tr>
<tr>
<td></td>
<td>MAA</td>
<td>19.37</td>
<td>4867.76</td>
</tr>
<tr>
<td>20</td>
<td>Unknown 1</td>
<td>6.03</td>
<td>440.20</td>
</tr>
<tr>
<td></td>
<td>Decane</td>
<td>4.26</td>
<td>374.40</td>
</tr>
<tr>
<td></td>
<td>Unknown 2</td>
<td>12.78</td>
<td>705.20</td>
</tr>
<tr>
<td></td>
<td>R-MHB</td>
<td>14.49</td>
<td>688.20</td>
</tr>
<tr>
<td></td>
<td>S-MHB</td>
<td>14.21</td>
<td>476.40</td>
</tr>
<tr>
<td></td>
<td>MAA</td>
<td>19.27</td>
<td>5778.36</td>
</tr>
<tr>
<td>50</td>
<td>Unknown 1</td>
<td>6.05</td>
<td>94.80</td>
</tr>
<tr>
<td></td>
<td>Decane</td>
<td>7.27</td>
<td>351.90</td>
</tr>
<tr>
<td></td>
<td>Unknown 2</td>
<td>12.79</td>
<td>950.40</td>
</tr>
<tr>
<td></td>
<td>R-MHB</td>
<td>14.55</td>
<td>228.70</td>
</tr>
<tr>
<td></td>
<td>S-MHB</td>
<td>14.26</td>
<td>151.70</td>
</tr>
<tr>
<td></td>
<td>MAA</td>
<td>19.28</td>
<td>7342.02</td>
</tr>
<tr>
<td>100</td>
<td>Unknown 1</td>
<td>6.06</td>
<td>86.40</td>
</tr>
<tr>
<td></td>
<td>Decane</td>
<td>7.28</td>
<td>351.70</td>
</tr>
<tr>
<td></td>
<td>Unknown 2</td>
<td>12.80</td>
<td>992.30</td>
</tr>
<tr>
<td></td>
<td>R-MHB</td>
<td>14.58</td>
<td>176.40</td>
</tr>
<tr>
<td></td>
<td>S-MHB</td>
<td>14.28</td>
<td>123.50</td>
</tr>
<tr>
<td></td>
<td>MAA</td>
<td>19.28</td>
<td>7279.40</td>
</tr>
</tbody>
</table>

* catalyst was washed with 20 wt% NaOH solution prior to the hydrogenation reaction to remove the aluminium from the catalysts.
Chapter 4  
Hydrogenation of MAA over TA-RNi Catalyst

By using the *in-situ* modification, the effect of the amounts of TA (% wt/wt RNi) added to the reaction media on the hydrogenation of MAA to R-MHB were investigated. The results from Table 4.3 raise questions about the products at the 12.78 minute peak. As it appeared when ≥10% TA is added in the *in-situ* modification reactions, which suggests they are products of the MAA reacting with methanol or the enol form of MAA.

The area looked at next was how the TA concentrations affected the peak areas of the unknown peaks at 6 and 12 minutes, Figure 4.7 shows that an increase in the concentration of TA increases the peak areas for both unknown at 6 and 12 minutes with the peak area at 12 minutes being most affected. It is possible that the peak area at 6 minutes at 50% TA is anomalous as the result does not fit with rest of data.

![Graph showing the effects of TA on peak areas of unknown peaks at 6 and 12 minutes.](image)

**Figure 4.7:** The effects TA on the standardised peak area of the unknown peaks at 6 and 12 minutes.

Using the 6, 12, 14 and 18 minute peaks to calculate the R-MHB yield of the reaction; it showed the variation across the different concentrations of TA. The peak area of the GC spectrum was used to calculate the yield. The calculation is shown broken down in Table 4.4. The trend of how the concentration of TA affects the yield of the reaction, Figure 4.8, shows that there is a general trend with the highest yield being at the 10% TA concentration. Both graphs show the lower the yield the
higher the peak area, of the peak at 12 minutes. This shows that the peak at 6 and 12 minutes are related and a derivative of MAA. This justifies and explains using the 12 minutes peak area in the yield calculation.

**Table 4.4: Yield calculation for 10 % TA.**

<table>
<thead>
<tr>
<th>Expected compound</th>
<th>Retention time (Mins.)</th>
<th>Peak area / A. U.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unknown 1</td>
<td>6.054</td>
<td>49.80</td>
</tr>
<tr>
<td>Unknown 2</td>
<td>12.814</td>
<td>302.3</td>
</tr>
<tr>
<td>R-MHB</td>
<td>14.396</td>
<td>3027.70</td>
</tr>
<tr>
<td>S-MHB</td>
<td>14.085</td>
<td>1473.8</td>
</tr>
<tr>
<td>MAA</td>
<td>18.187</td>
<td>4867.76</td>
</tr>
<tr>
<td>Total peak area</td>
<td>-</td>
<td>9721.36</td>
</tr>
<tr>
<td>Yield (%)</td>
<td>-</td>
<td>31.14</td>
</tr>
</tbody>
</table>

**Figure 4.8:** *The effect of tartaric acid concentration on the % yield of reaction.*

Quick room temperature reactions were carried out to investigate the products at the 6 and 12 minute.
Table 4.5: Elution times and the areas of compounds after stirring for 10 minutes

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Peak Area / A.U.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unknown 1</td>
</tr>
<tr>
<td>Methanol + MAA</td>
<td>608.9</td>
</tr>
<tr>
<td>Ethanol + MAA</td>
<td>716.3</td>
</tr>
<tr>
<td>Propanol + MAA</td>
<td>596.0</td>
</tr>
<tr>
<td>Toluene + MAA</td>
<td>413.5</td>
</tr>
<tr>
<td>THF + MAA</td>
<td>1002.7</td>
</tr>
</tbody>
</table>

Figure 4.9 shows the possible products when the hydrogenation reaction is performed, ketal and hemiketal intermediates are formed. These parallel reactions are reversible equilibrium reactions. [97-99]

