Optimisation and Characterisation of Nickel Based Nano-Catalysts for the Dry Reforming of Methane with Carbon Dioxide

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“It has pleased no less than surprised me that of the many studies whereby I have sought to extend the field of general chemistry, the highest scientific distinction that there is today has been awarded for those on catalysis.”

• Wilhelm Ostwald
Declaration

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; and any editorial work, paid or unpaid, carried out by a third party is acknowledged.

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Abstract

Two of the main components of biogases, methane and carbon dioxide, are regularly flared or released into the environment due to the compositions of these gases being unsuitable for further processing using currently available technologies. One process that can utilise the two aforementioned gases (in ratios not suitable for current commercial technologies) is catalytic dry reforming, which involves the conversion of these two gases into syngas (carbon monoxide and hydrogen). This process however is not commercially viable due to the lack of discovery of a suitable (economic) catalyst. The aim of this research project was to develop a nickel supported material which showed a significantly increased catalytic ability compared with conventionally prepared materials within the dry reforming reaction, thus increasing the economic viability of the reaction in the hope it will one day be used in industry.

The work undertaken in this thesis has been split into three distinct sections. The first two sections concentrate on improving monometallic Ni catalysts by considering the effect of improved supports over two distinct classes of carrier. The third section focuses on further optimisation of the materials reported in the previous sections by considering the positive doping effect of the lanthanide ytterbium (Yb) on the reported catalysts.

In chapter three the preparation, characterisation, activity and stability of Ni-incorporated mesoporous alumina (MAl) materials with different Ni loading (7, 10
and 15 wt %) are discussed. These catalysts were prepared by a template assisted hydrothermal synthesis method and tested as catalysts for dry reforming of methane under different conditions (nickel loading, gas hourly space velocity (GHSV), reaction temperature and time-on-stream (TOS)). The most active catalyst tested (Ni(10wt%)/MAI) showed a very high stability over 200 h compared to a Ni(10wt%)/\(\gamma\)-Al\(_2\)O\(_3\) prepared using a wet-impregnation method which had a significant loss in activity after only ~4 hours of testing. The high stability of the Ni/MAI materials prepared by the template assisted method was due to the Ni nanoparticles in these catalysts being highly stable towards migration / sintering under the reaction conditions used (700°C, 52000 mL.h\(^{-1}\)g\(^{-1}\) GHSV). The low susceptibility of the Ni nanoparticles in these catalysts to migration / sintering was most likely due to a strong Ni-support interaction and / or active metal particles being confined to the mesoporous channels of the support. The Ni/MAI catalysts also had significantly lower amounts of carbon deposited compared to the catalyst prepared using the co-precipitation method.

In chapter 4 the preparation, characterisation, activity and stability of Ni-incorporated silica sol-gel (SiO\(_2\) SG) materials with various Ni loading (10, 20 and 30 wt %) are discussed. These catalysts were prepared using in-situ deposition of Ni with the preparation of a sol-gel with increased pore size, and tested for catalytic ability in the dry reforming of methane. It was found that all Ni/SiO\(_2\) SG materials showed a comparable initial activity and very high stability over 15 h reaction period (700°C, 52000 mL.h\(^{-1}\)g\(^{-1}\) GHSV) compared to a Ni(10 wt %)/SiO\(_2\) prepared using a wet-impregnation method, which lost all ability to catalyse the reaction after a very short testing time (6 h). The high activity and stability of the Ni/SiO\(_2\) SG materials
were attributed to the decreased Ni particle size with increased distribution, and the increased resistance to sintering of the Ni nanoparticles. The increased distribution and smaller average size of the Ni nanoparticles was a result of the high surface area of the SiO$_2$ SG support and deposition technique used, which subsequently trapped the majority of Ni particles within the pore structure of the sol-gel.

In chapter 5 the preparation, characterisation, activity and stability of Ni(10 wt %)/MAI and Ni(10 wt%)/SiO$_2$ SG materials with different Yb doping concentrations (1 – 4 wt %) are discussed. These catalysts were prepared by in-situ deposition of Yb and Ni to support preparation, and tested for catalytic ability in the dry reforming of methane. The materials showed a further increased conversion of CO$_2$ and CH$_4$ over the whole 15 h reaction time over undoped materials. The further increased activity and stability of the Yb doped Ni/MAI materials were thought to be due to the decreased Ni particle size and increased Ni-support interaction observed in the characterisation of these materials. The increased stability in the Yb doped Ni/SiO$_2$ SG materials over the undoped catalyst was recognised as an effect of increased resistance to inactive carbon deposition over time. The role of the Yb was proposed to be a ‘seeding’ of the nucleation of the Ni nanoparticles across the reported support materials, leading to an increased dispersion and further increased Ni-support interaction.
Chapter 1

Introduction & Aims of Research

A general introduction to the dry reforming of methane is given in this chapter indicating the significance of the reaction, equilibrium conversions of reactants to high energy products, and specific uses of products for further processing. A brief introduction to catalysis is proceeded by specific examples of typical catalysts used in the target reaction, and recent development in both monometallic and bimetallic catalysts supported on different materials, in an attempt to maximise product yield whilst minimising catalyst deactivation through consequential carbon deposition. The aims of the reported research are given and justification provided for specific goals and the overall scope of the project.
1.1 Introduction

Depleting levels of fossil fuels are a continual topic of interest. Crude oil has long been used around the world as a fuel source in transport, industry and in the production of electricity. The high dependence of our economy on declining fuel sources such as crude oil continues to drive interest in the use of alternative fuel sources. Biogas which is produced from anaerobic digestion of biomass; such as landfill, urban and agricultural wastes, peat and wood\(^1\), is one of the most promising renewable energy sources available. Biogas primarily consists of carbon dioxide and methane in various concentrations, depending on the source. Typically biogas consists of; 25-50% CO\(_2\), 50-70% CH\(_4\), 1-5% H\(_2\), 0.3-3% N\(_2\), and a small concentration of various impurities\(^2\). One of the principal limitations with using biogas for various fuel applications is the variability in composition. Conventional heat engines require CH\(_4\) concentrations higher than 50% to operate efficiently, and biogases are regularly flared or released into the atmosphere when classified as unsuitable for such uses\(^3\). The methane and carbon dioxide released into the atmosphere contribute significantly to greenhouse gas emissions, whilst being wasted as potential energy sources\(^4\). Hence ways of converting biogas, which contains methane in concentrations that is currently not suitable for use, into a useable product(s) is of interest.
1.2 Carbon Dioxide Reforming of Methane

Investigations into using CO$_2$ and CH$_4$ as reactants for producing useful compounds culminated in the discovery that these gases can be converted to high energy syngas; which is comprised of hydrogen and carbon monoxide. Research into this process began in 1928$^5$ and the process is now commonly referred to as carbon dioxide reforming or dry reforming of methane.

Dry reforming of methane is a highly endothermic process and hence is only thermodynamically feasible at high temperatures and low pressures (reaction 1.1).

\[
\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2 \text{CO} + 2 \text{H}_2 \quad \Delta H = 247 \text{ kJ mol}^{-1} \quad (1.1)
\]

The H$_2$:CO product ratio resulting from dry reforming of methane is directly affected by the tendency of the H$_2$ produced to further react via the reverse water gas shift (RWGS) reaction (reaction 1.2). Under typical operating conditions this, as expected, results in H$_2$/CO ratios less than one.

\[
\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \quad \Delta H = 41 \text{ kJ mol}^{-1} \quad (1.2)
\]

The standard equilibrium conversions of both CO$_2$ and CH$_4$ and the product ratio for the dry reforming reaction has been calculated using a developed modelling program ‘ARLSOLGASMIX’ over a range of temperatures using a feed ratio of 1:1:1.8 CO$_2$:CH$_4$:He (Figure 1.1)$^6$
A key aspect of the dry reforming reaction is that the H₂/CO product ratio approaches unity; where the reverse water gas shift reaction is limited. This is a key advantage over other reactions such as the partial oxidation of methane (reaction 1.3) and steam reforming of methane (reaction 1.4) where H₂/CO product ratios of 2 and 3 are generally obtained. Lower product ratios are a requirement for such further reactions as the Fischer-Tropsch synthesis for the production of long chain alkanes (reaction 1.5), and hydroformylation/oxo synthesis (reaction 1.6).

\[
\text{CH}_4 + 0.5 \text{O}_2 \rightarrow \text{CO} + 2 \text{H}_2 \quad \Delta H = -36 \text{ kJ mol}^{-1} \quad (1.3)
\]

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3 \text{H}_2 \quad \Delta H = 206 \text{ kJ mol}^{-1} \quad (1.4)
\]

\[
2n \text{CO} + (n+1) \text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + n \text{CO}_2 \quad (1.5)
\]

\[
\text{RCH=CH}_2 + \text{CO} + \text{H}_2 \rightarrow \text{RCH}_2\text{CH}_2\text{CHO} / \text{RCH}_3\text{CHCHO} \quad (1.6)
\]

Figure 1.1: (A) Equilibrium conversions of CO₂ (○) and CH₄ (●) and (B) product ratios of H₂/CO (□) and H₂O/CO (●) for simultaneous CO₂ - CH₄ reforming and RWGS reactions as a function of temperature. Reaction conditions: \(P_{\text{tot}} = 1 \text{ atm; CH}_4/\text{CO}_2/\text{He} = 1/1/1.8\).
In order to both limit the effect of the reverse water gas shift reaction on the \( \text{H}_2/\text{CO} \) product ratio in the dry reforming reaction and simultaneously increase the yield of products, suitable catalysts have been employed which improve the rate of the target conversions and inhibit side reactions from occurring. In industry the need for highly efficient catalysis is driven by economic viability, where operating costs must be kept to a minimum whilst the effectiveness of a reaction in converting low value reactants to products of greater significance must be maximised. By catalysing the dry reforming reaction with more effective catalytic materials, research into this process is effectively driving towards the use of lower operating temperatures, whilst maintaining a high conversion of both \( \text{CO}_2 \) and \( \text{CH}_4 \) to high energy syngas with a product ratio close to unity.

### 1.3 An Overview of Dry Reforming Catalysis

Numerous materials have been investigated as potential catalysts for the carbon dioxide reforming reaction. A summary of some of the many catalysts that have been investigated over the last 30 years is given in Table 1.1.
Table 1.1: List of Materials Used to Catalyse the Dry Reforming Reaction

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The most effective catalysts in the dry reforming reaction are those that include a highly active metal paired with a suitable thermally stable support. Even when these individual components are considered and combined, the active phase must be deposited correctly and interact specifically with the support in order to maintain a high activity over time\textsuperscript{74,81}. These specifics are discussed in detail in the following sections.

From the numerous metals / materials that have been investigated for catalysing the dry reforming reaction it has been found that a number of metals can successfully catalyse this reaction when deposited on suitable supports. The order of activity for several of the most active metals researched has been reported to be Rh, Ru > Ir > Ni, Pt, Pd > Co > Fe, Cu\textsuperscript{74,82}. From the aforementioned order of elements listed it can be seen that the noble metals Rh, Ru and Ir have the highest activity, whilst two of the three elements with the next highest activity are also noble metals (Pt and Pd). Of the numerous outstanding catalysts developed, all however have experienced significant issues with regards to carbon deposition, which at optimal reaction conditions has the tendency to manifest on the surface sites of active catalysts and decrease the catalytic ability of the material\textsuperscript{83}. The extent to which specific catalysts are impacted by carbon deposition is discussed in detail in a later section (section 1.4.4).
1.3.1 Dry Reforming Reaction Mechanism

Two main mechanisms have been proposed for the dry reforming of methane over group VIII catalysts. The Eley-Rideal mechanism has been accepted as a viable reaction route; whereby CH₄ molecules are adsorbed onto active metal sites before they dissociate into H₂ and surface carbon species⁸⁴,⁸⁵. The surface carbon then reacts directly with incoming CO₂ species to produce CO. An alternate mechanism has been suggested, where adsorbed CH₄ molecules decompose to H₂ and CHₓ species⁴¹. Subsequently, incoming CO₂ molecules adsorb to nearby active metal sites or the interface between the active metal cluster and the support structure, depending on the characteristics of the support, before being broken into CO and surface oxygen, or OH species. From here the surface groups containing oxygen react with the CHₓ groups to form further CO and H₂. If no oxygen is free to react with CHₓ in this mechanistic route, it will react either with itself or the metal particle and result in bulk or filamentous carbon being deposited. On the other hand, when there is too much oxygen compared to the CHₓ, the oxygen will react with the reduced metal particle to produce the metal oxide, which has been shown to be less efficient in the activation of CH₄ reactants⁸⁶. Nakamura et al. showed that on a basic support such as alumina (Al₂O₃), the latter mechanism is consistent, where CO₂ is activated on the support in the vicinity of the active metal particle forming a carbonate species⁸⁷. The carbonate is then reduced by a CHₓ species resulting on the active particles, which forms the CO. Bitter et al. proved that a similar mechanism occurs on supports that are neither acidic nor basic such as zirconia (ZrO₂)⁸⁸. However, on acidic supports such as silica (SiO₂), the dry reforming reaction is believed to take place via a Langmuir-Hinshelwood mechanism⁷⁴. In this route the dissociative adsorption of
CO₂ also occurs mainly on the active metal clusters, and the adsorption may become limited as the reaction proceeds; where dehydrogenated carbon deposits accumulate and eventually undergo ageing and graphitisation on the metal surface. In the long-term the high concentrations of these carbonaceous residues may block the metal surfaces, thus leading to a continuous loss of activity by carbon deposition, where incoming CH₄ molecules become inhibited by the coking⁸⁹. This is discussed in more detail in the following section. Overall based on the research conducted to date it is generally accepted that both suggested mechanisms discussed here, and variations of these, can occur depending on the catalyst type used; specifically the nature of the active metal sites and the paired support structure¹³,⁸⁸,⁹⁰,⁹¹.

### 1.3.2 Carbon Deposition on Dry Reforming Catalysts

It is well known that carbon deposition is an integral component of the dry reforming reaction. Carbon deposition is primarily a result of the cracking of methane (reaction 1.7) and can also occur from the Boudard reaction (reaction 1.8) at lower reaction temperatures. These reactions together form the basis of the overall reaction pathway for conversion of CH₄ and CO₂ to syngas in the dry reforming reaction⁵.

\[
\begin{align*}
\text{CH}_4 & \rightleftharpoons \text{C} + 2\text{H}_2 \quad \Delta H = 75 \text{ kJ mol}^{-1} \quad \text{(1.7)} \\
2 \text{CO} & \rightleftharpoons \text{C} + \text{CO}_2 \quad \Delta H = -172 \text{ kJ mol}^{-1} \quad \text{(1.8)}
\end{align*}
\]
Carbon deposits manifesting from the above reactions are thermodynamically favourable when reacting CO₂/CH₄ in equal ratios at temperatures up to 1000°C at a reactor pressure of 1atm, and as high as 1100°C at pressures around 10atm (Figure 1.2)⁹². Operation of reactors at high temperatures when utilising a molar equivalence of CO₂/CH₄ or subsequently using feedstock ratios far greater than unity at lower temperatures are necessary in order to completely prevent carbon deposition, however in industry it is desirable to carry out the reaction at lower temperatures and at a feedstock ratio close to unity, for both economical and safety reasons⁹³.

![Figure 1.2: Carbon deposition in the dry reforming of methane as a function of temperature and CO₂/CH₄ feed ratio](image)

It has recently been reported that not only the amount of carbon deposited from methane decomposition and Boudard reactions will influence the activity / stability
of catalysts used during the reaction, but also the form of carbon deposited\textsuperscript{14}. Several research groups have shown that there are four main forms of carbon deposited during the reaction, $C_\alpha$, $C_\beta$, $C_\gamma$ and inactive carbon; namely amorphous, filamentous, graphitic carbon and bulk carbon\textsuperscript{46,50}. Wang et al. reported that $C_\alpha$ deposits were found to be primarily produced from CH$_4$ decomposition, whilst $C_\beta$ formation was usually a result of CO disproportionation\textsuperscript{94}. It has been reported that of these carbon types, amorphous carbon is the most active, being consumed rapidly by the Boudard reaction (reaction 1.3). Filamentous and polymorphic graphitic carbon develop from catalysts with particular morphologies, and generally do not have an immediate negative effect on catalyst activity but block active sites through encapsulation over prolonged formation period\textsuperscript{50}. Filamentous carbon species generally take longer to poison catalysts than polymorphic species. It is well known that bulk carbon causes a more rapid loss of activity through quick physical coverage of the active sites, and these inactive carbon types are generally not consumed in the Boudard reaction, hence rendering the catalyst less than optimal over various lengths of time\textsuperscript{95}.

1.3.3 Other Reasons for Catalyst Deactivation

During the course of the dry reforming reaction, catalyst deactivation can occur not only through physical blockage of active sites by carbon deposition as mentioned earlier, but also through changes in the active material morphology; such as thermal degradation and sintering\textsuperscript{96}. At high temperatures the pore structure of a catalyst support may collapse, and the size and shape of the active metal crystallites can change through physical migration or sintering (Figure 1.3a and b). This decreases the catalyst surface area and consequently the number of available active sites\textsuperscript{89}. 
Sintering is a complex process which depends on temperature, catalyst support composition, support porosity, and type of active metal of a catalyst. A good understanding of the sintering mechanism is crucial in considering deactivation over time caused by migration of active metal particles and in order to design catalysts with resistance to such effects at temperatures that would otherwise significantly change the morphology of supported metal particle clusters. The two mechanisms for active metal particle sintering that have been suggested are atom migration and cluster migration to coalescence, which can both significantly reduce active metal surface area (Figure 1.3b). Atom migration involves the emission of metal atoms from metal clusters before subsequent capture of these atoms by neighbouring clusters, changing active site location. Cluster or particle migration has been suggested where poorly bound metal clusters or groups of atoms migrate over support surfaces before coalescing into larger clusters, thereby reducing the active metal surface area over time. The type of sintering can be determined by analysing the sintering kinetics by the equation:

\[-d(D/D_0)/dt = k_s(D/D_0)^n\]  

(1.9)

Where \(k_s\) is the sintering rate constant, \(D_0\) is the initial dispersion and \(n\) is the sintering order. Lower values of \(n\) indicate atomic migration, whilst values of \(n\) greater than 2 indicate particle migration. Under typical dry reforming reaction conditions larger values of \(n\) are prevalent, which indicate regular particle cluster migration and a subsequent loss of active surface area, through cluster growth and consequential blocking of pores or defect sites. A supported metal catalyst will generally show some sintering when the temperature is roughly half of the active metal melting point, and due to the necessity of high temperatures when running
In the dry reforming reaction, these occurrences are regular throughout common catalyst materials. Inhibition of catalysts can be caused by either competitive inhibitors, or non-competitive inhibitors. Competitive inhibition occurs when two molecules compete for the same active site on the catalyst surface, whereas non-competitive inhibition occurs when properties of the active sites are changed by a molecule binding at an allosteric site. Poisoning occurs when an inhibitor bonds irreversibly to a catalyst, such as coking from severe carbon deposition, which can render active particles useless in a reaction (figure 1.3c).

Figure 1.3: Deactivation of a catalyst by; a) support breakdown through thermal degradation; b) active phase sintering through atom and cluster migration to form larger particles; c) inhibition of active particles through coking.
1.3.4 Overview of Catalyst Development and Testing for the Dry Reforming of Methane

As discussed earlier a number of noble metals have been found to be active catalysts in the dry reforming reaction. The noble metals have also proven to be less sensitive to carbon deposition over time, particularly Rh based catalysts; which at suitable conditions show very minimal carbon deposition over long periods of operation\textsuperscript{30,70}. However, these materials have the significant drawbacks of having high cost and limited availability, and hence there has been considerable interest in the development of cheaper non-noble metal based catalysts.

Ni based catalysts in particular have received a significant amount of interest due to the promising activity and selectivity that has been achieved when used in the dry reforming reaction\textsuperscript{81}. It is well known that monometallic Ni based catalysts used in this reaction show a reasonable initial activity towards the conversion of CO\textsubscript{2} and CH\textsubscript{4} into syngas, however suffer from deposition of inactive carbon species on the surface of the material during time on stream, affecting catalyst stability and rendering the catalyst less active than optimal.