- **Unknown 1: the 6 minute peak**
  The peak at around 6 minutes is produced with all the solvents tested (Table 4.5), therefore it is possible product would be the -enol form of the methyl acetoacetate. As discussed in Chapter 1 Section 1.8.2 the MAA can exist in the diketo form or as an enol the methyl acetoacetate, illustrated in Figure 1.13.
Wilson, Jones and Baddeley studied the absorptions of methyl acetoacetate onto chirally modified surfaces prepared at the liquid-solid interface using surface vibrational spectroscopy in the form of reflection absorption infrared spectroscopy (RAIRS). [56] They have shown that the tautomeric form of methyl acetoacetate (MAA) is very sensitive to the nature of the chirally modified surface. In particular, for the Ni/(R,R)-tartaric acid Ni/(S)-glutamic acid, and Ni/(S)-aspartic acid systems, it was determined that, following modification under conditions where enantioselectivity is optimised, MAA preferentially adopts the diketo tautomeric form. The preparation of chirally modified Ni catalysts involves treatment in an aqueous solution of modifier at a well-defined pH followed by washing and filtering. In the case of (S)-glutamic acid they also showed that, under conditions where the catalyst becomes enantioselective towards (S)-MHB, the enol tautomeric form of MAA dominates on the Ni surface. [56] Therefore it is possible that the MAA had undergone tautomerisation in acidic condition in the presence of tartaric acid in the solution giving a higher yield of S-MHB. This explains the results obtained from hydrogenation of MAA using the in-situ modification method, Table 4.3.

- **Unknown 2: the 12 minutes peak**

The peak at 12 minute is produced only with methanol; therefore could be a product of the MAA reacting with methanol. Having a sharp single peak means that only one product is being produced. In order to investigate this preliminary reaction was conducted under the hydrogenation conditions at 70 °C and pressure of 8 bar for 24 hours, results tabulated in Table 4.6 as a control reaction.

**Table 4.6: Control reaction for in-situ hydrogenation.**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Expected compound</th>
<th>Retention time (Mins.)</th>
<th>Peak area / A. U.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>Unknown 1</td>
<td>6.035</td>
<td>1153.1</td>
</tr>
<tr>
<td></td>
<td>Decane</td>
<td>7.302</td>
<td>346</td>
</tr>
<tr>
<td></td>
<td>Unknown 2</td>
<td>12.824</td>
<td>432.8</td>
</tr>
<tr>
<td></td>
<td>MAA</td>
<td>19.122</td>
<td>6438</td>
</tr>
</tbody>
</table>

As expected hydrogenated MAA in methanol would only give both peaks at 6 and 12 minutes. This confirms the product at 12 minute is due to the reaction between MAA and methanol.
Sung-Hyun Ahn and co-worker studied homogeneous asymmetric hydrogenation of MAA using an immobilisation catalyst Ruthenium catalytic complex supported on Al₂O₃. [100] Their results show the formation of a ketal product, shown in Figure 4.9. It is possible that a ketal product is what is causing the peak at around 12 minutes as it is not a chiral product this would explain the single sharp peak that was produced. This could to be confirmed by isolating this product and performing further reactions. Another possible method would be to run GC-MS. This would determine the mass of the unknown peaks meaning that the products may deducted, this was not possible due time constraints.

In the reaction performed by Sung-Hyun and co-workers it was noted that the ketal tended to be formed at the start of the reaction and then converted to the correct product, R-MHB, as the reaction progressed. [100] A possible explanation for this occurrence in the reaction performed using the ex-situ modified catalyst for the hydrogenation and not for in-situ modified experiments. This may have been due to the acidic conditions introduced by addition of TA. Sung-Hyun and co-workers used a lower temperature of 60 °C and a much higher pressure of 40 bar. The much higher pressure may have been the cause for the ketal to continue the reaction and convert to MHB.

Lukáš Bartek et al. also studied the homogeneous asymmetric hydrogenation of MAA in methanol using a ruthenium catalyst and also reported formation of ketal and hemiketal intermediates. [98] However, they did not report the hydrogenation of these compounds. However, in 2009 Eva Öchsner and co-workers showed that the hemiketal intermediate actually converted into the correct enantiomeric product. [97] They studied the asymmetric hydrogenation MAA in methanol using ruthenium-phenylphosphepine catalyst, to deduce possible reaction pathways for the asymmetric hydrogenation of MA. [97] This was done by comparing the experimental kinetic results with several possible models. Looking at all three Sung-Hyun, Lukáš Bartek and Eva Öchsner and co-workers reactions suggest only the alcoholic solvents opens an additional pathway to the MHB and the temperature and pressure play an important role. This is consistent with the experimental fact that the asymmetric hydrogenation of MAA is significantly accelerated in alcoholic solvents at high pressure and temperature. To determine if this is what happening in the
experiment as methanol was used as solvent - other solvents such as toluene, tetrahydrofuran, dichloromethane or chloroform are used. All of these suggest that high hydrogen pressure is one of the essential parameter for obtaining a high optical. Due to the university regulation the experiments were performed at a lower pressure, 8 bar or below, it is possible therefore that the ketal was produced and isolated.

**4.3.1.7. Performance of the ex-situ and in-situ modified catalysts**

The method of *in-situ* modification (addition of TA to the reaction media) makes the enantioselective hydrogenation procedure with the RNi catalyst less complicated, because the process of modification in an aqueous solution prior to the hydrogenation can be omitted.

*Figure 4.10* shows the % MAA converted, for both an *in-situ* and *ex-situ* modification including the product at 12 minute retention time. It shows as the concentration of TA is increased % conversion for the *ex-situ* modified catalyst also increased from 53% to 98%. The highest % conversion was achieved with 50% TA. However, for the *in-situ* modified catalyst the % conversion decrease with increased concentration of TA from 51% to 17%. The highest % conversion was achieved in the region of TA amount of between 10-20 % (wt/wt RNi).
Figure 4.10: Tartaric acid concentration effects on the % conversion of products (including the peak at 12 minutes) using the ex-situ and in-situ modified catalysts.

Figure 4.11: Tartaric acid concentration effects on the % enantiomeric excess of R-MHB for hydrogenation of MAA using ex-situ and in-situ modified catalysts

Figure 4.11 shows that the increase in concentration of TA would increase the enantiomeric excess for the both in-situ and ex-situ modification methods. However,
for the ex-situ modification the enantiomeric excess reaches at 50% TA and plateaus. As discussed in Section 4.1 this indicates that the excess TA was washed off during our washing step. On the other hand, the process of modification in an aqueous solution prior to the hydrogenation was omitted in the in-situ modification method, therefore at high TA coatings there is an excess amount of TA present in the reaction media that may not be able to adsorb on the catalyst surface. At higher concentrations of TA, the yield decreased and enantiomeric excess increased. There were several effects acting together. With an increase of the tartaric acid concentration, higher degree of its adsorption on the catalyst surface occurred and the catalyst surface coverage ‘θ’ increased. Simultaneously, nickel from the catalyst was leached into the reaction media. The amount of nickel leached to the reaction media was monitored by AAS using PerkinElmer Analyst 400 atomic absorption spectrometer, Figure 4.12. This could also be examined visually, as the color of the solution changed from clear to light green. It is noticeable from Figure 4.12 that during the modifications, the in-situ modification produced higher Ni leaching up to 50% TA in comparison to the ex-situ modification. TA concentration > 50 % produced same amount of nickel into the reaction media. Keane’s work showed that as the concentration of TA increased as did the amount of Ni leaching into the solution [23].