Strategies to improve the overall activity and stability of active metal catalysts for use in the dry reforming reaction have focused on preparing materials with optimum metal dispersion and particle size, supported on a suitable carrier material; which provides strong metal-support interaction. In order to achieve these objectives, most recent research has focused on the investigation of the use of different support
materials for active metal components, and the addition of dopants to such catalysts; in the form of structural and chemical promoters, and their overall effect on the dry reforming reaction. Specific research on the aforementioned strategies, which focuses predominantly on Ni based catalysts, is discussed in the proceeding sections.

1.4 Recent Research in Dry Reforming Catalysis

1.4.1 Influence of Activation of Nickel Sites and Nickel Loading

1.4.1.1 Pre-Treatment

In catalytic material preparation the thermal treatment process, especially the calcination temperature, highly affects the development of support surface properties and the phase structure of the material prepared. The difference in activity of a catalyst material in a previous study was found to be related to activation and calcination temperatures used after preparation of the material\textsuperscript{99}. In the above mentioned study, different types of carbon formed on catalyst surface, where the simple increase of calcination time had no appreciable effect on the reaction rate, but the specific temperature of the pre-treatment promoted the catalyst activity and enhanced overall performance, by an increase in the deposition of active phases of carbon. Al-Fatish et al. studied the effect of calcination temperatures on dry reforming catalysts supported on $\gamma$-Al$_2$O$_3$\textsuperscript{100}. It was observed that the calcinations directly enhanced catalyst stability; which increased as calcination and reaction temperatures were increased. They found that a catalyst must subsequently be activated by reduction before primary use; where the optimum activation of the
catalyst occurred by rapid reduction of metal oxides with diluted hydrogen gas at temperatures around 700°C.

By choosing a suitable support structure, as well as appropriate reduction and reaction temperatures, Savaia et al. showed it was possible to suppress side reactions occurring simultaneously with the dry reforming of methane\textsuperscript{101}. Through Ni supported on phyllosilicates (Ni\textsubscript{3}Si\textsubscript{4}O\textsubscript{10}(OH)\textsubscript{2}·nH\textsubscript{2}O) they showed that small, regular sized Ni\textsuperscript{0} particles would form on the surface of the catalyst, only upon reduction at temperatures above 700°C, whilst some of the unreduced support remained as a carrier. If the temperature of reduction for the catalyst was too low, transitional metal structures would result; which were less active in the reaction. In contrast, Juan-Juan and colleagues found that the activity of a Ni/Al\textsubscript{2}O\textsubscript{3} catalyst was not dependant on pre-treatment conditions, but this factor had a noticeable effect on the amount of deposited coke and hence the overall stability of the materials, due to the influence these conditions had on the Ni particle size and structure\textsuperscript{102}. Beebe et al. have demonstrated the structure sensitivity of CH\textsubscript{4} dissociation on Ni surfaces, where diverse pre-treatment conditions were used to determine the activity decreased in the crystal order Ni[110] > Ni[100] > Ni[111]\textsuperscript{103}. Perez-Lopez et al. found that amongst the thermal pretreatment effects, the reduction temperature was revealed as the most important stage, where it showed a strong influence on the activity and selectivity for the dry reforming of methane. In agreement with previous studies, they found that the direct activity of the materials observed could be considered practically independent from the calcination temperature, where the influence of this parameter was restricted to the specific surface area values with the change of temperature\textsuperscript{99}. In
a study on reduction temperature effect on a Co/TiO₂ catalyst, Nagaoka et al. discovered that whilst the catalytic activity was strongly affected by reduction temperatures used, the coke deposition on the material could also be somewhat controlled by this pre-treatment\textsuperscript{104}. They found that a suitable reduction temperature specific to the catalyst being studied (850°C) had the effect of reducing the active metal particles sufficiently, whilst remaining low enough as to limit the sintering effects seen in higher temperature pre-treatments; giving the catalyst resistance to coking over long reaction periods.

1.4.1.2 Preparation

In a review on catalyst preparation techniques, Blanchard et al. found that the surface density of the nickel particles, the catalyst activity, and its life span are highly dependent upon the catalyst preparation protocol\textsuperscript{106}. They showed that for ceramic supports impregnated with active particles from parent nitrate solutions, the initial nitrate solution concentration, the duration of the impregnation and the specific surface of the ceramic support all have a considerable influence on the size range of the deposited nickel particles; which in-turn significantly affects inactive carbon deposition rate. They also found the crystalline arrangement of the Ni resulting from the preparation and pre-treatment techniques have a significant influence on the solubility of carbon in the nickel phase, and the chemical link between the nickel particles and the support showed a significant impact on Ni sintering on the surface of the catalyst. Pelletier and colleagues found that impregnated Ni species tended to block the pores of their alumina-aluminium phosphate supports, significantly
reducing the surface area of the prepared catalysts. They conversely found that precipitated Ni catalysts had a stronger metal-support interaction and a minimal loss of surface area when Ni was deposited by this technique, which resulted in a stable catalyst material which showed a relative activity in the dry reforming reaction for over 250 h of reaction time.105

There have been an extensive range of novel catalyst preparation techniques explored recently in an effort to maximise activity and stability of materials in the dry reforming reaction. Shen and colleagues prepared a Ni/Mg-Al2O3 by a template assisted route involving pluronic P123 surfactant, producing a unique material which contained a rigid and highly ordered mesoporous support structure.107 They concluded that such a highly ordered mesoporous structure would not only see a high dispersion of small metallic particles, but the existence of the ordered mesopores could decrease the Ni reduction temperature by 50–100 °C; meaning less energy was used to fabricate a substantially more active and stable catalyst than previously seen in literature. Recently Daza et al. used a self combustion fabrication technique which improved the surface area and support basicity giving a higher activity and stability than co-precipitation methods.108 Hua and colleagues have used a dielectric-barrier discharge plasma technique to prepare a Ni/MgO catalyst with smaller active particle size and an enhanced Ni dispersion than seen in conventionally reduced Ni/MgO catalysts.109

Preparation methods that produce desired physical material properties are of primary importance, but equally vital are techniques that are simple to follow and highly repeatable when fabricating dry reforming catalysts. A new and simple method to
prepare alumina containing mainly mesopores has been described by Fajardo et al\textsuperscript{110}. Through a simple template assisted fabrication followed by polymer elimination through thermal treatment, they were able to produce spherical Al\textsubscript{2}O\textsubscript{3} particles with a specific high surface area of around 464 m\textsuperscript{2}/g. When suitably calcined and reduced these catalysts showed a high metal dispersion and stability over time, similar to materials that were prepared by more strenuous fabrication methods. Golcalves et al. recently found that certain catalysts could be prepared by using a sol-gel process, in which a Ni/SiO\textsubscript{2} catalyst showed far superior quality in the dry reforming of methane\textsuperscript{111}. They found that using this method could produce a catalyst that had a greater surface area than previously reported SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} supported materials, and showed a significant increase in catalyst stability. Zhang and colleagues directly deposited nano-sized Ni particles into a mesoporous TiO\textsubscript{2}/SiO\textsubscript{2} support by adding the parent Ni salt to the sol before using a template agent to stabilise their catalyst material in an alteration of a similar preparation technique. They found this technique gave a very strong Ni-support interaction; which prevented the active phase from sintering into larger particles, also maximising the stability of the catalyst over long periods of time\textsuperscript{62}. Contreras-Andre et al. used a simple one-step sol-gel method for the fabrication of Pt/Sn-Al\textsubscript{2}O\textsubscript{3} which gave enhanced activity and stability over previously reported catalysts due to superior support acidity and Pt dispersion\textsuperscript{112}. They noted however that using a sol-gel method may produce catalysts in which active particles were partially buried in the bulk of the alumina, leading to the loss of active sites which were not accessible to the reactants. The sol-gel method of preparation has also been employed to create Ni/CaO, Ni/Sm\textsubscript{2}O\textsubscript{3} and a series of Ni/Sm\textsubscript{2}O\textsubscript{3}–CaO catalysts with increased dispersion and active particle uniformity\textsuperscript{113}. 
1.4.1.3 Metal Loading

Optimal active metal loading is well known to be relative to the activity and stability of catalyst material being investigated in research on the dry reforming reaction. Bradford and Vannice concluded that in various Ni loaded catalysts, the optimal Ni loading is different from one catalyst to the other. Pompeo et al. worked on a 2-4% Ni/\(\alpha\)-Al\(_2\)O\(_3\) produced by impregnation, and reported that deactivation occurs within the first 40 h due to inactive carbon accumulation. Moreover, they indicated that these catalysts deactivated at high metal loadings, but at much lower rate. Blanchard and colleagues found when an excess of active metal is present on the support, access by the reactant gas to the support becomes limited, and carbon actually forms more rapidly by methane dissociation, deactivating the catalyst. Therefore they concluded that a balance between optimum active metal loading and stability is required; where a high concentration of active metal loading may result in a greater activity in the reaction but a decreased stability over time.

1.4.2 Support Effect on Dry Reforming Catalysts

1.4.2.1 Influence of Surface Area

It has been shown that support materials may participate in the dry reforming reaction in a significant way when paired with a suitable active phase. Recent research on the influence of support materials for Ni based catalysts has shown that
suitable high surface area supports can be effective in increasing Ni dispersion and thermal stability, hence decreasing the deactivation over time of the catalysts due to sintering and migration effects\textsuperscript{95,115,116}. In contrast to conventional oxide supports and macroporous materials, mesoporous materials such as zeolites have the distinct advantages of having easily accessible nanometer-sized pore structures, high surface area and adjustable metal composition and type through suitable preparation techniques; providing good opportunities to develop novel catalysts with significantly improved catalytic performance\textsuperscript{117}. Frontera et al. studied zeolite supported Ni catalysts and found that they allowed for the formation of smaller, highly reducible Ni oxide species which reduced the deactivation of the material over time\textsuperscript{41}. Within the dry reforming reaction a very high selectivity toward H\textsubscript{2} was reported when Ni was supported on MCM-41 mesoporous materials, superior to that of Ni/SiO\textsubscript{2} catalysts and comparable to the performance of highly active Ru/SiO\textsubscript{2} catalysts\textsuperscript{118}. Ni/Al\textsubscript{2}O\textsubscript{3} aero-gel catalysts also tend to show higher activity than SiO\textsubscript{2} supported catalysts primarily due to an increased surface area support\textsuperscript{40,119}. Wei et al. investigated Ni catalysts supported on nano-sized ZrO\textsubscript{2}, MgO and γ-Al\textsubscript{2}O\textsubscript{3} supports in an effort to prepare higher surface area materials, and found that the catalysts showed high thermal stability and had strong anti-carbon properties due to high preparative control; which resulted in highly dispersed active metal sites that interacted to a strong degree with the support structure\textsuperscript{120,121}. Parkhomenko and colleagues recently prepared a mesoporous silica-based material named TUD-1; an attractive catalyst support for the dry reforming reaction due to its regular pore size and distribution, high specific surface area, and hydrothermal stability at high reaction temperatures\textsuperscript{66}. They found that the porous nature of the material had a positive effect on the Ni dispersion throughout the catalyst, and therefore the
stability increased due to a resistance to coking. The incorporation of active metals directly into the framework of mesoporous molecular sieves has been shown to combine the benefit of a high surface area support, and the availability of highly distributed active metal sites to the reaction being studied. Daza et al. created high surface area Ni/Mg-Al mixed oxides promoted with Ce, and proved that mixed oxide materials can be precursors to Ni particles less than 10 nm when used as a support structure. This gave rise to a greater dispersion at a lower concentration of the active phase over the support material, hence minimising inactive carbon deposition, whilst maintaining a high distribution over time in the reaction.

1.4.2.2 Active Metal-Support Interaction

It has been shown that whilst individually the active component and catalyst support play separate roles in the dry reforming reaction, equally importantly the support-active phase interaction plays a key role in determining the activity and long term stability of the catalyst as a whole. Gronchi et al. studied the catalytic activities of Ni and Rh metals supported on SiO₂ and La₂O₃. It was shown that deactivation of both the supported metal types deeply depended on the support used, and the interaction that arose between the active Ni particles and the oxides they were dispersed upon. They concluded that one should aim to optimise a catalyst so as to promote a close contact of the reactants or their derived species through a high dispersion of the active phase, whilst maintaining easily reduced active particles.
1.4.2.3 Oxygen Supply

It has been discovered that for a support to be effective in the dry reforming reaction, it must have the ability to supply limited oxygen to the active metal phase\textsuperscript{122}. Appropriate supports supply oxygen to molecules bound to the active metal during the reaction and can accordingly limit carbon deposition through subsequent oxygenation of deposited carbon species. When compared to irreducible oxides, such as Al\textsubscript{2}O\textsubscript{3} or SiO\textsubscript{2}, the use of ZrO\textsubscript{2} can result in attractive process benefits owing mainly to its redox behaviour, with the added benefits of ease of reducibility and high thermal stability\textsuperscript{72}. CeO\textsubscript{2} is also well known for its high oxygen storage and transport capacity, where it is able to release oxygen under oxygen poor environments and quickly re-oxidise under oxygen rich environments. Laosiripojana and colleagues found that redox reactions occur on the CeO\textsubscript{2} surface between the gaseous components in the system and the lattice oxygen (O\textsubscript{x})\textsuperscript{116}. Amongst these reactions, the rapid redox reactions of carbon compounds such as CH\textsubscript{4}, and CO with lattice oxygen (reaction 1.9 and 1.10) can prevent the formation of carbon species from the methane decomposition (reaction 1.7) and Boudard reactions (reaction 1.8) even at low inlet carbon dioxide concentration.

\[
\text{CH}_4 + \text{O}_x \rightleftharpoons \text{CO} + \text{H}_2 + \text{O}_{x-1} \tag{1.9}
\]

\[
\text{CO} + \text{O}_x \rightleftharpoons \text{CO}_2 + \text{O}_{x-1} \tag{1.10}
\]

However, the beneficial redox abilities of CeO\textsubscript{2} supported catalysts are known to decline under high temperatures and strong reducing conditions, where the catalyst activity can be rapidly hindered through thermal degradation and loss of lattice
Further severe formation of nano-fibre whisker type carbon is common across these materials which has been observed to irreversibly deactivate the catalyst over time\textsuperscript{124}. Kambolis et al. were able to show that binary oxides of CeO\textsubscript{2}-ZrO\textsubscript{2} and Ni catalysts supported on these materials presented improved stability through increased oxygen content of the support\textsuperscript{58}.

There is however a limit to how much oxygen a support may provide to the dry reforming reaction before it becomes detrimental to the catalyst activity. If an oversupply of oxygen is provided it may rapidly re-oxidise the previously reduced metal species, and hence reduce the number of active sites available. Active metal phases may however be somewhat resistant to re-oxidation through suitable metal-support interaction and the morphology of the active particles themselves. Pereniguez et al. studied Ni/La\textsubscript{2}O\textsubscript{3} catalysts for the dry reforming reaction and were able to show the presence of an amorphous NiO phase in the sample, together with a crystalline LaNiO\textsubscript{3} phase\textsuperscript{43}. The increased catalytic performance of the catalyst observed was explained by the high resistance of the nickel particles to be re-oxidized in the latter phases once reduction pre-treatment was applied to the material.

### 1.4.2.4 Influence of Acidity

The acidity of the support used for dry reforming catalysts has been shown have a significant influence on coke formation\textsuperscript{125}. There are various oxide supports with different acidic natures commonly used in the dry reforming of methane; basic supports such as alumina (Al\textsubscript{2}O\textsubscript{3}); acidic supports such as silica (SiO\textsubscript{2}); and neutral type supports which are neither basic nor acidic, such as zirconia (ZrO\textsubscript{2}). Each
support type shows different reaction and mechanistic properties (as discussed in section 1.3.1), which in turn has implications for their long term activity and resistivity to carbon deposition\textsuperscript{114}. In particular deactivation of catalysts has been shown to be attenuated or even suppressed when Ni is supported on a metal oxide with a strong Lewis basicity\textsuperscript{34,111,126}. Metals supported on the basic La\textsubscript{2}O\textsubscript{3} are particularly active within the reforming reaction because they promote CO\textsubscript{2} adsorption through increased surface basicity, thus increasing the rate of production of synthesis gas\textsuperscript{127}. Whilst Ru supported on La\textsubscript{2}O\textsubscript{3} is still one of the most active catalysts known in the dry reforming of methane, Ni supported on La\textsubscript{2}O\textsubscript{3} has shown to be less stable over time in the reaction.

Catalyst supports which are neither acidic nor basic such as ZrO\textsubscript{2} may show improved catalytic activity when compared to acidic or basic supports. Zirconium oxides usually have surface areas of 50 m\textsuperscript{2}/g or less, which is rather low compared with conventional supports such as SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3} or TiO\textsubscript{2}\textsuperscript{115}. ZrO\textsubscript{2} tends to be rapidly deactivated from high levels of carbon deposition due to the relatively low surface areas of the material\textsuperscript{86,128,129}. Higher surface areas are attainable with the preparation of amorphous zirconia (200–300 m\textsuperscript{2}/g), but this is usually achieved at the expense of much lower thermal stability\textsuperscript{130}.

1.4.2.5 Al\textsubscript{2}O\textsubscript{3}

Al\textsubscript{2}O\textsubscript{3} is one of the most commonly explored support structures in the dry reforming reaction, not only due to its high basicity; promoting a high conversion of CO\textsubscript{2}, but due to its versatility through many different structural forms and various adaptations.
of previously reported morphologies. Ni/Al₂O₃ remains one of the most widely used catalysts in dry reforming research however in its most common α-phase it is well known to lack thermal stability at high reaction temperatures; which results in the sintering of metals on its surface, and subsequently its basic sites may contribute to the catalyst’s deactivation by coking¹³¹. In a study on Mo₂C active phase catalysts, Darajuta et al. found that Al₂O₃ was superior to ZrO₂, SiO₂ and TiO₂ in supporting the active particles of the material for the dry reforming of methane. The γ-Al₂O₃ phase was deemed to be the most suitable support structure due to its high surface area; resulting in a greater dispersion of active particles, and its increased thermal stability compared to other forms of Al₂O₃²⁸. Similarly Hou et al. used the same impregnation conditions, but studied Al₂O₃ supports with different phases; α-Al₂O₃ and γ-Al₂O₃, and found that the γ-phase was far superior as a support structure for active metals due to both its rigidity at elevated temperatures, and its high surface area. Co/Al₂O₃ catalysts have shown to give relatively high performance, but tend to deactivate rapidly from carbon deposition¹³². Ru/Al₂O₃ has been shown a stable catalyst presenting no coke deposition over time, but its performance is lower than that of the other Al₂O₃ supported catalysts¹³³.