![Figure 4.12](image.png)

**Figure 4.12:** Concentration of Ni leaching in solution against the concentration of tartaric acid, ex-situ and in-situ modification.
Leached nickel in the presence of TA in the solution could perform a homogenous hydrogenation reaction of MAA in the \textit{in-situ} modification. \cite{101} In other words, when using the \textit{in-situ} modification process for the hydrogenation of MAA the reaction is heterogeneous as well as homogenous. This explains the occurrence of a high enantiomeric excess using the \textit{in-situ} modification method.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.13.png}
\caption{Tartaric acid concentration effects on the \% yield of R-MHB for hydrogenation of MAA using \textit{ex-situ} and \textit{in-situ} modified catalysts.}
\end{figure}

Results of the present study shown in Figure 4.13 indicated that the addition of TA to the reaction media gave a low optical yield for the \textit{in-situ} modification. This finding showed that the \textit{in-situ} modification has the same tendency as the conventional \textit{ex-situ} modification. The maximum yields for the \textit{in-situ} and \textit{ex-situ} were achieved at different concentrations of TA. With an \textit{in-situ} modified RNi the maximum yield of 28.9\% was achieved at 10\% TA concentration, although there is little difference from 0\% to 20\% TA. An \textit{ex-situ} modified RNi reaches a clear maximum yield of 72.2\% at 50\% TA.

\subsection*{4.2. Conclusions}

The work is engaged in the study of \textit{ex-situ} and \textit{in-situ} chiral modification of Raney nickel catalyst using (R,R)-(+-tartaric acid. From the acquired data, a considerable influence of modifying conditions on the resulting enantioselectivity of the catalyst is
evident. To achieve the highest optical yields of MAA hydrogenation, it is necessary to optimise the parameters of modification. These parameters have to be optimised to create the optimal amount of the complex of nickel and tartaric acid on the catalyst surface.

The amount of TA affects the enantiomeric excess of R-MHB greater than 50% wt/wt RNi TA is optimal for achieving the highest enantiomeric excess. The excess TA was washed off during the washing step in the ex-situ modification process, whereas in the in-situ modification process the excess amount of TA in the reaction media would allow the homogenous hydrogenation reaction in combination with leached Ni ions. Hence, the enantiomeric excess for the in-situ modified catalyst is almost double that produced by the ex-situ modification process.

Solvent type has a significant effect on the enantiomeric excess used in this enantioselective hydrogenation reaction, as expected methanol is the most suitable for achieving the highest enantiomeric excess at 70 °C. However, the reaction with methanol did not produce the expected results for the in-situ modification method; two unknown products were identified. With further analysis, the probable products were the enol and the ketal from a reaction between the solvent methanol and MAA. To resolve this problem the reaction requires high pressure and longer reaction time.

The hydrogen pressures from 2 to 8 bars range have no effect on the enantioselectivity of R-MHB. Another factor that was investigated was the durability or shelf life of the catalyst activity and selectivity. There was steady drop in enantioselective ability as the storage period increase. The data obtained in this work infer that a chiral modification of Raney nickel catalyst using tartaric acid is a very complex process, which depends on an accurate optimisation of the modifying conditions.
Chapter 5

Hydrogenation of MAA over TA-Ni Catalyst

The Raney nickel catalyst is typically stored in an alkaline environment. Therefore, it was necessary to wash it several times with distilled water before modification as described in Chapter 4 section 4.1. However, this step was omitted for synthesised nickel nanoparticles with or without support. All the other procedure such as pre-modification, washing and modification for the synthesised Ni nanoparticles were carried out same as for Raney nickel (RNi), described in Chapter 4 section 4.1.

5.1. Preliminary experiments

Nickel nanoparticles are reported to be highly active catalysts for the hydrogenation of unsaturated carbonyl compounds. First, experiments for the hydrogenation of methylacetoacetate (MAA) were attempted on SiO$_2$ supported ‘one-microemulsion’ nickel oxide (30 wt% loading) without the modifier rather than the expected pure nickel nanoparticles. These experiments were conducted using Radley Carousel reactor under varying reaction conditions without success. In the first experiment the catalyst was used without calcination, which may be the reason for no reaction. Subsequent hydrogenation experiments were conducted with calcined catalyst at 450 °C for 4 hrs. In these experiments no hydrogenation was observed. It may be that the hydrogen pressure was not sufficient to hydrogenate MAA or it may well be due to the oxide layer on the nickel. Subsequently, a high pressure reactors were used to do this reaction using SiO$_2$ supported without (R, R)-tartaric acid and showed no hydrogenation. This may be a result of the formation of a very stable nickel silicate phase which was not fully reduced to nickel metal at 450 °C, and unreduced nickel silicate remained on the surface. Even the reduced nickel surface in this catalyst could be contaminated by the silicon. These effects disrupted the adsorption of tartaric acid on the nickel surface, and result in little or no activity of the catalyst. On the other hand, the pure nickel produced using the reduction method was found to be active, shown in Table 5.1 data and Figure 5.1. Therefore, the catalysts produced using the reduction method are further studied for the enantioselective hydrogenation of methylacetoacetate (MAA) to methyl 3-hydroxybutyrate (MHB).
Figure 5.1: GC spectrum for the MAA hydrogenated solution using (2R, 3R)-Tartaric acid modified pure nickel. Modifying conditions: \( C_{TA} = 0.2 \text{ mol/L, } pH = 5.1, T = 100 \degree C, t = 24 \text{ hrs; reaction conditions: solvent (25 mL), MAA (12.5 mL), catalyst (0.5 g), } H_2 (8 \text{ bar}) \text{ at 70}\degree C. \)

Table 5.1: Elution times of reaction mixture from the Rт-\( \text{YDEX}_{\text{TM}} \) column 30 m, 0.32 mm ID, 0.25 \( \mu \)m.

<table>
<thead>
<tr>
<th>Retention time / mins</th>
<th>Identity</th>
<th>Peak Area / A.U.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.06</td>
<td>- enol tautomeric form of MAA</td>
<td>359.8</td>
</tr>
<tr>
<td>7.28</td>
<td>Decane (internal standard)</td>
<td>270.6</td>
</tr>
<tr>
<td>12.82</td>
<td>-Ketal</td>
<td>65.4</td>
</tr>
<tr>
<td>14.15</td>
<td>S - MHB</td>
<td>554.4</td>
</tr>
<tr>
<td>14.42</td>
<td>R - MHB</td>
<td>1300</td>
</tr>
<tr>
<td>18.24</td>
<td>MAA</td>
<td>4983.3</td>
</tr>
</tbody>
</table>

5.2. Hydrogenation of MAA over TA-Ni Catalyst

Hydrogenation of MAA with an unmodified catalyst proceeds to the formation of racemic mixture (50:50) of methyl-(3R)-hydroxybutyrate (R-MHB) and methyl-(3S)-hydroxybutyrate (S-MHB). The catalyst modified with (R,R)-TA produced a higher content of R-MHB, while the catalyst modified with (S,S)-TA produced a higher content of S-MHB. Using antipodal enantiomer under the same modifying conditions, the yield of the reaction was nearly coincident, Figure 5.2. The reactions were carried out using the ex-situ modified catalyst.
Figure 5.2: The effect of antipodal modifier on the % yield of reaction. Modifying conditions: $C_{TA} = 0.2 \text{ mol/L}$, pH 5.1, $t = 24$ hrs; reaction conditions: solvent (25 mL), MAA (12.5 mL), catalyst (0.5 g) and $H_2$ (8 bar) at 70°C.

The BET surface area and the pore volume of each sample with or without support were determined by N$_2$ adsorption at -196°C (Micromeritics Gemini V Surface Area and Pore Size Analyser) previously degassed at 150°C for 2 hr using a Micromeritics Flowprep 060. The results of the properties of the pure supports are shown in Table 5.2.

Table 5.2: Physical properties of the supports prior to adsorption of Ni nanoparticles.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface / m$^2$ g$^{-1}$</th>
<th>Pore volume / cm$^3$ g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-Al$_2$O$_3$</td>
<td>86.25</td>
<td>0.042</td>
</tr>
<tr>
<td>Colloidal SiO$_2$</td>
<td>169.66</td>
<td>0.0071</td>
</tr>
<tr>
<td>C</td>
<td>282.45</td>
<td>unsuccessful</td>
</tr>
</tbody>
</table>
5.3. Hydrogenation of MAA over TA-Ni supported Catalyst

In heterogeneous catalysis, porous support bodies are widely used to obtain a good dispersion of the nano-sized active metal. Only the surface of the metal nanoparticle is active and it is essential to maximise the surface to volume ratio achieved by using the supports. Metal surface atoms gain significant mobility at high temperature due to large surface energy contribution. Nano-sized metal particles have strong tendency to sinter, therefore to prevent sintering, the nanoparticles are supported on a support, usually either an oxide such as SiO₂, γ-Al₂O₃ or porous carbon materials. These supports play multiple roles: it facilitates the preparation of very small particles, prevents sintering during catalytic activity that is often relatively high temperatures and under chemically reactive atmosphere and also improves the overall mechanical properties and stability of the system, allowing packing in large reactors. Furthermore, there are several examples in which the support-metal interaction also influences the catalytic activity of the metal nanoparticles.

Table 5.3 shows the specific surface area and pore volume of Ni on various supports, 50 wt % nickel loading were done to each support. The results show that the specific surface area and pore volume decreases with nickel loading, this may be due to blockage of the support pores by Ni. Ni supported on C and on γ-Al₂O₃ showed the highest (210.71 m² g⁻¹) and the lowest (64.04 m² g⁻¹) specific surface area, respectively.

Table 5.3: Physical properties and crystallite size of the catalysts with different support.

<table>
<thead>
<tr>
<th>Supports</th>
<th>BET surface / m² g⁻¹</th>
<th>Pore volume / cm³ g⁻¹</th>
<th>Crystallite size D / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>48.10</td>
<td>0.11</td>
<td>16</td>
</tr>
<tr>
<td>Ni-γ-Al₂O₃</td>
<td>64.04</td>
<td>0.92</td>
<td>13</td>
</tr>
<tr>
<td>Ni-Colloidal SiO₂</td>
<td>181.60</td>
<td>0.09</td>
<td>15</td>
</tr>
<tr>
<td>Ni-C</td>
<td>210.71</td>
<td>0.105</td>
<td>14</td>
</tr>
</tbody>
</table>

Table 5.4 shows the specific surface area and pore volume of *ex-situ* modified Ni on various supports and as expected there is a slight decrease in the surface area and pore volume distribution, except for Ni supported on the colloidal SiO₂. This may be due to the removal off the polymer that is present in colloidal SiO₂ during washing.
Table 5.4: Physical properties of the modified catalysts with different support

<table>
<thead>
<tr>
<th>Supports</th>
<th>BET surface / m² g⁻¹</th>
<th>Pore volume / cm³ g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>MNi</td>
<td>13.83</td>
<td>0.007</td>
</tr>
<tr>
<td>MNi- γ-Al₂O₃</td>
<td>61.53</td>
<td>0.030</td>
</tr>
<tr>
<td>MNi-Colloidal SiO₂</td>
<td>201.31</td>
<td>0.103</td>
</tr>
<tr>
<td>MNi-C</td>
<td>205.23</td>
<td>0.090</td>
</tr>
</tbody>
</table>

Figure 5.3 shows the enantiomeric excess (ee) of nickel nanoparticles supported on various supports. The results show that the Ni supported on γ-Al₂O₃ and C showed the highest (60.64%) and the lowest (30.64%) ee. This is the higher active catalyst in comparison to C and colloidal SiO₂. This may suggest that the activity of the carbon-supported catalyst is lower than that of the alumina-supported catalyst, or it may simply be due to the reaction being stopped before it had reached completion.

The sizes of the nickel nanoparticles on colloidal silica support and carbon supports are almost the same (14-15 nm), however on γ-Al₂O₃ is slightly smaller. Therefore, if the support had no effect on the hydrogenation the enantiomeric excess for R-MHB should have been the same. The results in Figure 5.3 show that the activity MNi-γ-Al₂O₃ > MNi-colloidal SiO₂ > MNi-C > pure MNi. This suggests the supports play important role on the hydrogenation process. The higher content of the supports exist in the nickel, the higher the BET surface is and the lower the enantiomeric excess is achieved.
Figure 5.3: The effect of varying the support on the % enantiomeric excess of R-MHB for hydrogenation of MAA. Modifying conditions: $C_{TA} = 0.2 \, \text{mol/L}$, pH 5.1, $t = 24 \, \text{hrs}$; reaction conditions: solvent (25 mL), MAA (12.5 mL), catalyst (0.50 g pure nickel and 1.0 g supported) and $H_2$ (8 bar) at 70°C.