1.4.2.6 NiAl₂O₄

As early as 1966 it was discovered that under certain conditions, the formation of highly stable spinel nickel (NiAl₂O₄) occurs at high temperatures across certain high surface area Al₂O₃ supported materials¹³⁴. The formation of NiAl₂O₄ occurs as high surface area Ni/Al₂O₃ is heated up close to 800°C, where Ni particles directly interact with the alumina support under inert conditions. The formation of NiAl₂O₄
has been shown to favour steady conversion of products to reactants, since it inhibits
the formation of carbonaceous deposits\textsuperscript{104}, although it is still unclear if the NiAl\textsubscript{2}O\textsubscript{4}
phase is itself active in the dry reforming reaction\textsuperscript{135-137}. Ni present throughout this
material is highly dispersed and it has been suggested that these species continuously
reduce to active forms of NiO and Ni\textsuperscript{0} slowly over time\textsuperscript{146}. Because of the high
dispersion of the active phase throughout the material, the resulting particle size is
small and consistent; resulting in mostly active forms of carbon being deposited
during the reaction. The Ni particles are held rigidly within the matrix of the material
thus limiting sintering effects at the high temperatures required of the dry reforming
reaction. Fidalgo et al. found that whilst the CH\textsubscript{4} interacted with the bound Ni\textsuperscript{0}/NiO
particles reduced from the NiAl\textsubscript{2}O\textsubscript{4} phase, the incoming CO\textsubscript{2} tended to react with the
initial carbon deposits from the activated CH\textsubscript{4} rather than the support structure or the
active particles themselves, giving continuously regenerating active sites\textsuperscript{138}.
MgAl\textsubscript{2}O\textsubscript{4} has also been suggested as a similar dry reforming catalyst which reduces
coke formation through a similar mechanism to NiAl\textsubscript{2}O\textsubscript{4} materials\textsuperscript{136}. This material
offers a desirable combination of properties for use in catalysis, due to its high
melting temperature (2135 °C), good chemical stability and mechanical strength. It
has been studied extensively for viability in the steam reforming reaction and found
as to be one of the highest performing materials in terms of both activity and stability
in the reaction. Corthals et al. found that the higher basicity of the support structure
in the MgAl\textsubscript{2}O\textsubscript{4} compared to other alumina based catalysts led to an increase in
resident CO\textsubscript{2} molecules, increasing the frequency of the reverse Boudard reaction
(reaction 1.8) which in-turn decreased the concentration of surface carbon species\textsuperscript{32}.
Guo and colleagues reported on a catalyst that contained a combination of both Ni
and Mg in a spinel form with the Al\textsubscript{2}O\textsubscript{4}\textsuperscript{59}. They found in the Ni-Mg/Al\textsubscript{2}O\textsubscript{4} material
that after use in the reaction, the Ni particle sizes remained similar to those both before pre-treatment and the reaction itself; indicating that minimal active phase sintering occurred under reaction conditions. Alvara et al. fabricated a similar catalyst containing 5 wt.% Ni supported on the Mg/Al₂O₃ support which exhibited stable performance for over 50 h of reaction. Whilst γ-Al₂O₃ supported metals have been shown to have a higher activity than metals bound in Al₂O₄ materials, the significantly lower carbon deposition rate occurring when using the NiAl₂O₄ catalysts makes them active for far greater reaction periods, hence outweighing the slightly lower activity.

1.4.2.6 Other Supports

Alkaline earth metal oxides, such as MgO, CaO, SrO or BaO can act as both supports or structural promoters when doped into other catalysts. Ni supported on MgO was found to be a viable dry reforming catalyst by Djaidja et al., where only a small concentration of Ni was required to give good activity, even at relatively low reaction temperatures. Low carbon deposition occurred at elevated temperatures; most likely due to the high reducibility and increased dispersion of the impregnated active metal on the support structure compared with previously reported catalysts.

Recently there has been an increase in exploration of catalyst supports in the dry reforming reaction composed of a mixture of oxide materials. These catalysts see some benefits of each support type included and tend to show an improved initial activity in the reaction. The better catalytic activity of Pt/ZrO₂/SiO₂ catalysts have
been explained by Reddy and colleagues as a result of a higher dispersion of Pt particles, and a greater thermal stability of the mixture of ZrO2 and SiO2 compared with using either oxide as a support on its own21. Nickel-containing Mg–Al layered double hydroxides have been considered by Tsyganok and colleagues in the dry reforming of methane. Such catalysts did not require regular pre-treatment to show a high activity in the reaction, however required several hours to reach maximum potential in the reaction term141,142. Pompeo et al found that a Ni/Al2O3-ZrO2 catalyst showed very good performance in the dry reforming reaction, where initial activity was comparable to that of a Ni/γ-Al2O3 catalyst but stability was increased by the ZrO2 component; which allowed the formation of more active and less hindering carbon types over the reaction period143.

Perovskite type catalysts have received recent attention in recent dry reforming catalysis research. With a general structure similar to calcium titanium oxide (CaTiO3) comprising of two cations joined to three identical anions (ABX3), they are well defined structures which produce very small and well dispersed active metal particles and are highly resistant to deactivation through carbon formation43,144. Valderrama et al. found that the combination of well dispersed Ni particles and availability of oxygen through La2O3 phase in a La1-xSrRxNiO3 perovskite type mixed oxide greatly improved the resistance to carbon deposition across the material for long periods in the dry reforming reaction145. Lima et al. found that whilst LaNi1-xFe3O3 perovskite type oxides were less active than conventional dry reforming catalysts, the long term stability through the ability to deter carbon formation far outweighed the decreased conversions seen in the materials146.
A large variety of carbon supported catalysts have been analysed for activity in the dry reforming reaction, including activated carbons, carbon blacks, and chars from biomass residues. This is interesting considering an intermediate of the reaction is carbon itself, deposited in various forms, which may somewhat self-catalyse the reaction when forming in close proximity / on active particles during the reaction. However carbon supported catalysts have previously been shown to exhibit low CO$_2$ reactivity, and thus most carbon based materials are not good catalysts for the dry reforming reaction.

1.4.3 Bi-Metallic Dry Reforming Catalysts

Research into viable materials for dry reforming catalysts has revealed that the addition of certain promoter materials may assist in giving the catalyst unique morphological properties / increase initial and long term activity. A number of research groups have conducted studies on the influence of dopants on the activity and stability of previously reported dry reforming catalysts in an attempt to develop improved catalysts for the reaction. Promoters are generally classified as either being chemical or textural in nature. Most promoters explored for dry reforming catalysts are generally chemical in nature. These chemical promoters are most commonly in the form of alkali and alkaline earth metals, or metal oxides.
1.4.3.1 Active Promoters

Whilst ruthenium and rhodium are known to be highly active in monometallic catalysts in the dry reforming reaction, they can also be used as activity promoters when doped in smaller concentrations on already active materials. Pietraszek and colleagues added the highly active metals Ru and Rh to Ni/CeZr fluorite type catalysts\textsuperscript{64}. They discovered that whilst Ni/CeZr materials rapidly lost activity due to carbon deposition, Ni-Ru/CeZr and Ni-Rh/CeZr remained active over long periods due to a decrease in the deposition of non-active carbon types. Recently Wu et al. showed that the addition of Rh to a Ni/BN catalyst led to a dramatic increase in the activity of the catalyst, and some increase in the stability\textsuperscript{151}. Yasyerli and colleagues found that monometallic Ni/MCM-41 catalysts prepared by a one-pot synthesis method did not perform well in the dry reforming reaction\textsuperscript{152}. They found however that when these materials were doped with Rh, the catalytic activity and stability increased dramatically. In contrast, Parkhomenko et al. found that the addition of Rh to similarly prepared Ni/TUD-1 catalysts led to no improvement in catalyst activity or stability, but led to a decreased dispersion of Ni compared to the undoped catalyst, due to a subordinate stability of active particles in the silica matrix\textsuperscript{66}.

Platinum and palladium have also been explored as chemical promoters for previously reported catalysts in the dry reforming reaction\textsuperscript{14}. Pt has been added to Ni/\(\gamma\text{-Al}_2\text{O}_3\) by Ozkara-Aydinoglu and colleagues, where it was found that both activity and stability in the dry reforming reaction were dependant on the specific amount of Pt loaded. They found with low amounts of loading, small Pt-Ni alloy particles would form, being more easily reduced and producing less detrimental
carbon deposits. Similarly, Garcia-Dieguez and colleagues studied the effect of Pt promotion for Ni supported on nano-sized $\gamma$-Al$_2$O$_3$ carriers and agreed that the Pt-Ni clusters that formed were superior to either Pt or Ni individually as active sites due to their small and regular size$^{153}$. Pt promoted fluorite-like oxides (PrCeZrO, GdCeZrO and LaCeZrO) supported on a corundum substrate have been studied by Sazonova et al., where a high activity was seen in the dry reforming reaction, however the reverse water gas shift reaction was found to be increasingly rapid, affecting the $\text{H}_2/\text{CO}$ ratio in the produced syngas$^{154}$. Steinhauer and colleagues prepared a set of Ni-Pd bimetallic catalysts supported on various carriers$^{155}$. They found that the addition of Pd similarly led to a higher activity within the dry reforming reaction, however at high loadings there was a significant increase in coking. When the catalyst was loaded with more than 10% metal content the dry reforming reactor was reported to be completely plugged by carbon nanotubes. Damyanova and colleagues studied a series of bimetallic Pd-Ni catalysts supported on MCM-41$^{45}$. They found that the synergetic effect between deposited Pd and Ni particles resulted in a material with superior activity and stability to monometallic catalysts. They noted that a catalyst with a higher Ni content but a constant Pd concentration of 0.5% resulted in a coagulation of active surface clusters, showing a higher activity, but less resistance to carbon deposition; where a suitable intermediate active particle concentration must be targeted to give a maximum activity whilst minimising deactivation via carbon deposition.

Various other dopants have been investigated for their activity promoting abilities in the dry reforming reaction including cobalt and molybdenum, with various effects discovered. Co-Ni bimetallic catalysts have been shown to have a greater catalytic
performance than either Co or Ni monometallic catalysts. Recently Chen et al. reported that homogenous alloys were formed when Co was added in sufficient quantities to Ni supported on aerogels, which led to a decrease in carbon deposited. This was mainly attributed to the complementary properties of both a smaller metal particle size and a stronger metal-support interaction. Gonzalez and colleagues prepared a series of Ni-Co bimetallic catalysts supported on mesoporous SiO$_2$ materials. They found that the selectivity of the catalyst towards H$_2$ depended on the specific bimetallic composition of each material. They attributed the difference in selectivity of each catalyst to the change in the support-active phase interaction across various metal loading percentages. In a similar study on Ni-Co systems, San-Jose-Alonso et al. found that catalysts with a higher ratio of Co to Ni showed to be most active in the dry reforming reaction, but produced the most coking through inactive carbon deposition. They discovered that catalysts loaded with appropriate concentrations of both metals showed a high activity and stability through the deposition of active forms of carbon rather over non-active forms. Mo has been recently discovered as a positive chemical promoter for dry reforming catalysts. Arkatova and colleagues found that the addition of Mo to NiAl intermetallic materials would promote the formation of a Ni-Mo active phase and through carbon deposition; a Mo$_2$C phase, which was easily converted to dry reforming products.

### 1.4.3.2 Textural Promoters

Textural promoters generally facilitate the preparation of well dispersed active phases and may also assist in keeping these phases stable through the reaction period; but unlike active promoters they do not play an active part in the reaction.
Several interesting textural promoters for dry reforming catalysts have been explored recently. These include: lithium, manganese, potassium, strontium, magnesium, calcium, yttrium, cerium, niobium, and barium. Pompeo et al. studied the effect the addition of Li had on a Ni/SiO₂ catalyst. They found that the addition of Li promoted morphological and textural modifications of the support structure as expected. As the addition of Li did not present any difference in the activation energies calculated for the dry reforming reaction over the materials prepared, they concluded that this dopant played no part in the reaction itself, but only in the physical properties of the support. Choi et al. studied the performance of a Ni/Al₂O₃ catalyst modified by the addition of Co, Cu, Zr, Mn, Mo, Ti, Ag and Sn. They found that when compared to a monometallic Ni/Al₂O₃ material, each dopant had a different effect on the catalysts performance, where materials doped with small amounts of Co, Cu and Zr showed a different increase in activity, whilst the addition of Mn reduced the carbon deposition occurring on the catalyst surface. K and Sr have been studied as viable textural promoters in Ni/Al₂O₃ and Co/Al₂O₃ catalysts. Whilst both promoters show an improvement over monometallic Ni catalysts, K appeared to be more effective as an additive; where an increase in dopant concentration produced a decrease in the percentage of deposited carbon, although this was also shown to decrease catalytic activity through both coverage of active sites and an increase in active particle size. K was also used as a promoter in a Ni/MgO system by Frusteri et al. who found that it decreased the initial reactivity of the catalyst, but with the significant benefit of a higher stability over time due to a lower portion of whisker carbon build up on the surface of the catalyst, and a higher proportion of active carbon types being deposited. Juan-Juan et al. studied the addition of K to a Ni/Al₂O₃ catalyst and found that addition of a very small
concentration resulted in the benefit of a high long term stability during the reaction\textsuperscript{126}. However they found that in materials with a higher concentration of K, these particles inhibited the active Ni sites by gradually migrating to the surface of the material. Hou et al studied the influence of doping MgO into mesoporous Ni/Al\textsubscript{2}O\textsubscript{3} prepared by a co precipitation method and found that this not only led to significantly improved stability, but also an increased activity compared to the undoped catalyst\textsuperscript{161}. Bouarab and colleagues studied Co/SiO\textsubscript{2} catalysts modified by MgO\textsuperscript{69}. They noted the formation of a silicate adlayer (Mg\textsubscript{2}SiO\textsubscript{4}) at high MgO loading, which favoured the development of small metallic Co particles over time, preventing their coalescence under reaction conditions, similar to the properties of spinel MAI\textsubscript{2}O\textsubscript{4} materials. In a similar discovery Fe and Mg have been added to SiO\textsubscript{2} supports to create the unique structure of olivine ((Mg, Fe)\textsubscript{2}SiO\textsubscript{4})\textsuperscript{181}. The dopants were seen to stabilise deposited Ni particles in these materials, reducing sintering during reaction periods and resulting in very low carbon deposition over time. The Fe showed a further effect of being present as free oxide types, which although is normally beneficial in the reaction, enhanced the rate of the reverse water gas shift reaction (reaction 1.2) leading to a decrease in H\textsubscript{2}/CO ratio.

Certain textural promoters will not only give the benefit of a decrease in inactive carbon deposition rate in the dry reforming reaction, but can assist in limiting the thermal degradation of the support structure itself. ZrO\textsubscript{2} has three known polymorphs: monoclinic (m-phase, below 1170 °C), tetragonal (t-phase, between 1170 and 2370 °C), and cubic (c-phase, above 2370 °C)\textsuperscript{162}. Rezai et al. found that the main reasons for catalyst deactivation was thermal degradation of the support, specifically a phase transformation from tetragonal ZrO\textsubscript{2} morphology to monoclinic.
morphology during the reaction at high temperatures. Recently it has been shown that the addition of textural promoters to the ZrO₂ supports in common high temperature cubic and tetragonal phases can lead to a stabilisation of these phases at increased temperature. Stabilisation occurred with the addition of selected dopants including: CaO, MgO, Y₂O₃ and CeO₂, all which showed an increased thermal solidity. Bellido et al. studied the effect of Y₂O₃ addition to a Ni/ZrO₂ catalyst and also found that this addition assisted in stabilising surface oxygen vacancies, which lead to an increase in reduction of the support and an increased interaction with Ni particles; which were also reducible at lower temperatures. They also found that the proximity of the surface oxygen vacancies and the active Ni particles improved the rate of removal of deposited carbon species; due to active oxygen species from CO₂ developing in the vicinity of C₃ on the Ni clusters. CaO has also been explored as a dopant in Ni/ZrO₂ catalysts by Bellido et al. who found that the added CaO similarly helped to promote surface oxygen vacancies which, when paired with active Ni sites would lower the reduction temperature of the NiO species and also promote active oxygen from CO₂ molecules; reducing the deposited carbon amounts. They further discovered that there was a balance between CaO concentration and activity of the catalyst, where a concentration greater than 8 molar % would result in a greatly decreased activity within the dry reforming reaction. In a study on Co catalysts supported on ZrO₂ promoted with various metal additives, Ozkara et al. found that the type of additive used could affect both active metal dispersion and catalytic activity. The addition of ZrO₂ as a textural promoter itself has been seen to greatly improve the stability of Ni/Al₂O₃ catalysts. Therdthianwong et al. showed that the addition of ZrO₂ enhanced the dissociation of oxygen intermediates in the dry reforming reaction, and although the overall activity of the
catalyst dropped, the stability over time was greatly improved\(^{164}\). Liu and colleagues have studied the effect of Zr, Ti, and Mn, promotion on MCM-41 supported Ni catalysts\(^{118}\). They found a negative effect on the samples that contained Ti and Mn, where they suspected active Ni sites became encapsulated or covered by TiO\(_x\) and MnO\(_x\) species; which prevented the incoming reactant gases from reaching the active phase of the material. They reported that Zr in the form of Zr\(^{4+}\) was able to assist both in direct activation of CO\(_2\) species, and in anchoring of the Ni particles; enhancing the structural stability by reducing sintering of the active phase.

Sr and Ca were used as structural promoters in mixed perovskite type structures studied by Khalesi et al. (Ca\(_x\)La\(_{1-x}\)Ni\(_{0.3}\)Al\(_{0.7}\)O\(_3\) and Sr\(_x\)La\(_{1-x}\)Ni\(_{0.3}\)Al\(_{0.7}\)O\(_3\)), who found that the addition of Sr aided with the resistivity to coke deposition, whilst Ca had a similar effect through the added basicity it provided to the material\(^{165}\). Nb has recently been used as a promoter by Alvarez et al. in a La\(_2\)Ni\(_{0.8}\)Nb\(_{0.2}\)O\(_4\) perovskite type catalyst, for the dry reforming of methane\(^{166}\). Although some of the Nb was reported to replace the active Ni sites in the material, the catalyst remained active and stable across the reaction period studied. Recently, Ba has been added to a Ni/\(\gamma\)-Al\(_2\)O\(_3\) catalyst by Garcia-Dieguez et al., who observed that the incorporation of Ba did not have an effect on the activity or stability of the material, but instead prevented the formation of spinel NiAl\(_2\)O\(_4\) by lowering the reduction temperature of the active particles\(^{53}\).
1.4.3.3 Lanthanide Doping

Very recently there has been detailed research reported on promoting dry reforming catalysts with elements from the lanthanide series. Whilst earlier research showed such lanthanides as Ce and La to be effective textural / activity promoters in the dry reforming reaction, it has very recently been found that other lanthanides, including praseodymium, samarium, and neodymium may also have favourable effects on catalysis of the reaction. Foo et al. recently discovered that the addition of Ce, Pr and Sm to Ni/Al₂O₃ catalysts did not affect the CH₄ or CO₂ consumption, however they did play a major role in increasing H₂ and CO production rate⁵⁵s. They suggested the increase in product yield could be directly related to a better utilisation of deposited carbonaceous species, through decreased metal particle size and hence a higher distribution of active particle clusters. Ozkara-Aydinoglu and colleagues studied the effect of La and Ce promotion on Co/SiO₂ catalysts⁷². They found that La modified materials exhibited high stability but moderate activity, whilst Ce promoted materials maintained a high activity through several hours of reaction time. Bouarab and colleagues found that the basicity of a Co/SiO₂ catalyst was directly related to the addition of La to the material; in the form of La₂O₃¹⁶⁷. The textural promotion prevented active Co particle sintering by avoiding particle coalescence, therefore maximising the stability of the catalyst at high temperatures required of the reaction. Junke et al. investigated dry reforming using La doped Ni-Al₂O₃ catalysts and reported that the addition of La limited carbon deposition to mostly active forms, hence reducing the formation of non-active filamentous and bulk carbon⁵⁰. They reported the aforementioned results were achieved primarily due to the limitation of
the Ni particle size, being less than 15 nm due to the addition of the lanthanide promoter.

Ce has been shown to have other beneficial effects as a promoter on catalyst performance such as; improving the reducibility of the active phase, improving the dispersion of the active phase, and high oxygen storage capability which can limit carbon deposition over time in the reaction. Montoya et al. reported that the addition of CeO not only increased stability, but also limited active metal-support interaction when used as a dopant, hence causing an ease of reducibility of the catalyst and resulting in high dispersion of small active Ni particles, which showed even less carbon deposition over time and a greater overall activity. Ce has been shown not only to promote reduction of Ni, but also to increase the amount and strength of the basic sites of Ni/Mg–Al catalysts. Daza et al. found that a 1% to 10% increase in doping percentage of Ce caused no considerable effect on the catalytic activity and selectivity, or of the size of active crystallite, in the materials prepared, but resulted in a greater inhibition of the coke formation. Similarly, Foo et al. found that by adding Ce to Co-Ni/Al₂O₃ catalysts they could improve the resistivity to carbon build up, but could not increase catalyst activity. They found that only deposited Cₐ was active towards oxidation from the CeO₂ present, where Cₐ still remained inactive in the reaction as reported in undoped materials. Nandini et al. showed that addition of CeO₂ to a Ni/γ-Al₂O₃ catalyst led to a decrease in the Ni particle size, thus an increase in the dispersion of the active phase. They also proposed that the improved stability observed was due to the paired oxidative properties of the CeO₂, where it assisted in gasifying surface carbon without affecting the structure of the Ni, even at high temperatures. Recently Li and
colleagues also found that adding CeO₂ to a high surface area Ni/Al₂O₃-ZrO₂ catalyst assisted in oxygen promotion of the catalyst surface; reducing carbon deposition greatly⁷⁹. Through suitable elemental selection and specific preparation methods they were able to create a catalyst which showed a high degree of active metal dispersion with strong metal to support interaction, high activity, and high stability; through the inhibition of inactive carbon deposition. As with noble metal doped catalysts, Daza et al. found that doping Ce into the catalyst showed a limit with optimal loading; where a suitable concentration was required to encourage the beneficial effects on the material, whilst an excess would inhibit the active sites of the catalyst through blockage and over oxidation¹⁷⁰.