5.3.1. Performance of the ex-situ and in-situ modified supported catalysts

The effect of the ex-situ and in-situ modified catalysts on the hydrogenation of MAA to R-MHB is shown in Figure 5.4. For these reactions C supported catalysts were used with 50 wt % Ni loading. The results show that the catalyst behaves in a very similar way to the ex-situ and in-situ modified RNi catalysts. The ex-situ modified catalysts reduced the catalyst’s activity slightly in comparison to in-situ modified catalysts.

The results from Table 5.5 raise questions about the products at the 6.07 and 12.78 minutes peak as these peaks were not seen for ex-situ modified catalyst when RNi was used. The retention times for these products are same as those produced when in-situ modified RNi catalysts were used, suggests same products.
Figure 5.4: GC results for the hydrogenation of MAA using the in-situ and ex-situ modified Ni catalyst. Modifying conditions: $C_{TA} = 0.2$ mol/L, pH 5.1, $t = 24$ hrs; reaction conditions: solvent (25 mL), MAA (12.5 mL), catalyst (1.0 g C-supported Ni) and $H_2$ (8 bar) at 70°C.

Table 5.5: GC results for the hydrogenation of MAA using the ex-situ and in-situ modified Ni catalyst under 8 bar at 70°C for 24 hrs.

<table>
<thead>
<tr>
<th>Modification</th>
<th>Identity</th>
<th>Retention time / Mins</th>
<th>Peak Area / A. u</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-enol</td>
<td>6.07</td>
<td>453.30</td>
</tr>
<tr>
<td></td>
<td>Decane</td>
<td>7.28</td>
<td>337.60</td>
</tr>
<tr>
<td></td>
<td>-Ketal</td>
<td>12.82</td>
<td>82.40</td>
</tr>
<tr>
<td></td>
<td>R-MHB</td>
<td>14.37</td>
<td>514.50</td>
</tr>
<tr>
<td></td>
<td>S-MHB</td>
<td>14.06</td>
<td>273.10</td>
</tr>
<tr>
<td>Ex-situ</td>
<td>MAA</td>
<td>19.38</td>
<td>6726.60</td>
</tr>
<tr>
<td></td>
<td>-enol</td>
<td>6.07</td>
<td>630.50</td>
</tr>
<tr>
<td></td>
<td>Decane</td>
<td>7.28</td>
<td>337.60</td>
</tr>
<tr>
<td></td>
<td>-Ketal</td>
<td>12.82</td>
<td>361.02</td>
</tr>
<tr>
<td></td>
<td>R-MHB</td>
<td>14.37</td>
<td>74.90</td>
</tr>
<tr>
<td></td>
<td>S-MHB</td>
<td>14.06</td>
<td>30.90</td>
</tr>
<tr>
<td></td>
<td>MAA</td>
<td>19.38</td>
<td>6044.40</td>
</tr>
</tbody>
</table>

5.4. Ni-TA Interaction

From previous studies [21, 50, 54, 102] it is well known that the metal-substrate interaction influences the reactivity and enantioselectivity of nanoparticles. Therefore, the used scanning transmission X-ray microscopy combined with near-
edge X-ray absorption fine structure spectroscopy (STXM/NEXAFS) to investigate the adsorption of the chiral modifier, namely (R,R)-tartaric acid, onto individual nickel nanoparticles. Pure nickel nanoparticles that were used in this set of experiments were synthesised using the reduction method as described in Chapter 3 Section 3.2. This investigation will collect detailed in-situ photoabsorption spectra of species involved in the enantioselective hydrogenation reaction of MAA. This will contribute to the understanding of the mechanism of this important and topical enantioselective heterogeneous hydrogenation reaction.

Earlier in Chapter 3 Figure 3.12 we showed the $1 \times 1 \, \mu\text{m}$ STXM image of Ni nanoparticles deposited on a clean Si$_3$N$_4$ window at photon energy of 854.5 eV. The image showed the presence of four pure nickel nanoparticles of ~90–140 nm in diameter. The Red line in Figure 3.12 indicates typical in line profile (line length = 1 $\mu\text{m}$) used for NEXAFS acquisition and covers both the nanoparticle and the background region used for normalisation. Information from the background of the sample was used to normalise the spectra for variations in X-ray beam intensity with photon energy and time. The accuracy of the positioning system in the STXM endstation on the PolLux beamline and also the distinct spatial configuration of groups of nanoparticles meant that it was possible to return to the same individual nanoparticle several times - even after the sample plate had been removed from the analysis chamber and replaced at a later time. This allowed examination of exactly the same nanoparticle under a number of different conditions and comparison of distinctly different nanoparticles under the same conditions.

Figure 5.5 shows normalised Ni L$_{2,3}$-edge NEXAFS from three different nanoparticles (i-iii) and also, for comparison, from Raney Nickel (iv). The three nanoparticles chosen covered a range of sizes from (i) ~90 nm to (ii) ~170 nm and finally a larger nanoparticle of (iii) ~300 nm to conduct a particle size effect on the adsorption mode of the TA. It is well known that RNi typically consists of very large but porous particles, due to the presence of aluminium. [103, 104] As described in Chapter 4 Section 4.1 the aluminium being leached from the solid in either a ‘pre-modification’ stage or under reaction conditions. The STXM experiment was conducted in a transmission mode, therefore, a crystallite of ~$500 \times 900 \, \text{nm}$ RNi was chosen for this study. A thicker sample would not allow transmission of the
radiation. Figure 5.5 shows that the dominant features of all the spectra are the resonances at 853–854 eV and ~871 eV, which correspond to the Ni L₃ and L₂ adsorption edges, respectively. For all but the smallest of the nanoparticles the maxima of the L₃ adsorption edge fall at 853.3 eV, in the case of spectrum (i) the (90 nm) particle the maximum is shifted to higher photon energies by ~0.4 eV. This higher photon energy shift may be the result of oxide layer on Ni under ambient condition although P-XRD analysis of the sample did not show evidence of a NiO phase. It is likely that a Ni catalyst could be exposed to air unintentionally, even for the shortest period, before it is modified for use in a catalytic reaction. As such, this spectrum may be of additional importance. The fact that a small shift is observed in the L₃- and L₂-edges but that the spectra retains all of the characteristics of the ‘clean’ nickel nanoparticles suggests that it would still perform as desired catalytically.

Figure 5.5 also shows a clear difference in the shape of the 853.3 eV peak for the spectrum (iii) the largest of the nanoparticles and (iv) the Raney Nickel sample with an apparent high photon energy shoulder appearing at ~856 eV. Both the position and the shape of the L₃-edge of 3d metals are strongly reliant on the empty 3d and 4s states. The full width–half maximum (FWHM) of the nickel L₃ adsorption edge for the pure, bulk metal is 2.3 eV. Senkovskiy et al. found that a Ni₅₀Ti₅₀ had the L₃ adsorption edge at 853.4 eV which was shifted from 852.7 eV. [105] This suggest that the current work where the L₃ adsorption edge for untreated Raney Nickel (nominally a Ni₁₋ₓAlₓ where 0.1 ≤ x ≤ 0.5) was found to be 853.3 eV. This resonance also appears to have a larger FWHM than any of the corresponding ‘pure’ metal nanoparticles.

Figure 5.7 shows C K-edge NEXAFS taken under different conditions either before (i) or after (ii)-(vi) the adsorption of TA. Spectra (i) shows NEXAFS of a nickel nanoparticle before the adsorption of any additional species. It can be used in conjunction with the XRD pattern Figure 3.9 to confirm that the nanoparticles were not only pure nickel but also had clean surfaces that were not contaminated with a cellulose residue from the synthesis procedure. Spectra (ii) represents the results of C K-edge NEXAFS after the adsorption of tartaric acid from aqueous solution and subsequent washing onto a completely clean (as received) Si₃N₄ window and spectra
(iii) represents the results of C K-edge NEXAFS after adsorption of the tartaric acid onto nickel nanoparticles deposited onto an alumina-coated window (~10 nm thickness Al₂O₃). All these three spectra (i) to (iii) are used as ‘control’ samples, the results of which put the later results into context. All the other spectra show resonances instantly recognisable as originating from small organic molecules containing multiple order bonds. Table 5.6 summarised all the assignments and associated transitions.

![Graph](image)

**Figure 5.5:** Ni L₂,₃-edge NEXAFS from: (i) ~90 nm Ni particle; (ii) ~170 nm Ni particle; (iii)~300 nm Ni particle; and (iv) ~500 nm Raney Nickel particle. [106]

**Figure 5.7** (ii) shows a weak signal with resonances at 285.2 eV and 286.9 eV and several smaller, ill-defined, features between ~289 and 302 eV. The presence of the 285.2 eV peak suggests that the tartaric acid molecule has undergone a chemical change upon adsorption involving the formation of a C=C double bond. The appearance of a C 1s→π* resonance can be explained two ways. First, a condensation reaction whereby the C=C bond is formed between the two chiral centres leading to the loss of H₂O and ultimate loss of all chirality from the modifier.
molecule. Second a keto-enol tautomerisation as shown in Figure 5.6 which represents an equilibrium between two constitutional isomers, the keto- and enol-forms. In the latter case the chirality of just one of the chiral centres is lost to sp\(^3\) hybridization. All the data suggest that this is more likely to be keto-enol tautomerisation as this has been observed previously under similar conditions. Ghoria \textit{et al.} showed the keto-enol equilibrium constant of malonic acid using STXM and showed a strong dependence on the relative humidity of the aerosol that deliquesced particles of the organic suspended in. [106] The higher the relative humidity, the greater the amounts of the enol form present - they concluded that similar carboxylic acids may also exist in predominantly enol forms.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5_6.png}
\caption{Keto-enol equilibrium showing the tautomeric forms of tartaric acid.}
\end{figure}

Despite the weak signal seen in Figure 5.6 (ii) the resonances appear at the expected photon energies (see Table 5.6) and suggest that a very small amount of TA adsorbs, in approximately equal amount of the keto- and enol-forms, on the clean Si\(_3\)N\(_4\) window. This was verified using the background signal obtained from the extended line profile (Figure 3.9) to normalise the signal from the nanoparticles.
Figure 5.7: C K-edge NEXAFS of: (i) ‘as produced’ Ni nanoparticle showing lack of surface contamination; (ii) tartaric acid adsorbed onto a clean Si₃N₄ window; (iii) tartaric acid adsorbed onto a Ni deposited onto an alumina coated Si₃N₄ window; tartaric acid adsorbed onto (iv) ~90 nm, (v) ~170 nm and (vi) ~300 nm Ni nanoparticles deposited onto a clean Si₃N₄ window. [106]

Table 5.6: C K-edge NEXAFS assignments. [106]

<table>
<thead>
<tr>
<th>Energy / eV</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>285.2</td>
<td>C 1s→π*ₐ(C=C)</td>
</tr>
<tr>
<td>286.9</td>
<td>C 1s→π*ₐ(C=O)</td>
</tr>
<tr>
<td>288.7</td>
<td>C 1s→σ*ₐ(C-H)</td>
</tr>
<tr>
<td>294.5</td>
<td>C 1s→σ*ₐ(C-C)</td>
</tr>
<tr>
<td>301.1</td>
<td>C 1s→σ*ₐ(C-O)</td>
</tr>
</tbody>
</table>

Despite the weak signal seen in Figure 5.7 (ii) the resonances appear at the expected photon energies (see Table 5.6) and suggest that a very small amount of TA adsorbs, in approximately equal amount of the keto- and enol-forms, on the clean Si₃N₄
window. This was verified using the background signal obtained from the extended line profile (Figure 3.9) to normalise the signal from the nanoparticles.

**Figure 5.7** (iii) shows the adsorption of TA onto nickel nanoparticles deposited onto an alumina-coated window (~10 nm thickness Al$_2$O$_3$). Subtraction of the background signal from the signal of the nanoparticle itself results in an almost flat and featureless spectrum. This can only be a result of subtracting two almost identical C K-edge NEXAFS signals and indicates that tartaric acid adsorbs onto alumina and the nickel nanoparticle in a similar mode and to a similar extent.