Whilst lanthanum and cerium are reported to be textural type promoters in dry reforming catalyst materials, praseodymium and neodymium have very recently been found to also directly affect catalyst activity. Gamba and colleagues doped a Ni/Al₂O₃-PVA catalyst with Pr and found the promotion actually assisted in both CH₄ and CO₂ turn over frequencies¹⁷⁵. They found that whilst there was no correlation between Pr concentration and Ni particle size, there was a correlation between Pr amount and carbon deposition rate owing to the transport of electrons through the Pr⁴⁺/Pr³⁺ pair. Nd has very recently been screened in an artificial neural network program to determine its effect as a promoter in the dry reforming reaction by Tian et al., who proposed that it would promote both activity and stability when added to a Re-Co/SrCO₃ catalyst¹⁷⁶.
1.4.4 Research on Carbon Deposition in Catalytic Dry Reforming of Methane

Carbon deposition type, and the rate at which this occurs is well known to be highly dependent on the material being used as a catalyst, and the reaction conditions employed. When using Ni based catalysts, there have been two proposed mechanisms for specific carbon deposition routes which directly affect active Ni particles; carbon transport through the bulk of Ni particles, and carbon transport along graphene formed interfaces. Whisker carbon develops in higher pressure systems, where once released in the methane decomposition reaction at surface sites, carbon diffuses through Ni clusters growing from active particles, hence forming tube or whisker type structures which can have a negative effect on catalyst activity by slow encapsulation. Helveg et al. recently discovered an alternate carbon deposition mechanism through in situ TEM imaging, which showed that under low pressure conditions graphene layers encapsulated Ni particles bound to the support structure. This was shown to lead to a change in adsorption energy of the C and Ni; allowing the active particles to diffuse through the graphene layer towards the surface of the material, before the particles would re-form into small clusters on the outer surface of resulting nanofibres. In this mechanistic study it was shown that Ni particles elongate and contract during carbon nanofibre growth when being transported to the growing catalyst surface, and whilst the deposition of carbon occurred rapidly, deactivation of the material was prolonged.

Chen and colleagues researched carbon deposition on mesoporous Al$_2$O$_3$ and found that the deposited carbon rate and type was highly structure sensitive. They concluded that whilst the reforming activity depends on the active metal particle
dispersion and size, carbon deposition is highly sensitive to the morphology of the
catalyst and can therefore be controlled by careful selection of preparation
conditions; primarily calcination temperature. Junke et al. opposed this statement,
concluding that although the catalyst textural properties had an effect on carbon
deposition, it was the active metal size in a Ni/La$_2$O$_3$-Al$_2$O$_3$ catalyst that was overall
responsible for the carbon deposition type, which in-turn determined the overall and
long term activity of the catalyst as a whole$^{50}$. They found that Ni particles less than
15 nm in diameter suppressed the formation and deposition of filamentous carbons,
decreased the amount of carbon deposition as a whole, and resulted in more active
C$_x$ species which showed a better activity for further oxidation to CO and
consequently a higher stability of the catalysts. Kim et al. agreed in that larger metal
particles regularly favour inactive carbon formation and accumulation, whilst smaller
active particles gave rise to more active species$^{180}$. The relationship between the
amount of the accumulated deposited carbon and the particle size in their spent
catalysts supported this notion. Guczi et al. found that on highly stable NiAl$_2$O$_4$
materials, the catalyst was only deactivated after long periods of time when graphitic
carbon eventually inhibited the reaction taking place on or neighbouring to active
sites$^{95}$. They found that it was plausible to assume that active carbon types first
deposited on Ni sites as amorphous NiC$_x$, but later if they remained on the catalyst
surface through lack of incoming CO$_2$ molecules, would change to non-active carbon
types such as graphitic carbon and carbon nanotubes; in fact it was only with
selected promoters that this deactivation step could be inhibited. On a similar
MgAl$_2$O$_4$ catalyst, Guo et al. agreed that graphitic carbon was most likely the non-
active form of carbon that lowered the activity of the catalyst over time, but in a
Ni/MgAl$_2$O$_4$ catalyst, CO$_2$ had a unique reactivity with all deposited carbon types to
some degree due to the carbonate, bidentate and formate species occurring on the MgAl$_2$O$_4$ surface$^{135}$. 

A balance between activity and carbon deposition has been shown to be important in selecting materials for catalysis in the dry reforming reaction. In a study on Pt supported catalysts Nagaoka et al. made a comparison study of Pt/Al$_2$O$_3$ and Pt/ZrO$_2$ materials$^{181}$. It was revealed that the rate of CH$_4$ decomposition on Pt/Al$_2$O$_3$ was greater than on Pt/ZrO$_2$, but accordingly whilst Pt/Al$_2$O$_3$ displayed higher initial activity, in the long run the Pt/ZrO$_2$ catalyst remained more stable due to better balance between carbon formation and its successive oxidation by the activated CO$_2$; occurring at the perimeter of the metal-support interface. Horvath et al. studied Ni, NiRh, and NiCo catalysts supported on Ce-Zr oxides and found that due to the reaction being performed at high temperatures, sintering of metal particles naturally occurred and the resulting clusters were subsequently removed from the support by the growing carbonaceous filaments$^{182}$. They discovered that these delocalised particles were then surrounded by network of nanotubes or encapsulated by graphitic layer, but there remained a small amount of Ni still available as an active phase; where it was included within the oxide matrix and hence these materials remained slightly resistant to sintering. They showed that in comparison to the research of Nagaoka, there was no direct relationship between the catalytic activity of the materials used and the amount of surface carbon remaining after the reaction, indicating the importance of the deposited carbon utilisation, where CO can be alternatively produced by oxidation of active carbon deposits.
1.5 Research Objectives

Whilst Ni supported materials are the most commonly used catalysts in the dry reforming of methane, a Ni catalyst which shows both a high activity and reasonable stability over time still remains elusive. Efforts into improving on the catalytic performance of these materials has mainly focussed on the optimisation of the support material over which the Ni is distributed, and the positive effect of dopants on the materials abilities in the reaction. The main aim of this research project was to develop Ni based dry reforming catalysts with high activity and stability when used at a relatively low reaction temperature.

Specific aims of the project were as follows:

- Prepare and characterise Ni based materials that have not been previously used in the dry reforming reaction

- Investigate the influence of the following on the activity and selectivity of the aforementioned catalysts:
  - Support type
  - Doping

- Investigate the following physical and chemical properties of prepared materials prior and after catalyst testing:
  - Type of Ni / Ni sites
  - Size / morphology of Ni
- Surface area
- Thermal stability

• Investigate the influence of the physical and chemical properties of tested materials on catalytic ability in the dry reforming of methane in terms of;
  - Activity
  - Stability
  - Product ratio
1.6 References

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(60) Richardson, J. T.; Paripatyadar, S. A.; Applied Catalysis A: General 1990, 61, 293.

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The experimental aspects of the research discussed in this thesis are outlined in this chapter. These include catalyst preparation and characterisation, catalyst activity analysis system design and specifics, and catalyst testing method.
2.1 Materials

2.1.1 Chemicals Used in Preparation of Catalysts

Table 2.1 lists the chemicals used in the preparation of all materials presented in this thesis and the supplier through which the chemicals were obtained.

Table 2.1: List of chemicals and suppliers for materials preparation

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel nitrate hexahydrate (Ni(NO₃)₂).6H₂O</td>
<td>Merck</td>
</tr>
<tr>
<td>Ytterbium nitrate pentahydrate (Yb(NO₃)₃.5H₂O)</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>γ-Al₂O₃ powder</td>
<td>Puralox-Catalox</td>
</tr>
<tr>
<td>SiO₂ powder</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Aluminium isopropoxide (Al(OPr')₃)</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Nitric acid (HNO₃) 0.1M diluted from concentrated batch</td>
<td>Merck</td>
</tr>
<tr>
<td>Polyethyleneoxide-polypropyleneoxide-</td>
<td>BASF</td>
</tr>
<tr>
<td>polyethyleneoxide (Pluronic 123)</td>
<td></td>
</tr>
<tr>
<td>Tetraethyl orthosilicate (TEOS)</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Urea (CO(NH₂)₂)</td>
<td>Merck</td>
</tr>
</tbody>
</table>
2.1.2 Chemicals Used in Catalyst Testing

Gases used for instrument calibration and catalyst activation and testing were obtained from Coregas. Table 2.2 lists the gases used and their purities.

Table 2.2: List of gases used in the activity analysis of prepared catalysts

<table>
<thead>
<tr>
<th>Gas</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>4.5 (99.995%)</td>
</tr>
<tr>
<td>H₂</td>
<td>5 (99.999%)</td>
</tr>
<tr>
<td>CO₂</td>
<td>4.5</td>
</tr>
<tr>
<td>CH₄</td>
<td>5</td>
</tr>
<tr>
<td>CO (reference)</td>
<td>4.5</td>
</tr>
</tbody>
</table>

2.2 Methods

2.2.1 Catalyst Pelletisation

Following calcination¹⁻³ (see Chapters 3.2.3, 4.2.3 and 5.2.3) all catalyst materials were pelletised to larger particles between 650 and 800µm in diameter with the use of a hydraulic press and sieves of varying mesh size. The particles were filtered through several sieves of decreasing diameter mesh to ensure an accurate distribution of diameter, where clusters with larger or smaller size than the desired range were rejected. The die used to press the catalysts was similar to that used in preparing KBr plates for IR analysis, where the pressure was limited to 5 tonne/m² in order to prevent degradation of physical attributes such as surface area and pore volume.
2.2.2 Catalyst Testing

2.2.2.1 Catalyst Testing System Components

The following is a list of the main components of the catalyst activity analysis system used in the catalyst testing throughout this thesis:

- GC – Shimadzu type 17A with TCD detector attachment
- Silica gel 60/80 packed GC column – Grace Davison Discovery Sciences
- 6-Way automatic switch (computer controlled, hydraulic pressure)
- Stainless steel connector components and flow switches – Swagelok
- 4-Way automatic switch
- Type K stainless steel thermocouple – Swagelok
- Custom designed quartz reactor tube with graded stainless steel-quartz end connections – Petersen Scientific Glass Blowing
- Vertical hinged tube furnace with separate programmable temperature controller and custom tube adaptors – John Morris Scientific
- Quartz wool – Petersen Scientific Glass Blowing
- MKS Mass flow controllers – John Morris Scientific
- Gases and dual stage pressure regulators – Coregas
- Teflon and stainless steel tubing – Swagelok
- Manual pressure relief switch – Swagelok
- Analogue pressure gauge – Swagelok
- Pressure relief valve (manual set, mechanical release, automatic reset) – Swagelok
- Heat tape
- Heat tape temperature controllers (x4) – John Morris Scientific
2.2.2.2 Catalyst Testing System

A schematic diagram of the catalyst testing system, which was designed and built in-house, is shown in figure 2.1.
Figure 2.1: Catalyst Activity Analysis System Overview
The reactor was a quartz tube (inner diameter: 7 mm, outer diameter: 13 mm) with gradual graded stainless steel end connections (5 gradual graded sections, 8 mm outer diameter stainless steel) as shown in Figure 2.2. The graded end pieces allowed for an airtight seal under pressures up to 15 atm whilst minimising the effect of thermal expansion difference occurring at the quartz-stainless steel interface, which would otherwise result in the degradation of the seal. The quartz reactor ensured the catalyst bed could be more precisely monitored than conventional stainless steel reactors, whilst restricting self catalysis of the reaction (as previously noted with steel materials⁴).
Catalyst bed temperature was measured with a removable type-k thermocouple to ensure a consistency between the furnace set temperature and the reactor, and the temperature gradient over the catalyst bed was analysed; where the differences between the
temperatures were determined to be negligible (see Appendix A). The reactor was held vertically by custom made brackets within the heating zone of a vertical split hinged furnace (maximum temperature: 1300 °C, single heat zone, heat zone length: 700 mm) as shown in Figure 2.3.

Figure 2.3: Reactor held within vertical hinged tube furnace
Ceramic tube adaptors were placed at the immediate ends of the furnace heat zone to both assist in holding the reactor in the centre of the heat zone, and to ensure the accuracy of reaction temperatures (where these adaptors minimised heat loss occurring from the ends of the furnace). The vertical-type hinged furnace was programmed using a custom temperature controller (Lindberg Blue, single zone with override safety trip switch).

Gas delivery for in-situ catalyst pre-treatment and delivery of dry reforming reactants was controlled by MKS type 1479-A mass flow controllers (single channel, metal-seal, maximum flow rate 200 sccm (He), 100 sccm (CO₂, CH₄, H₂)). These controllers were individually programmed by a computer system running a custom designed dos-based control program. Gases could be delivered across the catalyst bed, or bypassed directly to the attached gas chromatograph for delivery composition analysis; by the use of a 4-way hydraulic-driven automatic switch connected to the system prior to the reactor. All tubing before and after the reactor was heated to 100°C by four separate zones of heat tape, each connected to a separate temperature controller and monitored by an individual type k thermocouple. This ensured a consistency in gas delivery across the catalyst bed, where no vapours could be trapped in the reactor assembly and all products and remaining reactants would be consistently delivered into the GC for analysis.

A Shimadzu type GC-17A gas chromatograph loaded with a packed silica column (60/80, 15 m) was connected to the system for the in-situ analysis of output gas. A thermal conductivity detector (TCD) was used to analyse the gas composition through the use of a difference in thermal conductivity between an input He reference gas and the sample gas being analysed.
A 6-way automatic switch was also loaded inside the GC oven, to be used as the gas delivery method from the catalyst bed / bypass to the GC as seen in Figure 2.4; where a sample loop of precisely 2 mL volume was attached across the switch. When set to a ‘load position’ (Figure 2.4a), the incoming gases from the catalyst analysis assembly were allowed to continuously flow through and fill the sample loop, before the switch was changed to the ‘sample position’ (Figure 2.4b), where precisely 2 mL of sample was introduced to the carrier gas stream, so it could be subsequently carried through to the GC column for separation and quantitative analysis.

![Figure 2.4: Schematic of 6-way automatic switch in load position a), and sample position b).](image)

By using this sample delivery method, and keeping the temperature inside the GC oven at a constant temperature (70°C), an accurate sample volume was consistently delivered for analysis, which could be used to calculate percentage conversion of products to reactants, product ratios, and any deactivation that occurred over the catalyst materials over time.
Gas analysis was performed using Shimadzu Class GC-10 software paired to the TCD detector.

For safety, a manual pressure relief valve was connected to the system between the mass flow controllers and the reactor, and an analogue pressure gauge was connected to measure the pressure of the system at any given moment during the reaction period. The manual pressure release valve was set to 10 atm max pressure to ensure that if any significant blockages in the system occurred the resulting pressure in the ‘stream’ line would be released into a ‘vent’ line before the pressure relief valve reset. Prior to each catalyst testing experiment a manual flow switch was used to pressurise the system, ensuring that there were no leaks within the reactor. The system was contained under a fume hood with suitable negative pressure to ensure any escaping gases were promptly removed from the vicinity of the equipment.

### 2.2.3 Catalyst Testing Procedure

The pelletised catalysts to be analysed were held in place by quartz wool which was inserted into the reactor both before and after the catalyst bed, to allow no physical movement of the catalyst during analysis (whilst allowing the gases to flow unimpeded across the pelletised particles and through the reactor). The reactor was then filled at both ends with lengths of 2 mm diameter quartz rods, to allow sufficient pre-mixing and heating of reactant gases before flow across the pelletised catalysts and reduce dead volume in the reactor.
A pre-determined mass of pelletised catalyst material was loaded into the reactor tube as mentioned above before being reduced (activated) in-situ prior to reaction studies. In a typical reduction of the catalyst preceding reaction analysis, the pelletised catalysts were raised to a temperature of 700°C, where they were reduced under a hydrogenated environment (5% H₂ purity 5, 95% He purity 4.5) at a flow of 50 sccm for 2 h.

Testing of catalytic materials was conducted as follows unless stated otherwise: typically 105 mg of pelletised catalyst was placed in the centre of the reactor with quartz wool loaded either side as outlined in the section above. Whilst the catalyst was reducing, the reactant gases (1:1:2, CO₂ purity 4.5: CH₄ purity 5: He purity 4.5) were set to a total flow rate of 66 sccm, before being bypassed to the GC, where the reactants were analysed for composition. After two subsequent bypass analyses, the gases were allowed to flow across the catalyst bed and into the GC loading zone. Once every 26 mins, the 2 mL sample loop of the 6-way switch was allowed to enter the GC where separation of components allowed the sample to be analysed for qualitative and quantitative composition (as outlined in the following section). Each catalyst was exposed to a flow of reactant gases for a minimum of 6 h, before being cooled under an inert environment and collected for post run analysis.

### 2.2.3.1 Gas Conversion Analysis and Product (H₂:CO) Ratio

The conversions of CO₂ and CH₄ were calculated by using equations (2.1) and (2.2):

\[
\text{CO}_2 \text{ conversion } \% = \frac{[\text{CO}_2\text{in}] - [\text{CO}_2\text{out}]}{[\text{CO}_2\text{in}]} \times 100\% \quad (2.1)
\]

\[
\text{CH}_4 \text{ conversion } \% = \frac{[\text{CH}_4\text{in}] - [\text{CH}_4\text{out}]}{[\text{CH}_4\text{in}]} \times 100\% \quad (2.2)
\]

Where all percentage data of conversions and yield were calculated in mol%.
Production percentages of H\textsubscript{2} and CO were calculated from GC calibration curves; where standards comprised of various molar percentages of each gas were delivered to the GC (under standard operating conditions) before being analysed and collated into a curve of best fit for each gas as seen below in Figures 2.5 and 2.6 respectively:

Whilst it is expected that a linear concentration increase in each gas would subsequently result in a linear change in peak area for the specified gas, the non-linear response for H\textsubscript{2} is due to the fluctuation in current over the TCD detector when comparing the sample gas (H\textsubscript{2}) to the reference gas (He) which have similar (and therefore interfering) thermal conductivities (0.1805 and 0.1513 Wm\textsuperscript{-1}K\textsuperscript{-1} respectively). However, due to the relatively linear region occurring between the H\textsubscript{2} mol\% of 10 to 30\%, one can assume that the production percentage of H\textsubscript{2} can be accurately determined by solving the more complex equation (2.9):

\[
\text{H}_2 \text{TCD peak area} = -1.7467 \times (\text{H}_2 \text{ concentration \%})^3 + 201.48 \times (\text{H}_2 \text{ concentration \%})^2 - 1655.7 \times (\text{H}_2 \text{ concentration \%}) - 1459
\]  

(2.9)

Where the domain was limited between 10 and 30 mol\%

The CO production could be similarly solved by the formula (2.10):

\[
\text{CO TCD peak area} = 234125 \times \text{CO concentration \%}
\]  

(2.10)
Figure 2.5: GC calibration curve for H₂ product

Figure 2.6: GC calibration curve for CO product
The product ratios of H$_2$:CO were calculated by analysing the product percentages of H$_2$ and CO respectively and comparing products.

### 2.2.4 Catalyst Characterisation

#### 2.2.4.1 Temperature Programmed Reduction (TPR)

Temperature programmed reduction (TPR) is a simple experimental technique most commonly used for characterisation of the reduction of a metal oxide (MO) to form elemental metal (M$^0$) and water vapour in by the following mechanism:

\[
\text{MO(s)} + \text{H}_2(\text{g}) \rightarrow \text{M}^0(\text{s}) + \text{H}_2\text{O} \quad (2.7)
\]

In TPR of metal based catalysts a metal oxide catalyst precursor is exposed to a gradual temperature rise under a reducing gas atmosphere, generally containing a low concentration of hydrogen. The rate of flow of the reducing gas is kept constant throughout the temperature program and the outlet gas composition is measured via a TCD detector; so that the change in concentration of H$_2$ is therefore proportional to the rate of reduction of the MO species to the elemental M$^0$. Reduction peaks appear where the reduction rate of a species at a specific temperature passes through a maximum. Interpretation of TPR profiles is usually limited to the discussion of peak maximum temperatures and the number of peaks, indicative of the reducibility and number of species present. The chemical nature and environment of the species will determine the position of the peaks, and the area under the peaks represents the proportion of species being reduced at the specific temperature.
TPR experiments were performed using an apparatus built at RMIT University specifically for reduction characterisation studies of heterogeneous catalysts, as shown in the schematic diagram in Figure 2.7:

The reactor was a fixed bed quartz reactor (inner diameter 3 mm, outer diameter 5 mm, length 500 mm) where the catalyst was kept in place by quartz wool plugs. The catalyst bed was placed in the heating zone of a vertical split hinge furnace (Lindberg Blue; single heating zone 300 mm), and its temperature monitored by a stationary ‘type k’ thermocouple held in close proximity to the micro-reactor. A TCD detector similar to that used in the catalyst testing system (refer to section 2.2.3.2) was used to monitor the gas output. The gas feed to both the catalyst bed and a TCD detector was controlled manually by needle-valve flow controllers. 5 % molar H\textsubscript{2} balanced in Ar (Coregas) was split into two individual controllers and used for both a reducing environment and a direct TCD reference gas. The TCD filament was manually set to 100 °C under 3 A current for both reference and analysis.
In a typical TPR analysis, approximately 0.05 g of pelletised catalyst was weighed out and loaded in the micro-reactor. Before the commencement of TPR analysis the catalyst surface was activated as follows: the temperature of the catalyst bed was ramped from room temperature to 500 °C at a rate of 10 °C min\(^{-1}\) before being held for 2 h at this temperature, all under a flow of 50 mL min\(^{-1}\) pure Ar. The catalyst was then allowed to cool back to room temperature whilst maintaining the Ar flow. For the TPR analysis the activated catalyst was then exposed to a flow of reducing gas at a flow of 1 mL min\(^{-1}\) and ramped to 900 °C at a rate of 10 °C min\(^{-1}\). The reduction characteristics of the catalyst were determined from the difference in thermal conductivity present across the TCD detector due to the consumption of H\(_2\) from the reducing gas.
2.2.4.2 B.E.T. Surface Area Analysis

Brunauer-Emmett-Teller (BET) analysis provides specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure by a fully automated analyser. The technique uses external area and pore area evaluation to determine the total surface area in meters squared per gram of material (m²/g). The total surface area of the material can be calculated using equation (2.8):

\[
S_{\text{BET total}} = \frac{\theta_m N s}{V}
\]  

(2.8)

Where \(\theta_m\) is the monolayer adsorbed gas quantity as derived from a BET analysis plot, \(N\) is Avogadro’s constant, \(s\) is the adsorption cross section of the adsorbed species, and \(V\) is the molar volume of the adsorbate gas. Barrett-Joyner-Halenda (BJH) analysis can be used to further determine pore area and volume using adsorption and desorption characteristics using equation (2.9):

\[
v_{\text{adsorption}}(x_k) = \sum_{i=1}^{k} \Delta V_i(r_i \leq r_c(x_k)) + \sum_{i=k+1}^{k} \Delta S_i t_i(r_i > r_c(x_k))
\]  

(2.9)

Where \(v_{\text{adsorption}}(x_k)\) is the volume of adsorbate at relative pressure \((x_k)\), \(V\) is the pore volume, and \(t\) is the thickness of the adsorbed layer.

Prior to BET analysis the catalyst was calcined under identical conditions to catalyst testing pre-treatment (refer to chapter 2.2.2), and similarly reduced for 2 h at 700 °C under 5% H₂ (refer to chapter 2.2.4). Immediately preceding BET analysis, the material was raised to a temperature of 300 °C (in-situ to analysis) under a neutral He environment to
evaporate any residing water molecules and activate the surface of the catalyst. Nitrogen adsorption/desorption isotherms, BET surface area and pore volume measurements were conducted using N₂ as the adsorbate on a Micromeritics ASAP 2010 Surface Area Analyzer at 77K, attached to a computer running Micromeritics analysis software.

2.2.4.3 X-ray Diffraction Analysis (XRD)

X-rays have wavelengths in the angstrom range and are therefore sufficiently energetic to penetrate solids and probe their internal structure. X-ray diffraction analysis is therefore a powerful tool in identifying crystallographic information about solid catalysts, including bulk phases and monitoring the kinetics of bulk transformations. Diffraction of X-rays by crystal planes allows for the derivation of lattice spacing calculated by using the Bragg equation:

\[ n\lambda = 2dsin\theta \]  

(2.10)

Where \( n \) is the order of reflection, \( \lambda \) is the wavelength of radiation used, \( d \) is the distance between two lattice planes, and \( \theta \) is the Bragg angle. Sherrer showed that broadening of a specific diffraction line corresponding to a Bragg angle (\( \theta \)) can be directly related to crystal size using the relationship:

\[ L = \frac{K\lambda}{\beta\cos\theta} \]  

(2.11)
Where L is the measure of the dimension of the crystal in a direction perpendicular to the
crystal plane, K is the Sherrer constant of 0.89, \( \lambda \) is the wavelength of radiation used, \( \beta \) is
the peak width at half maximum height, and \( \theta \) is the angle between the beam and the reflecting plane.

X-ray diffraction studies were performed on a Bruker AXS D8 advance wide angle powder
X-ray diffractometer using a monochromatic CuK\( \alpha \) radiation source (\( \lambda = 1.54056 \)\( \text{Å} \)),
operating at 40 kV and 40 mA over a 2\( \theta \) range of 15 - 85°. Peak identifications were
carried out using and attached computer running Bruker D8 advance software.

2.2.4.4 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy is a quantitative analysis technique that is used to
measure the elemental surface composition, electronic and chemical state of a sample.
XPS spectra are obtained when a sample is irradiated with soft x-rays, where the number
of escaping electrons and their kinetic energy are detected and recorded. The electrons
detected are generally released from 1-10 nm from the surface of the sample, so this
technique is limited to the detection of surface species and states.
The binding energies of emitted electrons are calculated using equation (2.12):

\[
E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \varphi)
\]  

Where \( E_{\text{photon}} \) is the energy of the primary photon, and \( \varphi \) is the work function of the
spectrometer.
The composition and oxidation status of the surfaces of catalyst materials were explored using XPS analysis. A Thermo Scientific K-Alpha X-ray photoelectron spectrometer was used to analyze the surface composition of the catalysts. The spectra were obtained at room temperature with an Al-Kα radiation source. Samples were analysed under a pressure of 1 x 10⁻⁹ torr or less. The core levels were aligned with the carbon 1s binding energy of 285 eV. Analysis of the obtained XPS data were performed using an attached computer running appropriate software.

2.2.4.5 Transmission Electron Microscopy Imaging (TEM)

Electron microscopy techniques are used to determine both the size and shape of materials through a visual representation of the sample. A primary electron beam is fired at a loaded sample, which results in transmitted, diffracted, backscattered, secondary, and Auger electrons as seen in Figure 2.8.

![Diagram of electron microscopy](Figure 2.8: Electron microscopy primary and resulting electron beams)
In transmission electron microscopy (TEM) transmitted and diffracted electrons are collected by a suitable detector, presenting an image either on a screen which is luminescent due to a phosphorous coating, or on a recording medium such as a film. More recently digital recording devices have been used to capture and record images of the sample at various points; such as charge-coupled device (CCD) cameras.

Transmission electron microscope and high resolution TEM (HRTEM) images were recorded on JEOL 1010 TEM and JEOL 2010 TEM instruments at accelerating voltages of 100 kV. All samples were prepared by drop-casting onto strong carbon coated 200 mesh copper grids. Images were recorded on film before being developed and stored digitally through a film scanner.

2.2.4.6 Thermogravimetric Analysis (TGA)

Thermo gravimetric analyses (TGA) determines changes in the weight of a solid sample when temperatures are gradually elevated across the material. A gas is passed across a small mass of sample, contained within a micro pot-furnace, where the temperature of the sample is raised until one or more components of the sample decompose into a gas phase and are subsequently dissociated from the remaining solid sample. Due to the enclosed nature of the process, very small changes in weight can be recorded, and an accurate plot of loss of weight at various temperatures results.
TGA of spent catalysts were carried out using a Perkin-Elmer Pyris 1 TGA-7 run from room temperature to 850 °C with a linear heating rate of 10 °C.min⁻¹ under a flow of air. The furnace was held at 850 °C for a further 10 mins to ensure no further weight loss occurred after analysis was complete. Weight curves were analysed and derivatised using Perkin-Elmer TGA software installed on an attached computer.
2.3 References


This chapter presents a detailed description of the experimental results attained when nickel was supported on a high surface area mesoporous alumina with different metal loadings. The materials have been extensively characterised and subsequently tested for activity in the dry reforming reaction. A comparison of the above mentioned catalytic materials with equivalent material prepared by conventional wet-impregnation method has been assessed and the differences in observed activity are explored.
3.1 Introduction

Studies on the influence of the material used as a support on the activity and stability of nickel based catalysts for the dry reforming of methane are important for improving the understanding of the role of carrier, and for the subsequent development of improved dry reforming catalysts. As outlined earlier (refer to section 1.3) a number of different support materials have been used to prepare Ni based dry reforming catalysts. The most common supports include alumina, silica, zirconia and titania, each of which show different morphologies, active particle-support interaction and resulting performances over the dry reforming reaction\textsuperscript{1-7}.

Al\textsubscript{2}O\textsubscript{3} is the most commonly explored support structure in the dry reforming reaction, not only due to its high basicity; under suitable conditions promoting a high conversion of CO\textsubscript{2}, but also due to its versatility through many different structural forms and various adaptations of previously reported morphologies. Tang et al. found that the increased base strength of a Ni/Al\textsubscript{2}O\textsubscript{3} material caused CO\textsubscript{2} to be more easily adsorbed than on other supports, and hence when paired with well distributed Ni particles resulted in an increased initial activity\textsuperscript{8}. Hou et al. studied Ni supported on different morphologies of Al\textsubscript{2}O\textsubscript{3} and found that the catalytic ability of the materials could be improved when Ni was supported on \(\gamma\)-Al\textsubscript{2}O\textsubscript{3} compared to various other morphologies\textsuperscript{9}.

However whilst the beneficial physical properties of alumina supported materials are widely recognised when used as catalysts for the dry reforming reaction, several issues have recently been realised when using these materials for such purposes. Of these concerns, the most commonly overlooked problems are the lack of thermal stability inherent of these materials and the increased rate of inactive carbon deposition they allow.
The facile thermal agglomeration of active metal particles is known to regularly occur under standard dry reforming conditions when metals are deposited on the surface of a support structure with low thermal stability, where there is little resulting particle-support interaction\textsuperscript{10}. This is known to lead to rapid sintering of active metal particles deposited across the material, which may result in an increased build up of inactive carbon species. Kim et al. showed that Ni sintering occurred rapidly across a Ni/\(\gamma\)-Al\(_2\)O\(_3\) material at high temperatures, primarily due to a weak metal-support interaction. Further the highly basic nature of alumina can actually be detrimental to catalytic ability within Ni supported Al\(_2\)O\(_3\) materials. Where a highly basic support generally results in an increased rate of the Boudard reaction (reaction 1.8) compared to non-basic supports, when paired with a less active metal phase the methane decomposition reaction (reaction 1.7) may be limited, and hence a significant concentration of carbon is allowed to build up across the materials where the above mentioned reaction rates are unbalanced. Guo et al. found that the high Lewis basicity of a Ni/\(\gamma\)-Al\(_2\)O\(_3\) material resulted in a high level of inactive carbon deposition over time, where promoters were required to suppress the deactivation of the material\textsuperscript{11}. These factors have proved to limit the stability of alumina supported Ni catalysts in the dry reforming reaction; where a decrease in conversion of CO\(_2\) and CH\(_4\) over time greatly limits their effectiveness as suitable catalytic materials.

Whilst the sintering of active metal particles under severe reduction and reaction conditions seems to be inevitable, recently researchers have estimated that the degree of this thermal sintering could be minimised when active metals were loaded on carrier materials with certain physical properties. In 1992 a new group of materials emerged which saw an exciting potential application in the catalytic field. These materials were
those of mesoporous support structures, first reported in the form of MCM-41; a high surface area, highly stable silica based material with properties extremely suitable for catalytic application\textsuperscript{12}. The above materials consist of a rigid, thermally stable framework, with a greatly increased surface area due to the presence of pores with specific targeted morphologies which occur throughout the bulk of the material and lead to catalysts consisting of highly dispersed active metal particles. However MCM-41 has been shown to be a poor carrier when paired with Ni and used as a catalyst in the dry reforming reaction\textsuperscript{13}, where harsh reaction conditions and a weak metal particle-support interaction have been shown to allow a high degree of Ni particle sintering, and hence a decrease in reactant conversion over short periods of time.

Whilst research into optimisation of catalysts by using mesoporous supports is dominated by silica based mesoporous materials, recent research has seen some interest in the exploration of non-silica based mesoporous materials as catalyst components for various industrial reactions. These have included mesoporous zirconias for the autothermal reforming of ethanol\textsuperscript{14}, mesoporous carbons for the oxygen reduction reaction\textsuperscript{15}, mesoporous titanias for use in solar cells\textsuperscript{16}, and mesoporous aluminas for the steam reforming reaction\textsuperscript{9}. Very recently Hou et al. found that Ni deposited in situ to preparation of a mesoporous Al\textsubscript{2}O\textsubscript{3} showed a very high stability in the steam reforming of methane, where an increased Ni-support interaction paired with the thermally stable support stopped the high temperature sintering of metal particles\textsuperscript{9}.

The preparation of mesoporous materials made of metal oxides is simple, and synthesis parameters can be easily controlled to create a material with desirable properties. The typical synthesis consists of four major components: an inorganic metal oxide precursor,
organic template, solvent, and an acid (or base) to act as a catalyst. It is the specific morphologies of the inorganic precursor and organic template that determine the overall morphology of the mesoporous material.

The triblock co-polymer ‘P123’ surfactant 
(HO(CH₂CH₂O)₂₀(CH₂CH(CH₃)O)₇₀(CH₂CH₂O)₂₀H) has been successfully used as a templating agent in the preparation of such mesoporous materials as FDU-14 and SBA-15, where its suitability arises due to its amphiphilic nature, low cost, commercial availability, and self ordering properties. P123 may be used as a soft template in the preparation of high surface area mesoporous aluminas (MAI), where the molecule, alumina isopropoxide (Al(OPr)₃) is a suitable inorganic precursor. The reaction pathway of micellisation to the formation of the mesopores and subsequent self assembly of the mesoporous alumina material is presented in Figure 3.1. The hydrophobic center of the surfactant P123 primarily forms the core of a micelle structure whilst the hydrophilic ends form the corona. Al(OPr)₃ molecules adopt the mesoscopic morphology as a result of the micelle structure of the P123; where they are preferentially bound to the hydrophilic corona of the surfactant micelle. Subsequent self assembly of tube type structures occurs through intermolecular bonding between Al(OPr)₃, resulting in the fabrication of a highly ordered material consisting of rigid parallel mesopores. Subsequent calcination of the material removes the P123 soft template from within the mesopores, leaving a high surface area, rigid, thermally stable material.
Figure 3.1: Pathway of micellation, formation of mesopores and self assembly in mesoporous alumina preparation

Such materials have been shown to maintain the highly desirable physical properties of MCM-41 supports, in particular in facilitating a high distribution of active metal particles, whilst showing considerable active metal-support interaction\(^9\). This could lead to solutions to the main concerns with using Ni supported alumina materials as catalysts in the dry reforming reaction; highly distributed, thermally stable Ni particles which should allow for a maintained conversion of CO\(_2\) and CH\(_4\) over long reaction periods; and the preservation of high methane conversion (reaction 1.7) rates, which should prevent the build up of non-active carbon species across the materials. The above mentioned materials would prove to be a major benefit in the dry reforming reaction, where a maintained stability of highly active materials has shown to be elusive so far in catalyst development in this area.

A set of mesoporous alumina based Ni catalysts (Ni/MAI) were prepared with various Ni loading and compared to a Ni alumina material prepared via more common wet
impregnation method (Ni/γ-Al₂O₃ WI). The materials were characterised for physical properties, and tested for catalytic ability in the dry reforming reaction.

3.2 Experimental

3.2.1 Materials

Refer to section 2.1.1 for a list of materials used in catalyst preparation

3.2.2 Catalyst Preparation

3.2.2.1 Nickel Mesoporous Alumina

Mesoporous alumina (MAI) containing Ni was synthesized using an advanced template assisted method⁹ with modifications. In a typical synthesis of Ni(7)/MAI, 4.0 g of Pluronic P123 was dissolved in 30 ml of ethanol under stirring at room temperature, before 8.0 g of Al(OPri)₃ was added to the solution. Nickel precursor solution was made separately by dissolving 0.896 g of Ni(NO₃)₂.6H₂O in 10 ml ethanol and 6 ml concentrated HNO₃. The latter solution was added to the P123 solution under vigorous stirring. The mixture was stirred for a further 2 h. The final slurry was transferred into a polypropylene bottle, closed and heated in an oven for 12 h at 90 °C. The temperature of the PP bottle was finally brought down to 50 °C and the bottle was uncapped overnight to permit the remaining ethanol to evaporate. The obtained solid sample was ground to a fine powder and calcined using a specific pre-treatment cycle at 630°C for 2 h under static air. For the synthesis of Ni(10)/MAI and Ni(15)/MAI, the same procedure was followed using a predetermined amount of nickel nitrate and nitric acid.
3.2.2.2 Wet Impregnated $\gamma$-Al$_2$O$_3$

Ni was deposited through incipient wetness impregnation methods in 10% w/w concentration over commercial $\gamma$-Al$_2$O$_3$ as a comparison between novel preparation technique and the aforementioned conventional method. A commercial $\gamma$-Al$_2$O$_3$ was weighed out and subsequently impregnated with an aqueous solution of Ni(NO$_3$)$_2$·6H$_2$O to obtain materials with 10 wt% Ni. In a typical synthesis of 10% Ni across $\gamma$-Al$_2$O$_3$, 0.99 g of Ni(NO$_3$)$_2$·6H$_2$O was dissolved in excess ethanolic solution under constant stirring for 1 h. 2.0 g of commercial $\gamma$-Al$_2$O$_3$ was added to the solution and allowed to stir overnight, before being boiled down to a slurry. The resulting slurry was then transferred to a polypropylene bottle and dried in an oven at 90 °C for 12 h. The material was labelled Ni(10)/$\gamma$-Al$_2$O$_3$ WI.

3.2.3 Pre-Treatment of Catalysts

After preparation, all materials were calcined to remove any residing water molecules, convert the metal pre-cursors to their respective oxides and to remove any remaining template. For the catalysts consisting of mesoporous alumina (MAl) support material, the dried catalyst powders were placed in a ceramic boat and loaded into a quartz tube before being placed in the heating zone of a hinged tube furnace (Lindberg Blue; maximum temperature 1100°C). The material was heated up at a rate of 10°C per minute from room temperature to 110°C, before being held for 2 h to ensure all residing water was removed. The catalysts were then heated at a decreased rate of 2°C per minute to ensure minimal thermal shock to the material, to a temperature of 630°C and subsequently held at this temperature for a further 2 h. This heating process is represented below in Figure 3.2.
The material prepared by wet impregnation method (Ni(10)/\(\gamma\)-Al\(_2\)O\(_3\) WI) was also calcined under identical conditions to those listed above.

Following calcinations the catalysts were pelletised as outlined in Chapter 2.2.1

Reduction of the catalyst materials were performed in-situ immediately prior to the activity analysis, where subsequent to the loading of the pelletised material within the tubular reactor, the temperature was raised to 700°C and the catalysts were subject to a hydrogenated environment (5% H\(_2\) purity 5, 95% He purity 5) for 2 h.

### 3.2.4 Catalyst Testing

The catalysts were analysed under standard catalyst testing conditions as listed in section 2.2.2.
3.2.5 Characterisation / Analytical Methods

The freshly prepared materials were analysed by XRD and TPR prior to reduction; XRD, BET surface area analysis, TEM, and XPS methods after reduction; and XRD, TEM and TGA methods after activity analysis. These techniques are outlined in section 2.2.3.