**Figure 5.7** spectra (iv)–(vi) are dominated by prominent resonances due to C 1s→π* and C 1s→σ* transitions. All three spectra are very similar and differ only in that they represent adsorption resonances of tartaric acid adsorbed onto different sized particles; namely, the same (iv) ~90 nm, (v) ~170 nm and (vi) ~300 nm nanoparticles that were examined in Figure 5.7 (i–iii). In contrast to adsorption on the clean window (Figure 5.7 (ii)), when adsorbed onto nickel nanoparticles the ratio of the 285.2 eV and 286.9 eV resonances in NEXAFS suggests that the tartaric acid is predominantly in the enol form. The main difference between the three spectra is the improvement in the ‘quality’ of the data (i.e. a reduction in signal-to-noise) that results from the ability to average the signal over a larger number of points when collecting data from larger nanoparticles. Accordingly, we have shown that the adsorption of tartaric acid from aqueous solutions onto the three distinctly different nanoparticles presented here is unaffected by particle size. This is perhaps unsurprising due to the generally large size of the nanoparticles used in the study. If the spatial resolution of the instrument would allow investigation of nanoparticles in the 5–50 nm size range one might expect to see more pronounced differences caused by size effects and reduced terrace widths resulting in disruption of the long-range order of the adsorbed overlayer of chiral modifier molecules.

### 5.5. Conclusion

The types of support and the preparation methods affected the enantiomeric excess of the obtained product, methyl (R)-3-hydroxybutyrate. Ni supported on γ-Al$_2$O$_3$
catalyst gave the highest enantioselectivity, whereas the carbon-supported catalyst showed lower selectivity.

C-supported catalysts with 50 wt% Ni loading were used to investigate the effect of the two modification methods, the *ex-situ* and *in-situ* using *(R,R)-(+)*-tartaric acid. The results showed that the *in-situ* modified catalyst is more active in comparison to ex-situ modified catalyst, which was very similar to the *ex-situ* and *in-situ* modified RNi catalysts activity.

The scanning transmission X-ray microscopy combined with near-edge X-ray absorption fine structure spectroscopy spectra (STXM/NEXAFS) was used to investigate the adsorption of the chiral modifier, namely *(R,R)-tartaric acid, onto individual nickel nanoparticles. The C K-edge spectra strongly suggest that tartaric acid deposited from aqueous solutions undergoes a transformation on the metal surface akin to an enolisation, evidenced by the presence of strong C1s→π* resonances in the C=C region as well as the expected π* resonances at C=O photon energies. Furthermore, we were able to interrogate the Ni L\textsubscript{2,3}-edge resonances of individual metal nanoparticles which, combined with powder X-ray diffraction (PXRD) patterns showed them to consist of a pure nickel phase rather than the more thermodynamically stable bulk nickel oxide. Importantly, there appears to be no “particle size effect” on the adsorption mode of the tartaric acid in the particle size range $\sim 90 \text{ – } \sim 300 \text{ nm}$. 

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Chapter 6

6.1. Conclusions

A series of nanoparticles exhibiting NiO crystalline were synthesised using both ‘one-step’ and ‘two-step’ microemulsion methods. The diffraction peaks of the as produced samples using both methods were covered with organic residues and had on amorphous structure. After the calcination processes all the organic residues present in the catalyst surface were removed and the crystallinity in the materials improved. However, temperature treatment made those nanoparticles mobile on the support causing them to sinter and form larger particles. The Ni/SiO$_2$ (30 wt. % nickel) catalysts were produced and the catalytic properties were tested in the enantioselective hydrogenation of MAA. Our data showed no catalytic activity, this may be a result of the formation of a very stable nickel silicate phase which was not fully reduced to nickel metal at 450 °C, and unreduced nickel silicate remained on the surface. Even the reduced nickel surface in this catalyst could be contaminated by the silicon. These effects disrupted the adsorption of tartaric acid on the nickel surface and show no activity and enantioselectivity of the catalyst.

A synthetic route without any other protective agent and inert atmosphere protection has been successfully developed for the preparation of metallic nickel nanoparticles by hydrazine reduction. The NEXAFS and PXRD showed nanoparticle to consist of a pure nickel phase rather than the more thermodynamically stable bulk nickel oxide. In addition, the obtained nickel nanoparticles were isolated in the solid state and stabilised for several months in the atmosphere. Their physical characterization showed that they possess different sizes. From the catalytic test results, the nickel displayed hydrogenations of MAA. Our results showed that the types of supports and the preparation methods affected the enantiomeric excess of the obtained product, methyl (R)-3-hydroxybutyrate.

Various supported Ni catalysts were synthesised using the reduction method and found the γ-Al$_2$O$_3$ supported catalyst to be most active catalyst in comparison to catalyst supported on colloidal SiO$_2$ and C.

The enantioselective hydrogenation of methyl acetoacetate was carried out over a (R,R)-TA modified Raney nickel to find the optimum condition to achieve the
highest enantioselectivity of the catalyst. The experiments were carried out under various conditions such as different concentration of TA, temperature, pressure and different solvents to create the optimal amount of the complex of nickel and tartaric acid on the catalyst surface. It was found that the TA >50% wt/wt RNi is the optimal for achieving the highest enantiomeric excess. The excess TA was washed off during the washing step in the ex-situ modification process, where as in the in-situ modification process the excess amount of TA in the reaction media would help to precede the homogenous hydrogenation reaction in combination with leached Ni ions. Hence, the enantiomeric excess for the in-situ modified catalyst is almost doubled in comparison to the ex-situ modification process. Methanol was found to be the most suitable solvent for achieving the highest enantiomeric excess at 70 °C. However, reaction did not produce the expected results for in-situ modification method; two unknown products were identified. With further analysis, the probable products were enol form of the MAA and ketal from reaction between the solvent methanol and MAA, respectively.

The influence of hydrogen pressure on the enantioselectivity of R-MHB was insignificant when compared with other factors. We also investigated the enantioselective ability as the storage period increase. Our results indicate RNi can be modified and stored to be used for up to 3 days without hydrogenation effect on the reactivity or selectivity.

The enantioselective hydrogenation of β-keto-esters (methyl acetoacetate) in the presence of an adsorbed chiral molecule on the surface of nickel nanoparticle is an extremely complex system. The precise pathways of the reaction and the mechanism of this enantioselective control, however, have not been yet verified; though several models have been proposed to explain the activity (discussed in Chapter 1). We have shown that the possibility to use the excellent spatial resolution of STXM to interrogate L_{2,3}-edge resonances of individual, catalytically relevant, metal nanoparticles. The C K-edge spectra strongly suggest that tartaric acid deposited from aqueous solutions undergoes a transformation on the metal surface akin to an enolisation, evidenced by the presence of strong C1s→π* resonances in the C=C region as well as the expected π* resonances at C=O photon energies. Furthermore, the reproducibility and accuracy of the experiment allowed the same nanoparticles to
be located after the sample had been treated under several different conditions. Differences in the shape and position of the L$_3$-edge resonance could also be used to infer information about the electronic structure and surface state of the material. Importantly, there appeared to be no “particle size effect” on the adsorption mode of the tartaric acid in the particle size range ~90 – ~300 nm.