3.3 Results and Discussion

3.3.1 Characterisation of Mesoporous-Alumina Supported Nickel

The powder X-ray diffraction patterns of the prepared mesoporous-alumina catalysts prior to and after being reduced (at 700 °C under flowing H₂), along with the Ni(10)/γ-Al₂O₃ material prepared by wet impregnation are presented in Figure 3.3. No diffraction peaks due to Al₂O₃ were present in the catalysts that had not been reduced; hence the Al₂O₃ existed as an amorphous or poorly crystalline phase in these materials. After reduction the XRD patterns for all three Ni/MAI catalysts showed signs of Al₂O₃ crystallinity, as well as diffraction lines at 44.7°, 52.1° and 76.6° 2θ which were due to the [111], [200] and [220] planes of metallic Ni. The occurrence of diffraction lines of crystalline Ni only after the high temperature reduction of the catalysts indicates that the Ni/NiO clusters were deposited as very small and well dispersed particles during preparation, and remained as small sized particles after the calcination step used in the preparation of the materials, only becoming clusters large enough to be detected by this technique once reduced. The material prepared via wet impregnation technique showed no sign of Ni⁰ after reduction stages, indicating that either the Ni was not reduced under the conditions employed for
reduction, or easily re-oxidised to NiO during the analysis period by oxygen from the atmosphere (and due to its location on the exposed surface of the support\textsuperscript{19}). The lack of NiO peaks in the Ni/MAI materials indicates that the nickel species were completely reduced under the reduction conditions employed, or re-oxidation (due to oxygen in the immediate atmosphere) of the active particles did not take place as easily, and therefore these particles were more stable than across the wet impregnated sample.
Figure 3.3: XRD of Ni/MAI and Ni(10)/γ-Al₂O₃ WI materials
The Ni⁰ particle diameter in the reduced Ni/MAl samples was calculated based on the peak broadening for the Ni [111] diffraction line at 44.4⁰ – 44.9⁰. The Ni particle size, unit cell parameter and interplanar spacing of the prepared materials are presented in Table 3.1. It can be seen that the mean diameter of the reduced Ni⁰ particles increased with increasing nickel loading, indicating that the reduction step allowed some local sintering of Ni particles to form larger clusters; more so in the materials with higher initial Ni loading. The evidence of small Ni particle size may be somewhat in recognition to the “confinement effect” which has been shown to limit the in-situ growth of the active metal particles by effectively trapping them within the pores of a highly porous support, thus physically limiting the migration of active particles into larger clusters²⁰.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ni Particle Size (nm)</th>
<th>Unit Cell Parameter</th>
<th>Interplanar Spacing of 100 Plane [d₁₀₀] (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(7)/MAl</td>
<td>9.6</td>
<td>7.84</td>
<td>6.79</td>
</tr>
<tr>
<td>Ni(10)/MAl</td>
<td>10.9</td>
<td>9.26</td>
<td>8.02</td>
</tr>
<tr>
<td>Ni(15)/MAl</td>
<td>18.6</td>
<td>8.49</td>
<td>7.35</td>
</tr>
</tbody>
</table>

Figure 3.4 shows the nitrogen adsorption / desorption isotherms and Figure 3.5 shows the pore size distribution of the reduced Ni/MAl catalysts. The samples show typical type IV adsorption curves characteristic of ordered mesoporous materials with uniform pores²¹.
(Figure 3.4). The adsorption / desorption isotherms show a large increase in the relative pressure ($P/P_o$) from 0.65 to 0.9 due to the capillary condensation of nitrogen within the mesopores. The steepness of the inflection step reflects the uniform pore size distribution of the Ni-loaded mesoporous alumina samples. The isotherms for all the samples are similar in shape, however the inflection point of the step shifted to lower $P/P_o$ values with increasing Ni loading, which indicates that the Ni loading had a significant role in changing the channel shapes or creates small defects in the pore walls of the mesoporous alumina support.

Figure 3.4: BET isotherms of Ni/MAI materials
The specific surface area, pore diameter, and pore volume of the catalysts with increasing Ni loading which were determined using BET analysis are reported in Table 3.2 along with the properties of the Ni/γ-Al₂O₃ WI material. From the data presented it can be seen that a decline in pore diameter and pore volume occurred with increasing Ni loading from 7 wt% to 15 wt%. This was most likely due to increased metal loading occurring directly within the pores as a result of the increasing concentration of added Ni. The different observations for BET surface area with respect to increasing Ni loading; where the catalyst containing an intermediate amount of Ni had a higher surface area than the catalyst containing a lower amount of Ni is interesting based on the pore volume and diameter data. This observation is however consistent with the properties that were observed for the interplanar spacing and lattice parameter data (Table 3.1) and indicate that this intermediate level of Ni loading had a unique effect on the formation process of the highly porous support.
Representative HRTEM images of the calcined and reduced Ni(10)/MAl sample are shown in Figure 3.6. From the HRTEM images the ordered mesoporous and periodic structure of the Ni/MAl can be observed. Nickel particles could not be observed in the TEM images of the materials prior to reduction (Fig 3.4 a & b) due to their very small size / and high distribution. This result is consistent with the XRD analysis of the calcined (non-reduced) materials where no diffraction lines can observed for Ni. Ni nanoparticles can be clearly seen in the TEM images of the reduced samples, presented in Figures 3.4c & d where it can be observed that the Ni particles are evenly dispersed both on the surface of the mesoporous alumina support (Figure 3.4c) and throughout the internal structure of the Ni(10)/MAl sample.
Figure 3.6: HRTEM images of Ni/MAI material; a and b) calcined Ni/MAI; c and d) reduced Ni(10)/MAI

TPR profiles of the Ni/MAI and Ni/γ-Al2O3 materials prior to being reduced at high temperature are presented in Figure 3.7. These plots show that Ni\(^{x+}\) reduction to Ni\(^0\) occurred over a broad temperature range for all materials, indicating that these particles had various metal-support strength. The temperature at which maximum reduction occurred (\(T_{\text{max}}\)) increased slightly in the Ni/MAI materials as the nickel loading was increased above 7\% w/w. The peak maxima for Ni(7)/MAI, Ni(10)/MAI and Ni(15)/MAI are at 574, 594 and 585 °C, respectively; being greater than the peak maxima of 553 °C.
from the easily reduced surface NiO species in the Ni/γ-Al₂O₃ material prepared via wet impregnation. A small shoulder can be observed at lower temperatures when observing the plots of the two Ni/MAI samples with greater Ni loading; occurring between 300 and 425 °C. This was due to the primary reduction of a small percentage of free nickel particles on the outer surface of the material with very low metal-support interaction (see Appendix B); occurring as a result of high concentration of active particle loading. The lack of further H₂ consumption in the TPR profiles above 800 °C indicates all of the exposed Ni²⁺ in the catalyst was converted into metallic Ni, with the exception of the Ni(15)/MAI which shows a minor shoulder occurring around 850°C, which can be attributed to very strongly bound Ni; most likely occurring in spinel form (NiAl₂O₄)¹⁶. Given that this shoulder is relatively small compared to the Tₘₐₓ peaks it can be assumed that only a small percentage of the Ni²⁺ is bound in this form.

![Figure 3.7: TPR profiles of Ni/MAI and Ni(10)/γ-Al₂O₃ materials](image)

Figure 3.7: TPR profiles of Ni/MAI and Ni(10)/γ-Al₂O₃ materials
We therefore have identified three forms of Ni occurring within the materials explored:

- Weakly bound surface species (Ni/NiO)
- Strongly bound surface species (Ni/NiO); most likely occurring within the pore structure of the supports, and
- Very strongly bound spinel species (NiAl₂O₄)

XPS analyses of the reduced catalysts were conducted and the results obtained are presented in terms of the characteristic Ni peaks, and the surface atom percentage of Ni and Ni/Al ratios; in Figure 3.8 and Table 3.3 respectively. Preliminary analysis of the non-reduced catalysts showed that there was no change in the binding energy of all elements regardless of Ni loading.

Figure 3.8 shows the characteristic XPS profiles of the Ni peaks occurring in the reduced samples in the range of 844-870 eV; for the Ni(7)/MAl (a), Ni(10)/MAl (b), Ni(15)/MAl (c), and the Ni(10)/γ-Al₂O₃ WI (d) materials. The binding energy of Ni 2p₃/₂ and Ni 2p₁/₂ remained constant at 855.4-856.7 eV and 874.7-876.4 eV respectively. All samples showed evidence of Ni/NiO from the peaks mentioned above. The broad peak occurring at 862.4 eV was assigned to be the shakeup satellite peak. The overall Al 2p₃/₂ levels were 74.4 eV and the O 1s levels were 531.7 eV. The Ni(15)/MAl sample shows a minor peak occurring at 867.6 eV, due to the presence of a small amount of very strongly bound spinel Ni (NiAl₂O₄). This is consistent with the TPR results; where the shoulder occurring above 800°C indicates the inclusion of this species.
The near surface elemental composition of the Ni/MAI and Ni(10)/γ-Al2O3 WI materials were determined by quantitative XPS analysis and are given in Table 3.3. It is interesting to note that the surface / sub-surface concentration of Ni^{2+} in the samples remained almost constant as the Ni loading was increased; where an increase in loading would be assumed to result in a higher observed surface concentration of Ni/Ni^{2+}. A higher concentration of surface Ni atoms can be observed in the Ni(10)/γ-Al2O3 WI material, consistent with the preparation method, and the high ratio of surface Ni/Al species was expected for a material loaded with the full 10% wt Ni loaded across the surface of the support. These results further indicate that the majority of Ni species within the Ni/MAI materials were located deep within the pore structure of the material, or throughout the bulk of the support (in a strongly bound spinel form).
Figure 3.8: Binding energy peaks for Ni range from XPS analysis; a) Ni(7)/MAI; b) Ni(10)/MAI; c) Ni(15)/MAI; and d) Ni(10)/γ-Al₂O₃ materials
Table 3.3: XPS near surface atomic percent values for Ni and Al, and Ni/Al ratios in Ni/MAI and Ni(10)/\(\gamma\)-Al\(_2\)O\(_3\) WI materials

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ni (atom %)</th>
<th>Ni/Al ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(7)/MAI</td>
<td>1.1</td>
<td>0.027</td>
</tr>
<tr>
<td>Ni(10)/MAI</td>
<td>1.2</td>
<td>0.030</td>
</tr>
<tr>
<td>Ni(15)/MAI</td>
<td>1.1</td>
<td>0.030</td>
</tr>
<tr>
<td>Ni(10)/Al(_2)O(_3)</td>
<td>3.4</td>
<td>0.140</td>
</tr>
</tbody>
</table>

3.3.2 Alumina Supported Nickel Catalysts Evaluation

The influence of a number of factors on the performance of the prepared Ni/MAI catalysts in the dry reforming of methane was investigated. The factors investigated included; preparation technique, Ni loading, temperature and GHSV. Catalyst activity was observed in terms of conversion of reactant gases (refer to Chapter 2.2.4.2) and ratio of products (refer to Chapter 2.2.4.3), and stability was monitored in terms of activity drop over time. Subsequent analysis of carbon formation on the surface of the catalyst material after the reaction was also conducted.
3.3.2.1 Effect of Ni Loading and Support Type

The methane and carbon dioxide conversion results obtained using Ni/MAI catalysts with different Ni loadings and the Ni/\(\gamma\)-Al\(_2\)O\(_3\) catalyst prepared using a wet impregnation / precipitation method are presented in Figure 3.9 and Figure 3.10 respectively. The catalyst prepared using the wet impregnation method (Ni(10)/\(\gamma\)-Al\(_2\)O\(_3\) WI) clearly achieved significantly higher initial methane and carbon dioxide conversions in the first 6 hours of testing. This was most likely due to the higher concentration of surface Ni species in this material compared to the MAI materials (based on the XPS results on pages 98-101 obtained for the respective catalysts).

The Ni(10)/\(\gamma\)-Al\(_2\)O\(_3\) catalyst however was clearly not as stable as the Ni/MAI catalysts under the conditions used, as the methane and carbon dioxide conversions obtained with this material decreased dramatically after only 240 minutes of testing; whereas there was only a very slight decrease in both methane and carbon dioxide conversion that occurred for Ni/MAI catalysts over the entire testing period of 520 minutes. The poor stability of the Ni(10)/\(\gamma\)-Al\(_2\)O\(_3\) WI catalyst compared to the Ni/MAI catalysts was most likely due to sintering of the supported Ni; where a weaker active metal-support interaction was noted (in the TPR analysis on pages 96-98). This limited time of increased activity may also be due to rapid inactive carbon deposition; where this would block the active metal sites over a short period of time.

Of the Ni/MAI catalysts with different Ni loadings the Ni(10)/MAI performed slightly better than the other Ni/MAI catalysts. This was most likely due to this material having a
higher active metal surface concentration as compared to the other two Ni/MAI catalysts (based on the XPS analysis on pages 98-101).
Figure 3.9: CH₄ conversion % over Ni/MAI and Ni(10)/γ-Al₂O₃ materials at 700 °C, 5.2 x 10⁴ mL.h⁻¹.g⁻¹ GHSV gas flow, for 500 mins reaction period.

Figure 3.10: CO₂ conversion % over Ni/MAI and Ni(10)/γ-Al₂O₃ materials at 700 °C, 5.2 x 10⁴ mL.h⁻¹.g⁻¹ GHSV gas flow, for 500 mins reaction period.
Figure 3.11 shows the average H$_2$:CO product ratios recorded during the activity analysis of the Ni/MAI and Ni/$\gamma$-Al$_2$O$_3$ WI catalysts in the section above. It can be seen that the Ni/MAI catalysts outperformed the catalyst prepared by wet impregnation (Ni(10)/$\gamma$-Al$_2$O$_3$) in terms of significantly increased product ratios. Specifically out of the Ni/MAI materials the catalyst loaded with 10 %w/w Ni (Ni(10)/MAI) showed a further increased H$_2$:CO ratio of 0.78 over the Ni(7)/MAI (0.75) and the Ni(15)/MAI (0.72) materials.

![Figure 3.11: Average H$_2$:CO product ratio over Ni/MAI and Ni(10)/$\gamma$-Al$_2$O$_3$ materials over 500 min reaction period](image)

### 3.3.2.2 Effect of Temperature and Gas Hourly Space Velocity

The effect of reaction temperature was investigated using the best performed Ni/MAI catalyst from the initial screening tests (Ni(10)/MAI). The results from these tests (which were conducted using the same sample for each condition studied through gradually increasing the reaction temperature) and the conditions that were used are given in Figure 3.12. As expected, the methane and carbon dioxide conversions across this catalyst...
increased with increasing reaction temperature. The stability of the catalyst also increased
with increasing reaction temperature, as seen by the maintained short term activity; most
likely due to lower inactive carbon formation, owing to the increased rate of the
Boudouard reaction (reaction 1.8).

The effect of reaction temperature on the ratio of H$_2$:CO produced during temperature
investigation is given in Figure 3.13. There was a significant increase in the product ratio
with increasing temperature from 700 to 900 °C as expected. The lower H$_2$ production
observed at the lower reaction temperatures (500 – 700 °C) indicates that the ‘reverse
water gas shift reaction’ (reaction 1.2) may also have occurred simultaneously at a
significant rate with the CO$_2$ reforming reaction under these conditions.
The effect of gas hourly space velocity (GHSV) of reactant gas flow was investigated using a fresh Ni(10)/MAI catalyst (at a constant temperature of 700 °C), and these results are presented in Figure 3.14. As expected with lower GHSV, a higher conversion of both methane and carbon dioxide was observed due to an increase in residence time of the reactant gases across the active phase of the material. The product ratios of H₂:CO obtained across the above mentioned analysis is shown in Figure 3.15. It can be seen that the product ratio remained fairly similar across all GHSV values, indicating that the ratio is affected more by reaction temperature; and hence the influence of the ‘reverse water gas shift reaction’ (reaction 1.2) rather than GHSV.
Figure 3.14: Effect of GHSV on CH₄ and CO₂ conversion over Ni(10)/MAI catalyst at 700 °C at GHSV of: a) 80000 mL·h⁻¹·g⁻¹; b) 75000 mL·h⁻¹·g⁻¹; c) 50000 mL·h⁻¹·g⁻¹; d) 25000 mL·h⁻¹·g⁻¹; and e) 13000 mL·h⁻¹·g⁻¹.

Figure 3.15: H₂:CO product ratio over Ni(10)/MAI catalyst at 700 °C at various GHSV values.
3.3.2.3 Long term stability and carbon formation over Ni/MAI catalyst

The time-on-stream activity and product ratio obtained with the Ni(10)/MAI catalysts was investigated over 200 h at 800 °C using a GHSV of 52000 mL h⁻¹g⁻¹. Figure 3.16 shows the methane and carbon dioxide conversions over time-on-stream activity. From the data presented it can be seen that this catalyst had excellent stability, and achieved very good average methane and carbon dioxide conversions of about 80% and 89% respectively. An activity drop of about 2-3% was observed for both methane and carbon dioxide conversion only within the first few hours, which was most likely due to some instability in the carbon deposition / utilisation cycle during this period¹⁹. The selectivity of both H₂ and CO were also very stable over the whole 200 h reaction period, with a high H₂:CO product ratio close to 0.9 being maintained throughout the analysis.
Figure 3.16: Time on stream conversion analysis of CH₄ and CO₂ over Ni(10)/MAI catalyst at 52000 mL.h⁻¹g⁻¹ GHSV and 800 °C

3.3.3 Characterisation of Spent Catalysts

The spent catalysts from the dry reforming comparison tests (conducted at 700°C) were characterized by powder XRD, TEM, XPS and TGA. The powder XRD patterns of the spent Ni/MAI catalysts are presented in Figure 3.17. The diffraction peaks for metallic Ni were present at 2θ values of approximately 44.5°, 51.8° and 76.4° being due to the [111], [200] and [220] crystal planes. The XRD pattern for the spent Ni(15)/MAI catalyst showed a broad peak at ~26.2°, corresponding to the graphitic [002] lattice plane of carbon.
nanotubes. The build up of these less active carbon types such as graphitic carbon (C\textsubscript{\textgamma}) can be contributed to the existence of the larger Ni particles, where active metal sites are too large to produce highly active amorphous carbon (C\textsubscript{\textalpha}), yet still sufficiently small to limit deactivation due to complete blockage by bulk carbon\textsuperscript{20}. The peaks for γ-Al\textsubscript{2}O\textsubscript{3} became prominent after reaction in the materials indicating the formation of crystalline γ-Al\textsubscript{2}O\textsubscript{3} over the time frame the test was conducted (15 hours).

![Figure 3.17: XRD of spent Ni/MAI materials](image)

Figure 3.17 shows a representative TEM image of the Ni(10)/MAI catalyst after 200 h testing. This image provides clear evidence of the formation of carbon nano-tubes (CNTs) with graphitic morphology during the reaction. The CNTs have an outer diameter distribution between 30–40 nm.
The amount of carbon deposited on the spent catalysts was investigated using TGA and for the Ni(10)/MAI catalyst is presented in Figure 3.19. From this plot there are two main observable losses of weight occurring at 90 – 300 °C and 470 – 800 °C respectively. It can be assumed that the first loss of weight occurring at the lower temperature is that of adsorbed species of H₂O from the atmosphere, oxygen species from re-oxidised surface metal particles, and any amorphous carbon (Cₐ) that remained on the surface of the material after the conclusion of activity testing²². The weight drop which occurred at higher temperature (above 400 °C) can be observed due to more stable carbon species (C₇), which burn off at the elevated temperature under the reducing environment used to analyse the spent material. The derivative curve indicates this weight drop occurs at maximum rate around 520 °C.
The rate of carbon deposition on the spent catalysts was determined from the total weight of inactive carbon species detected by TGA (which occurred from 450 – 800 °C) compared to the time-on-stream, per gram of catalyst and is listed in Table 3.4. It can clearly be seen that the inactive carbon deposition occurred at a far greater rate on the Ni(10)/γ-Al₂O₃ WI catalyst compared to the Ni/MAI materials, further evidence that this had a negative effect on CH₄ and CO₂ conversion over time. Of the Ni/MAI catalysts, the Ni(10)/MAI far outperformed the Ni(15)/MAI and slightly outperformed the Ni(7)/MAI in terms of total carbon deposition over time. The lower rate of carbon deposition on the Ni(10)/MAI material which was on stream for 200 h would be due to the fact that the reaction was performed at a higher temperature, and therefore at a higher efficiency for a longer period than the Ni(10)/MAI catalyst with only 15 h reaction time. The above results show that this material far outperformed the wet impregnated material in terms of stability.
Table 3.4: Carbon formation rate over Ni/MAI and Ni(10)/γ-Al₂O₃ WI materials as determined by TGA analysis

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction Time (Hrs)</th>
<th>Rate of C Formation (g_{carbon}/g_{cat}/Hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(7)/MAI</td>
<td>15</td>
<td>1.1 x 10⁻³</td>
</tr>
<tr>
<td>Ni(10)/MAI</td>
<td>15</td>
<td>6.8 x 10⁻⁴</td>
</tr>
<tr>
<td>Ni(10)/MAI</td>
<td>200</td>
<td>3.6 x 10⁻⁴</td>
</tr>
<tr>
<td>Ni(15)/MAI</td>
<td>15</td>
<td>6.8 x 10⁻³</td>
</tr>
<tr>
<td>Ni(10)/Al₂O₃</td>
<td>15</td>
<td>3.1 x 10⁻²</td>
</tr>
</tbody>
</table>
3.4 References

(1) Fischer, F.; Tropsch, H. Brennstoff Chemie 1928, 3, 39.
Chapter 4

Investigations on Nickel Supported on Amorphous Silica

This chapter includes the characterisation of a prepared amorphous silica sol-gel support loaded with various amounts of nickel. The catalytic ability of the material is explored through both conversion of reactants and ratio of products within the dry reforming reaction, and a direct comparison made to a related material prepared by a conventional wet impregnation method. Post run analysis of the spent material is explored through several characterisation techniques and the high stability of the material is analysed in terms of carbon deposition rate during time-on-stream analysis.
4.1 Introduction

There are two main classes of supports utilised as carriers for active metal particles and subsequently used as catalyst supports in the dry reforming of methane: basic and acidic support materials. Each of these support types have been shown previously to have distinct influences when catalysing the above reaction with regards to:

- conversion
- stability
- and carbon deposition\(^1\).

Catalyst supports which have a basic nature, such as Al\(_2\)O\(_3\) have been proposed to lead to increased reaction rates when paired with highly active metals due to the difference in reaction site of both CH\(_4\) and CO\(_2\)\(^2\). CH\(_4\) has been shown to bind to the active metal particles before it is dissociated across the above mentioned materials, whilst the slightly acidic CO\(_2\) molecules preferentially bind to basic support sites (in close proximity to the active particles) prior to becoming activated. From here these intermediates are able to migrate and react to produce the high energy products desired of the reaction.

However a Langmuir-Hinshelwood mechanism has been shown to occur when utilising more acidic supports; where both CH\(_4\) dissociation and CO\(_2\) activation occur on active metal particle sites\(^3\). In this case, the dissociative adsorption of CO\(_2\) eventually becomes limited by the ability of these reactant molecules to adsorb to the active particle site; where this may become restricted by the build up of non-reactive carbon species, leading to a continuous loss of activity of the catalyst over time. For this reason, it has been shown that Ni based catalysts supported on acidic silica carrier materials show a much lower stability over time and hence lower overall activity in the dry reforming reaction compared to those supported on Al\(_2\)O\(_3\), La\(_2\)O\(_3\), TiO\(_2\) and various other
carriers of greater alkalinity\textsuperscript{4}. Schuurman et al. showed that Ni deposited on Al\textsubscript{2}O\textsubscript{3} supports were far more active in the dry reforming reaction due to a lower acidity\textsuperscript{5}. Gronchi et al. found that Ni deposited on SiO\textsubscript{2} was far outperformed in the dry reforming reaction by Ni deposited on La\textsubscript{2}O\textsubscript{3}\textsuperscript{6}.

Silica support materials are still however of interest for the catalysis of the dry reforming reaction due to the unique morphologies that can be utilised, leading to increased surface areas and a higher subsequent dispersion of the active phase\textsuperscript{7,8}. However it is also known that a support with a high surface area will most likely consist of a network of small pores, and therefore will suffer from poor intra-pellet diffusion of reactants and products\textsuperscript{9}, which can dramatically reduce the initial activity of the material. Tao et al. found that the ability of Pt supported catalysts were limited when deposited on commercial ‘Q-3’ SiO\textsubscript{2}, where only micropores of less than 3 nm were present throughout the support\textsuperscript{9}.

In an attempt to resolve the intra pellet diffusion limitation within SiO\textsubscript{2} supported catalysts, amorphous silicas have recently been explored, which contain a variety of pore sizes and a large internal surface. Ferriera et al. found that amorphous SiO\textsubscript{2} supports included both micropores and mesopores, which markedly improved metal dispersion through increased surface area\textsuperscript{10}. However a low metal-support interaction between the active phase and the SiO\textsubscript{2} material led to increased particle size, which deactivated the catalysts over time. Sol-gel materials are known to contain an increased surface area over conventionally prepared materials and a variety of pore sizes when specific precursors are utilised\textsuperscript{11}. In fact many authors report the sol-gel preparation method as the most efficient way of preparing suitable catalyst materials; which when utilised correctly results in an increased dispersion of active metals on finely tuned support structures\textsuperscript{12-15}. The sol-gel method has been used to produce silica based materials since as early as 1846,
and was extensively researched in the twentieth century for the production of various glasses by the polymerisation of molecular precursors from a solution\textsuperscript{16}. This preparation method is today a materials processing technique utilised in producing glass, ceramics, and catalysts with unique, highly controllable physical properties. In general, the sol-gel process involves the transition of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the suspension into a continuous liquid network (gel) phase. The resulting particle size and morphology of a sol-gel material can be precisely controlled when prepared using specific precursors to produce particles with mesopores and / or micropores which are extremely fine; therefore having an increased surface area and greater intra-pellet diffusion characteristics over materials prepared by common methods\textsuperscript{11}. The precursors for sol-gel materials are usually inorganic metals or metal compounds consisting of metal centres surrounded by selected ligands. The most common precursors are molecules that already have metal-oxygen bonds, namely metal alkoxides M(OR)\textsubscript{n} or oxoalkoxides MO(OR)\textsubscript{n}\textsuperscript{17}.

The reaction chemistry for the preparation of sol-gel materials can be described in terms of three basic reaction pathways; consisting of a hydrolysis and subsequent water or alcohol condensation stages as seen in reactions (4.1), (4.2) and (4.3) respectively:

\begin{align*}
\text{-M-OR} + \text{H}_2\text{O} & \rightleftharpoons \text{-M-OH} + \text{ROH} \\
\text{-M-OH} + \text{-M-OH} & \rightleftharpoons \text{-M-O-M-} + \text{H}_2\text{O} \\
\text{-M-OH} + \text{-M-OR} & \rightleftharpoons \text{-M-O-M-} + \text{ROH}
\end{align*}

(4.1) (4.2) (4.3)

The hydrolysis reaction (4.1) involves the simple replacement of alkoxide functional groups with hydroxide groups. Subsequent condensation reactions involving metal bound hydroxide groups act to produce metal oxide networks, with water (4.2) or alcohol (4.3)
produced as by-products. The properties of a prepared sol-gel material are not just dependent on precursors chosen as reactants, but also a number of factors that may affect both the hydrolysis and condensation reaction steps; particularly reaction pH, temperature and \( \text{H}_2\text{O/M ratio}^{17} \). After preparation the materials must be dried under suitable conditions in order to remove the liquid from the pores in the interconnected solid gel network; typically those of hypercritical conditions, ensuring that the network does not collapse but a low density aerogel is produced. The reaction is known to be catalysed at low pH values, for example by using strong acids such as HCl or HNO₃.

Under low pH, the general reaction pathway for the fabrication of silica sol-gel is shown in (4.4):

\[
\begin{align*}
\text{RO} & \quad \text{Si} \quad \text{OR} \\
\text{OR} & \quad \leftrightarrow \quad \text{RO} \quad \text{Si} \quad \text{OR} \\
\text{OR} & \quad \leftrightarrow \quad \text{RO} \quad \text{Si} \quad \text{OR} \quad \text{H}_2\text{O} \\
\text{OR} & \quad \leftrightarrow \quad \text{RO} \quad \text{Si} \quad \text{OR} \quad \text{H} \quad \text{OR} \quad \text{H}_2\text{O} \\
\text{OR} & \quad \leftrightarrow \quad \text{RO} \quad \text{Si} \quad \text{OR} \quad \text{OR} \quad \text{OR} \quad \text{OR} \quad \text{OR} \quad \text{OR} \quad \text{OR} \\
\text{OR} & \quad \leftrightarrow \quad \text{RO} \quad \text{Si} \quad \text{OR} \quad \text{OR} \quad \text{OR} \quad \text{OR} \quad \text{OR} \quad \text{OR} \\
\end{align*}
\]

(4.4)

Under acidic conditions it can be assumed that an alkoxide group is protonated in a rapid reaction step, withdrawing the electron density from a neighbouring metal atom, before it can be attacked by an incoming water molecule\(^{18} \). This results in the formation of a transition state with a penta-coordinate geometry, which decays by displacement of alcohol. Using an acid based sol-gel fabrication method uniformed mixed oxides can be formed, yielding primarily linearly branched polymers which subsequently entangle and form additional branches, resulting in gelation; thus the term sol-gel arises\(^{16} \). The versatility of the sol-gel preparation technique; due to the large number of organometallic precursors available and the low processing temperatures...
required of the process, gives rise to a large range of possible materials; each consisting of pure, homogenous nanoparticles with a limited size distribution and highly controllable physical properties\textsuperscript{19,20}.

Takahashi et al. studied SiO\textsubscript{2} sol-gel supported catalysts for the dry reforming reaction, and found that these materials possessed an increased surface area and highly distributed active phase. However they found that these materials showed a low thermal stability due to the small pore size inherent of the preparation procedure\textsuperscript{21}. Later the above supports were improved by the addition of urea during the preparation stages of the material by Tomiyama et al.\textsuperscript{22}. However increased Ni concentrations (up to 50 % wt) were required to produce a high conversion rate in the dry reforming reaction. Thermal decomposition of the added urea (once the wet gel product has been formed) was effective for the enlargement of the pore size of the silica gel, where the pH of the solution was increased by the generation of ammonia as the urea decayed. Tang et al. similarly found that the addition of citric acid during the preparation stages of SiO\textsubscript{2} sol-gel resulted in the formation of larger pores throughout the bulk of the material\textsuperscript{23}. They found that when added in sufficient amounts, the citric acid would change the pore structure of a Pt/SiO\textsubscript{2} material from microporous to mesoporous, which showed an increased intra-pellet diffusion when used in gas flow reactions, and hence a higher catalytic ability when used as a support.

Therefore sol-gel prepared materials are excellent candidates for suitable acidic SiO\textsubscript{2} supports for a dry reforming catalyst material; which when prepared to have an increased pore diameter should show a high initial activity and long term stability in the reaction even at increased active metal loading. In this chapter a sol-gel material containing both micropores and mesopores was prepared using a highly controlled combination of precursors. Ni was deposited throughout the carrier in various concentrations in-situ to formation of the sol-gel. The resulting novel materials
were characterised in depth and studied for catalytic ability in the dry reforming reaction, and the results are presented and discussed in comparison to a material prepared by wet-impregnation method.

4.2 Experimental

4.2.1 Materials

Refer to section 2.1.1 for a list of materials used in catalyst preparation

4.2.2 Catalyst Preparation

4.2.2.2 Nickel Silica Sol-Gel

Several Ni supported SiO₂ catalysts were prepared by homogeneous precipitation of nickel hydroxide in a sol-gel-derived wet silica gel. The preparation process consisted of two successive steps: gelation of silica in the presence of nickel nitrate and urea, followed by aging at higher temperature to decompose the urea. In a typical synthesis of Ni(10)/SiO₂ SG, 9.35g of tetraethyl orthosilicate (TEOS) was added dropwise to a mixture of 2g urea and 1.49g Ni(NO₃)₂·6H₂O both dissolved in 10g of 0.1M HNO₃ and 2.88g of citric acid under constant stirring. The resulting solution was transferred to a sealed polypropylene bottle and heated to 80°C for 5 days in order to both decompose the urea and increase the pH of the gel solution. The temperature of the PP bottle was then reduced to 50°C and the bottle left uncapped for 1 week. The obtained solid sample was ground to a fine powder
and calcined at 540°C for 2 h under static air. For synthesis of Ni(20)/SiO2 SG and Ni(30)/SiO2 SG the same procedure was followed using a predetermined amount of nickel nitrate.

4.2.2.2 Wet Impregnated Silica

For direct comparison to a material prepared by more conventional methods, a commercial SiO2 was wet impregnated with Ni as follows: 9.9 g of Ni(NO3)2·6H2O was dissolved in excess ethanolic solution under constant stirring for 1 h before 2.0 g of commercial SiO2 was added to the solution and allowed to stir overnight. The solution was boiled down to a slurry and then transferred to a polypropylene bottle and dried in an oven at 90 °C for 12 h. This resulted in material with 10% w/w Ni deposited on SiO2 labelled as Ni(10)/SiO2 WI.

4.2.3 Pre-Treatment of Ni/SiO2 SG Materials

After preparation, all prepared materials were calcined to remove any residing water molecules, break down the metal salts into their respective oxides, and remove any template. For the catalysts consisting of silica sol-gel support, the dried catalyst powders were placed in a ceramic boat and loaded into a quartz tube before being placed in the heating zone of a hinged tube furnace (Lindberg Blue; maximum temperature 1100°C). The material was heated up at a rate of 10°C per minute from room temperature to 110°C, before being held for 2 h to ensure all water evacuated the material. The catalysts were then heated at a slower rate of 2°C per minute to ensure minimal thermal shock to the material, to a temperature of 540°C and subsequently held for a further 2 h at this temperature as represented in Figure 4.1:
The material prepared by wet impregnation method was also calcined under identical conditions to those listed above.

Following calcinations the catalysts were pelletised as outlined in Chapter 2.2.1

Immediately prior to activity analysis, 0.105g of pelletised catalyst material was loaded into the reactor tube before being reduced in-situ before testing.

In a typical reduction of the catalyst preceding testing, the pelletised catalysts were raised to a temperature of 700°C under a diluted hydrogen environment (5% H₂ purity 5, 95% He purity 5) at a flow of 50scm for 2 h.
4.2.4 Catalyst Testing

The catalysts were analysed under standard catalyst testing conditions as listed in Chapter 2.2.2.

4.2.5 Characterisation / Analytical Methods

The freshly prepared materials were analysed by XRD and TPR prior to reduction; XRD, BET surface area analysis, TEM, and XPS methods after reduction; and XRD, TEM and TGA methods after activity analysis. These techniques are outlined in Chapter 2.2.3.

4.3 Results and Discussion

4.3.1 Characterisation of Ni/SiO₂ materials

The wide angle X-ray diffraction patterns of the prepared silica sol-gel catalysts prior to and after being reduced (at 700 °C under flowing H₂) and the Ni(10)SiO₂ material prepared via wet impregnation are presented in Figure 4.2. The presence of a broad band in all samples around 2θ = 22° indicates the presence of an amorphous phase, which not only existed somewhat in the sample prior to reduction, but clearly became more predominant in the samples after being reduced. Clearly the silica does not form a crystalline phase during reduction; but instead forms an irregular, somewhat unstructured type carrier. NiO peaks are observed in the calcined sample (prior to reduction), and occur with increasing
area subsequently in the reduced Ni(10)/SiO₂ SG, Ni(20)/SiO₂ SG and Ni(30)/SiO₂ SG materials at 43.3°, 37.2° and 62.8° 2θ. Interestingly only very minor NiO peaks are observed in the wet impregnated sample, indicating that the Ni species across the sample stay reduced, even under the oxygen rich environment immediate to the XRD sample holder. This indicates a slightly stronger interaction between the Ni particles and the support than simply weakly bound outer surface NiO species (which are easily re-oxidised) expected when prepared with the wet impregnation technique. Following reduction the XRD patterns for the silica sol-gel catalysts and the wet impregnated material (Ni(10)/SiO₂ WI) showed signs of crystalline Ni, with peaks occurring at 44.5°, 51.8° and a minor peak at 76.4° 2θ which are due to the [111], [200] and [220] planes of metallic Ni. The Ni peaks grow in area across the catalyst materials with an increase in loaded Ni as expected, and are roughly equivalent in the Ni(10)/SiO₂ SG and Ni(10)/SiO₂ WI materials. The ratio of the [111] peak of the crystalline Ni compared to the other crystal planes is more predominant in the Ni(10)/SiO₂ SG sample indicating that this loading of Ni paired with the unique preparation procedure results in a preference towards the formation of Ni crystals with [111] lattice planes. Ni silicate peaks representing strongly bound Ni₂SiO₄ are present in the sol-gel materials loaded with a high concentration of Ni (Ni(20)/SiO₂ SG and Ni(30)/SiO₂ SG), where the increased loading of Ni clearly results in the formation of these species.

Therefore there are three distinct Ni morphologies observable within the above samples:

- NiO species (most likely on the outer surface of the support) in the case of all Ni/SiO₂ SG materials both before and after reduction,
- Crystalline Ni species in the case of all reduced samples, and
Ni silicates in the materials loaded with a higher concentration of Ni (Ni(20)/SiO₂ SG and Ni(30)/SiO₂ SG).
Figure 4.2: XRD of Ni/SiO$_2$ SG and Ni/SiO$_2$ WI materials
The $\text{Ni}^0$ particle diameter in the reduced samples was calculated based on the peak broadening for the Ni [111] XRD diffraction line at 44.3° – 44.7°. The Ni particle sizes are presented in Table 4.1. It can be observed that the Ni particle size was significantly reduced in the sol-gel materials (Ni/SiO$_2$ SG) compared to the material prepared by wet impregnation / precipitation (Ni/SiO$_2$ WI). It can also be seen that the mean diameter of the reduced Ni$^0$ particles increased with increasing nickel loading in the Ni/SiO$_2$ SG materials.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ni Particle Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(10)/SiO$_2$ SG</td>
<td>8.9</td>
</tr>
<tr>
<td>Ni(20)/SiO$_2$ SG</td>
<td>9.1</td>
</tr>
<tr>
<td>Ni(30)/SiO$_2$ SG</td>
<td>13.7</td>
</tr>
<tr>
<td>Ni(10)/SiO$_2$ WI</td>
<td>20.4</td>
</tr>
</tbody>
</table>

Figures 4.3 and 4.4 show the nitrogen adsorption / desorption isotherms and pore size distribution of the reduced Ni/SiO$_2$ SG catalysts. The samples show typical type IV hybrid adsorption curves (Figure 4.3) characteristic of silica sol-gel materials containing both mesopores and micropores$^{24}$. The adsorption / desorption isotherms show a relatively large increase in the relative pressure ($P/P_0$) from 0.5 to 0.9 due to the capillary condensation of
nitrogen within the mesopores. The less steep inflection step compared to the previously reported materials (refer to section 3.3.1) reflects the deviation from uniform pore size, and indicates there is a larger range of pore types that exist throughout the bulk of the Ni/SiO₂ SG samples. The isotherms for the samples differ somewhat in shape, where the inflection step is less steep for samples loaded with a higher concentration of Ni, which indicates that the Ni loading had a significant role in changing the pore distribution within the material. The samples loaded with higher amounts of Ni (Ni(20)/SiO₂ and Ni(30)/SiO₂) also show a 2-stage hysteresis loop indicating the inclusion of closed or blocked pores which is expected given the high metal loading.