6.2. Future works

Trying to understand the mode of action of a catalyst is a fascinating but also very difficult endeavour for heterogeneous catalysts and even more so if the desired reaction is an enantioselective one. In most cases, at best one has a qualitative understanding of their mode of action, which is not surprising considering the complexity of the systems.

Through this study, we have observed the issue of nickel leaching using the ex-situ and in-situ modification methods, which was quantified using AAS. A potentially useful further study would involve the use of Inductively-coupled plasma mass spectrometry (ICP-MS) to accurately determine the absolute concentration of leached Ni after hydrogenation of MAA in various conditions at very short reaction times. The detection limit for Ni in ICP-MS is 400x better than using AAS (ICP-MS < 0.005 μg/L, AAS < 20 μg/L). [107] As shown by Kean and Webb, Ni leached from the catalyst surface can be extracted from the reaction mixture and used itself as an enantioselective hydrogenation catalyst. [101] This suggests some, possibly very small amount, of the enantioselectivity of the reaction may be provided by leached Ni. Similarly, McIntosh et al. have shown conclusively that the enantioselective differentiation step of the hydrogenation of isophorone occurs in the liquid phase and not on the metal surface. [108]

Only a very small number of studies concerning in-situ modification have been reported in the case of tartaric acid modified Ni system. [42] [109] All the parameters that can affect the reactivity and selectivity of the catalysts require optimisation (i.e. temperature, reaction time, pH of the solution containing the modifier) for each new catalyst and support combination. For the hydrogenation of MAA the solvents tested should include other short chain alcohols such as propanol
and butanol, along with solvent such as THF and toluene. Kukula et al. reported a highest optical yield (~57%) was obtained using THF. [47] The study showed that mixing MAA and methanol at room temperature and low pressure formed the product found at 12 minutes retention time using GC, however it was not produced using other solvents such as THF or toluene. If the product observed using GC at a retention time of 12 minutes was related to the ketal and hemiketal forms of the molecule, [98] alternative techniques may be best used to identify the product conclusively for example GC-MS or NMR after fractional distillation.

The present study showed that there was a steady drop in the enantioselective-directing ability of the modified catalyst as the storage period increase. Enantioselective ability dropped from 73% to 66% just after 3 days, then to 63% after 9 days. These results indicate RNi can be modified and stored to be used up to 9 days prior to use with a small decrease. However, little has been investigated for reusability of the ex-situ modified catalyst. A highly active and enantioselective, yet reusable, chirally modified nickel catalyst is highly desirable, therefore a series of experiments should be carried out to investigated the reusability of the catalyst. The procedure would consist of submitting the same catalyst repeatedly to hydrogenation reactions with fresh reagents (under the same conditions) and investigating the performance of the catalysts to monitor and degradation.

Several groups have contributed to the literature on Ni-based system and yet there is still no clear picture of the exact chemical nature of the adsorbed molecules or the surface structure and the state of the catalytically active Ni nanoparticles. Moreover, many of the previously reported studies are performed in ultra-high vacuum in the absence of a solvent; very little information is available on the active modified surface created under realistic reaction conditions. Through our study, we examined the adsorption of R, R-tartaric acid onto a ‘real’ catalyst sample consisting of Ni nanoparticle using STXM. [100] The C K-edge spectra strongly suggest that tartaric acid deposited onto the nanoparticle surfaces from aqueous solutions undergoes a keto-enol tautomerisation. Since the structure of most reaction intermediates are usually deduced from the observed effects of structural changes of the modifier and substrates and on the specific interactions of the species involved in the catalytic reaction [substrate(s), active site, and modifier]. Therefore, it is very important to
investigate further the modified surfaces created under realistic condition using vibrational spectroscopy and STXM. [104] Somorja and co-worker have shown the role of all the species present in the mechanism of ethylene hydrogenation using Pt(100) and Pt(111) and its intermediate by using infrared-visible sum-frequency-generation (SFG) vibrational spectroscopy with simultaneous gas-chromatographic kinetic studies. SFG allowed the identification of different surface intermediate present on Pt(100) and Pt(111) under reaction condition and thus, in combination with kinetics data and energetic calculations, led to a molecular level understanding of the different mechanisms behind this structure sensitivity.
7. References


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8. Appendixes

8.1. Gas Chromatography

8.1.1. Calibration

In each sample decane was added as an internal standard. For the calibration pure MAA, R-MHB, S-MHB and decane were all run through the GC under the same conditions as for the hydrogenated solutions. Three samples of same concentration were made to produce triplicate results so that error bars could be included.

![Graph](image.png)

\[
y = 46.033x \\
R^2 = 0.9998
\]
Figure 8.1: Calibration curve for MAA, R-MHB and S-MHB using average peak area, with error bars.
8.2. AAS

8.2.1. Calibration

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>Blank corrected Absorption</th>
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<tbody>
<tr>
<td>0</td>
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</tr>
<tr>
<td>0.625</td>
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<td>5</td>
<td>0.308</td>
</tr>
<tr>
<td>10</td>
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</tbody>
</table>

Figure 8.2: Calibration curve of AAS with Ni.
8.3. **Hydrogenation of MAA over TA-RNi Catalyst**

![GC spectrum for the MAA hydrogenated solution using (2R, 3R)-Tartaric acid modified RNi. Modifying conditions: \( C_{TA} = 0.2 \text{ mol/L}, \ pH = 5.1, \ T = 100 \degree C, \ t = 24 \ hrs; \) reaction conditions: solvent (25 mL), MAA (12.5 mL), catalyst (0.5 g), \( H_2 \) (8 bar) at 70°C.]

Figure 8.1: *GC spectrum for the MAA hydrogenated solution using (2R, 3R)-Tartaric acid modified RNi. Modifying conditions: \( C_{TA} = 0.2 \text{ mol/L}, \ pH = 5.1, \ T = 100 \degree C, \ t = 24 \ hrs; \) reaction conditions: solvent (25 mL), MAA (12.5 mL), catalyst (0.5 g), \( H_2 \) (8 bar) at 70°C.*