From the pore distribution plot (Figure 4.4) it can be seen that the sample containing 10 % w/w Ni (Ni(10)/SiO₂ SG) showed a large range of pores, mostly in the mesopore region (2-50 nm), with a small number of micropores. The samples containing a greater concentration of Ni (Ni(20)/SiO₂ SG and Ni(30)/SiO₂ SG) show an increased amount of mesopores with a small diameter (2-25 nm), however show no mesopores with greater diameter, again most likely due to a blockage of pores by the increased metal loading.
Figure 4.3: BET isotherms of Ni/SiO₂ SG materials

Figure 4.4: Pore size distribution of Ni/SiO₂ SG materials
The specific surface area, pore diameter, and pore volume of the sol-gel catalysts with increasing Ni loading are reported in Table 4.2. From the data presented it can be seen that the Ni/SiO₂ SG materials showed an increase in surface area, pore diameter and pore volume over the material prepared by wet-impregnation (Ni(10)/SiO₂ WI). A decline in average pore diameter and pore volume occurred within the Ni/SiO₂ SG materials with increasing Ni loading from 10 wt% to 30 wt%. This was likely due to increased metal loading occurring directly within the pore structure as a result of the increasing Ni, thus restricting both the average pore diameter and consequently the overall pore volume within the support structure of the material. The observed difference for BET surface area with respect to increased Ni loading; where the catalyst containing an intermediate amount of Ni showed a higher surface area than the catalyst containing a lower amount of Ni is interesting given the reduced pore diameter and volume within this material.

Table 4.2: BET surface area, average pore diameter and total pore volume of Ni/SiO₂ SG and Ni/SiO₂ WI materials

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET Surface Area (m²/g)</th>
<th>Avg Pore Diameter (nm)</th>
<th>Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(10)/SiO₂ SG</td>
<td>256</td>
<td>17.4</td>
<td>1.11</td>
</tr>
<tr>
<td>Ni(20)/SiO₂ SG</td>
<td>274</td>
<td>9.5</td>
<td>0.65</td>
</tr>
<tr>
<td>Ni(30)/SiO₂ SG</td>
<td>264</td>
<td>8.1</td>
<td>0.64</td>
</tr>
<tr>
<td>Ni(10)/SiO₂ W.I.</td>
<td>238</td>
<td>7.2</td>
<td>0.35</td>
</tr>
</tbody>
</table>
TEM images of the calcined and reduced Ni/SiO₂ SG samples are shown in Figure 4.5. From these images the non-regular structure of the SiO₂ material can be clearly noted, showing their amorphous and highly porous nature. As expected no Ni particles were observable prior to reduction; consistent with the XRD analysis of the samples, which indicates only a NiO phase existed prior to this preparation stage of the material (Figure 4.5a); most likely as very small and well dispersed particles throughout the bulk and across the surface of the support due to the in-situ deposition as a result of the preparation method used. After reduction, the Ni particles can be observed distributed throughout the support structure (Figure 4.5b). The aggregation effect of the surface Ni can be seen to have been greater across the catalysts with an increased loading of Ni; where these active clusters appear larger in the higher loaded materials (Figure 4.5c). This is in concurrence with the Ni particle size analysis, which highlights the increasing average Ni particle size trend with increasing Ni loading (across the Ni/SiO₂ SG materials).
TPR profiles of the SiO$_2$ samples prior to reduction pre-treatment are presented in Figure 4.6. It can be seen that there are two main temperature ranges of reduction common to the samples, occurring around 300-370°C and 600-700°C. The peak occurring at the lower temperature indicates the reduction of NiO species (see Appendix B), where this peak is smaller in the sol-gel materials compared to the material prepared by wet impregnation.
deposition (Ni(10)/SiO2 WI). The large area of this peak in the wet impregnated sample is expected, where the majority of NiO particles would be expected to reside on the surface of the support, with only a minor Ni-support interaction. However the slightly increased T_{max} of this peak to 370°C in this material is unexpected, but shows a slight increase in metal-support interaction within the weakly bound surface species of Ni (as in agreement with the lack of NiO peaks in the XRD analysis). The broadness of the peak at ~300°C (especially in the Ni(30)/SiO2 SG material) indicates that the surface phase of NiO occurs in a range of states, where they are bound / interact with the support at varying strengths. The peak occurring in all samples at a higher temperature (600-700°C) indicates Ni^{2+} species having a strong metal-support interaction, such as those located within the pore channels, or those species that were deposited directly within the framework of the support material; being in a chemically bound nature to the SiO_{2} groups (silicates). The dominant area of the latter peak in the sol-gel samples compared to the peak at lower temperatures is indicative that the majority of the Ni occurs in this higher bound arrangement within the Ni/SiO_{2} SG materials. The minor difference in T_{max} values observable at high temperatures in the Ni/SiO_{2} SG materials is indicative that there was a slightly increased interaction between the majority of Ni species within the samples with higher loading compared to the Ni(10)/SiO_{2} SG material, where the T_{max} of the peaks in the Ni(10)/SiO_{2} SG, Ni(20)/SiO_{2} SG and Ni(30)/SiO_{2} SG increased from 670 °C to 680 °C to 700 °C respectively.
XPS analysis of the reduced catalysts were conducted and the results obtained are presented in terms of Ni profiles in Figure 4.7, and surface atom percentages of Ni and Ni/Si ratios in Table 4.3.

Figure 4.7 shows the characteristic Ni XPS profiles for the Ni/SiO₂ SG and Ni(10)/SiO₂ W.I. materials across the binding energy range of 844 - 870 eV. The broad peaks occurring at 862.4-863.5 eV were recognised as the shakeup satellite peaks. Ni 2p₃/₂ peaks were present in all samples at binding energies of 856.1 – 857.4 eV. There is a third peak observable in the sol-gel materials with greater loading of Ni (Ni(20)/SiO₂ SG and Ni(30)/SiO₂ SG), occurring at 853.6 and 854.0 eV respectively, which can be attributed to the presence of Ni silicates (Ni₂SiO₄) in these materials (in agreement with XRD analysis).
There is a shift to higher binding energies (of around 0.4 eV) for the main Ni peaks in the Ni(10)/SiO$_2$ SG material compared to the Ni(10)/SiO$_2$ WI material due to the increased average interaction between the active metal and the support$^{25}$. A similar shift can also be noted from the Ni(10)/SiO$_2$ SG to the sol-gel materials with greater Ni loading, where the Ni$^{2+}$ states have a higher binding energy by a further 0.5 eV in the Ni(20)/SiO$_2$ SG and Ni(30)/SiO$_2$ SG materials; likely due to the effect of the above mentioned Ni silicates on the decreased reducibility of the material.

Table 4.3 shows the near surface atomic percentage of Ni and presents the Ni/Si ratios of the Ni/SiO$_2$ SG and Ni/SiO$_2$ WI materials. There is a general increase in surface Ni concentration in the Ni/SiO$_2$ SG samples compared to the material prepared by wet-impregnation (Ni(10)/SiO$_2$ WI). This is in agreement with the XRD and TPR results which show greater NiO peaks (from weakly bound surface Ni) in the Ni/SiO$_2$ SG materials compared to the Ni(10)/SiO$_2$ WI material. Again the Ni species within the wet-impregnated sample most likely reside within the pore structure of the commercial material and hence when not near the immediate surface of the support are not observable by XPS. As expected the percentage of Ni increased with increasing initial loading in the sol-gel materials, and the Ni/Si ratio also increased.
Figure 4.7: Binding energy peaks for Ni range from XPS analysis; a) Ni(10)/SiO$_2$ SG; b) Ni(20)/SiO$_2$ SG; c) Ni(30)/SiO$_2$ SG; and d) Ni(10)/SiO$_2$ WI materials
Table 4.3: XPS near surface atomic percent values for Ni and Si, and Ni/Si ratios in Ni/SiO<sub>2</sub> SG and Ni/SiO<sub>2</sub> WI materials

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ni (atom %)</th>
<th>Ni/Si ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(10)/SiO&lt;sub&gt;2&lt;/sub&gt; SG</td>
<td>0.5</td>
<td>0.01</td>
</tr>
<tr>
<td>Ni(20)/SiO&lt;sub&gt;2&lt;/sub&gt; SG</td>
<td>1.1</td>
<td>0.05</td>
</tr>
<tr>
<td>Ni(30)/SiO&lt;sub&gt;2&lt;/sub&gt; SG</td>
<td>1.6</td>
<td>0.07</td>
</tr>
<tr>
<td>Ni(10)/SiO&lt;sub&gt;2&lt;/sub&gt; WI</td>
<td>0.4</td>
<td>0.01</td>
</tr>
</tbody>
</table>

4.4 Silica Sol-Gel Supported Nickel Catalyst Evaluation

Typical catalyst screening (as described in Chapter 2.2.4) was used to analyse the performance of the set of prepared Ni/SiO<sub>2</sub> SG materials in the dry reforming reaction, and these results were compared to those of a conventionally prepared Ni(10)/SiO<sub>2</sub> WI material. The activity of the materials loaded with different Ni concentrations was monitored in terms of conversion of both CH<sub>4</sub> and CO<sub>2</sub> (see section 2.2.4.2) and product ratio of H<sub>2</sub>:CO (see section 2.2.4.3). The stability of these catalysts was observed with respect to any change in conversion over a significant reaction period. The spent catalysts were analysed for carbon deposition, where these used materials were explored through XRD, TEM and TGA analysis.

The methane and carbon dioxide conversion results obtained using Ni/SiO<sub>2</sub> SG catalysts with different Ni loadings and the Ni(10)/SiO<sub>2</sub> catalyst prepared using a wet impregnation
The catalyst prepared using the wet impregnation method (Ni(10)/SiO$_2$ WI) achieved a similar initial methane and carbon dioxide conversion in comparison to the similarly loaded Ni(10)/SiO$_2$ SG catalyst. Of the Ni/SiO$_2$ SG catalysts with different Ni loadings there was only a small difference in initial and overall CH$_4$ and CO$_2$ conversions, where the Ni(30)/SiO$_2$ SG performed slightly better that the Ni(20)/SiO$_2$ SG catalyst, which in-turn performed slightly better than the Ni(10)/SiO$_2$ SG material. This limited increase in activity with a 2 and 3 time increase in Ni loading was unexpected, where the benefit of using a catalyst loaded with a significantly higher concentration of Ni was expected to be far greater than the slight activity increase observed for the higher loaded materials. The trend cannot be related to surface area (which affects metal dispersion) in the case of these materials; as the Ni(20)/SiO$_2$ SG catalyst showed a superior surface area to the other sol-gel materials, yet did not perform as well as the Ni(30)/SiO$_2$ SG material. Therefore the difference in activity can only be attributed to the direct effect of increased Ni loading. The unexpected ceiling in activity across the catalysts with higher loading of Ni may have been due to an unforseen preparation induced intra-pellet diffusion limitation; where the excessive loading of the active metal within the pores of the support (as seen in the reduced BET pore volumes) may actually hinder the reactants from reaching a portion of the active metal sites loaded within the bulk of the carrier. Also the formation of Ni silicates within the catalysts (as observed in XRD analysis) loaded with an increased amount of Ni could decrease the availability of the particles as active metal sites. According to the high temperature peaks observable in the TPR, the Ni silicates and those Ni species with a higher support interaction may not be fully reduced at 700 °C when exposed for a short period of time. This is significant considering the catalysis of the dry reforming reaction was tested at a temperature of 700 °C.
It can be seen from the activity analysis curves that all Ni/SiO₂ SG catalysts remained fairly stable over the entire period testing was conducted (15 hours). There was only a very slight decrease in both methane and carbon dioxide conversion that occurred for all Ni/SiO₂ SG catalysts (0.9 – 5.3%) over the testing period. The Ni(10)/SiO₂ WI catalyst was clearly not as stable as the Ni/SiO₂ SG catalysts under the conditions used, even compared with the results of those materials with an increased metal loading (Ni(30)SiO₂ SG); as the CH₄ and CO₂ conversions obtained with the wet impregnated catalyst decreased significantly after only 80 minutes of testing (and subsequently blocked the reactor completely).

Although the difference in stability of the Ni(10)/SiO₂ SG was far enhanced compared to the Ni(10)/SiO₂ WI catalyst, there is some minor difference observable between the stability of the Ni(10)/SiO₂ SG material and those Ni/SiO₂ SG catalysts that were loaded with a higher concentration of Ni as seen in Table 4.4. The loss of activity across the Ni(10)/SiO₂ SG material was more than double (5.3%) compared to the Ni(20)/SiO₂ SG (0.9%) and Ni(30)/SiO₂ SG (2.2%) materials. The above results indicate that an increased dispersion of Ni (which can be directly linked to a higher support surface area) was the primary reason for a high stability in the materials; where the Ni(20)/SiO₂ SG could be seen to have a greater surface area than the Ni(30)/SiO₂ SG which had a greater surface area than the Ni(10)/SiO₂ SG catalyst (as observed in the BET results).
Figure 4.8: CH₄ conversion % over Ni/SiO₂ SG and Ni(10)/SiO₂ WI materials at 700 °C, 5.2 x 10⁴ mL.h⁻¹g⁻¹ GHSV gas flow, for 900 mins reaction period

Figure 4.9: CO₂ conversion % over Ni/SiO₂ SG and Ni(10)/SiO₂ WI materials at 700 °C, 5.2 x 10⁴ mL.h⁻¹g⁻¹ GHSV gas flow, for 900 mins reaction period
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Loss of Activity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(10)/SiO₂ SG</td>
<td>5.3</td>
</tr>
<tr>
<td>Ni(20)/SiO₂ SG</td>
<td>0.9</td>
</tr>
<tr>
<td>Ni(30)/SiO₂ SG</td>
<td>2.2</td>
</tr>
<tr>
<td>Ni(10)/SiO₂ W.I.</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 4.10 shows the H₂:CO product ratio observed over the catalyst tested during the 15 h reaction period. A significantly increased H₂:CO ratio was observed for the Ni/SiO₂ SG materials compared to that of the wet impregnated (Ni(10)/SiO₂ WI) sample. A minor increase in H₂:CO ratio can also be seen to have occurred with increasing Ni loading within the Ni/SiO₂ SG materials. This indicates the benefit of a higher loading of active particles and / or greater active particle-support interaction.
The spent catalysts generated from the tests discussed in the previous paragraphs were characterised by powder XRD, TEM imaging, and TGA. Figure 4.11 shows the XRD patterns of the spent Ni(10)/SiO2 SG, Ni(20)/SiO2 SG and Ni(30)/SiO2 SG catalysts. The diffraction peaks for metallic Ni were observed in all of the samples at 2θ values of 44.5°, 51.8° and 76.4° being due to the [111], [200] and [220] crystal planes of Ni subsequent to reaction. The characteristic Ni peaks showed a variance in ratio between the various lattice parameters across the samples with different Ni loading; where the Ni [111] plane was more dominant in the spent Ni(10)/SiO2 SG material, but less so in the materials with higher Ni loading. This is in agreement to the XRD analysis observations in the materials prior to catalysis testing (refer to pages 125-128)
The diffraction patterns of the Ni(20)/SiO2 SG and Ni(30)/SiO2 SG samples show evidence of NiO peaks remaining after the testing period, indicating that some species of Ni are easily re-oxidised (under oxygen rich conditions during the XRD analysis) due to weak particle-support interaction. Interestingly peaks pertaining to Ni2SiO4 became more apparent in the Ni(10)/SiO2 SG material subsequent to the reaction period. These peaks did not exist in the XRD analysis of the fresh material (see page 128), and therefore from the evidence presented it can be assumed that these species were formed under the harsh reaction conditions employed over time. This may be a further cause for the slight drop in activity noted of the Ni(10)/SiO2 SG (see page 139-142); where the formation of highly stable Ni2SiO4 subsequently reduced the number of Ni sites that would otherwise be active across the reaction.

All spent catalysts showed signs of carbon deposition with peaks occurring at 26.2° and a small shoulder at 42.12° 2θ due to the graphitic [002] and [100] lattice planes of carbon nanotubes. The above mentioned [002] peak was very intense in the spent Ni(10)/SiO2 SG material, but less so in the Ni(20)/SiO2 SG and less again in the Ni(30)/SiO2 SG catalysts. This is interesting based on the high activity of the Ni(10)/SiO2 SG material with respect to the comparatively low Ni loading, and the reduced Ni particle size in this material compared to those with greater Ni loading (as determined by extrapolation of XRD data). It has been previously assumed that the build up of graphitic carbon types are detrimental to a catalyst material, and these non-reactive species are a direct result of large Ni clusters on the surface of the support7. The evidence above indicates that it is not primarily the Ni particle size which results in the build up of graphitic carbon species on SiO2 sol-gel supports, but it is either due to the specific morphology of Ni within the catalyst; where a high proportion of Ni [111] crystal planes were seen to be present in this material, or due
to the majority of Ni species within this material showing a slightly weaker metal-support interaction; where a greater Ni-support interaction exists within the materials loaded with a higher amount of Ni (Ni(20)/SiO₂ SG and Ni(30)/SiO₂ SG) due to the initial presence of Ni silicates.

Figure 4.11: XRD of spent Ni/SiO₂ SG catalysts

Figure 4.12. shows representative TEM images of the spent Ni(10)/SiO₂ W.I and Ni(10)/SiO₂ SG catalysts. The spent Ni(10)/SiO₂ W.I. shows a high concentration of graphitic carbon nanotube fibres, all with a diameter of approximately 40 nm; where this inactive graphitic type carbon is known to be responsible for the deterioration of active sites on the spent catalyst over long reaction periods. The other factor commonly known to negatively affect activity of catalysts in the dry reforming reaction is the sintering of active particles. There indeed appears to be a large aggregation of surface Ni particles with high density which is most likely due to sintering at high temperatures of surface species of Ni (with low particle-support interaction). The inactive fibrous
carbon structures and sintering of Ni particles to larger clusters accounts for the poor stability over time observed for this material.

All sol-gel supported materials showed similar morphologies across TEM imaging, with a small quantity of wormlike carbon tubes of different morphologies and diameters growing from the surface of the support. The wormlike carbon has a very irregular diameter ranging from 5-50 nm (as seen in Figure 4.12 b), and seems to be loosely intertwined around various catalyst carrier particles. The irregular size and morphology of carbon across the above mentioned materials suggest less inactive species being deposited in the reaction period; where only small amounts of inactive filamentous carbon appear to be present, compared to the large concentration of carbon with various morphology; which are likely to be less detrimental to the reaction\textsuperscript{28}. Whilst the Ni particles appeared to be directly linked to the carbon structures in these spent catalysts, they did not appear to be separated from the SiO\textsubscript{2} SG support in the Ni/SiO\textsubscript{2} SG materials, whereas the wet impregnated (Ni(10)/SiO\textsubscript{2} WI) material shows some detachment of Ni particles from the support.
The amount of carbon deposited on the spent catalysts was investigated using TGA. The rate of carbon deposition on the spent catalysts was determined from the total weight of inactive carbon species detected by TGA compared to the time-on-stream, per gram of catalyst and is listed in Table 4.5. The carbon deposition rate across the Ni(10)/SiO₂ WI material was higher than that across all Ni/SiO₂ SG samples. The sol-gel supported catalysts with higher Ni loading (Ni(20)/SiO₂ SG and Ni(30)/SiO₂ SG) showed a lower overall carbon deposition rate than the Ni(10)/SiO₂ SG catalyst (in agreement with the XRD analysis). The fact that the Ni(30)/SiO₂ SG material showed less carbon formation over time than the Ni(20)/SiO₂ SG catalyst may be explained by the higher overall conversion of the material loaded with a greater amount of Ni.
Table 4.5: Rate of carbon formation over time across Ni/SiO$_2$ SG and Ni/SiO$_2$ WI catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Rate of C Formation ($g_{\text{carbon}}/g_{\text{cat}}/\text{Hr}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(10)/SiO$_2$ SG</td>
<td>$2.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>Ni(20)/SiO$_2$ SG</td>
<td>$7.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>Ni(30)/SiO$_2$ SG</td>
<td>$4.6 \times 10^{-3}$</td>
</tr>
<tr>
<td>Ni(10)/SiO$_2$ W.I.</td>
<td>$1.5 \times 10^{-1}$</td>
</tr>
</tbody>
</table>
4.5 References

Chapter 5

Studies on Ytterbium Doped Nickel Catalysts

This chapter begins with an outline and discussion of experimental results obtained from a similar study on the activity analysis of Ni/Al₂O₃ catalysts doped with a small concentration of single species from the full series of lanthanides. A detailed description of the experimental results attained when Yb was doped in various amounts in both Ni(10)/MAl and Ni(10)/SiO₂ SG materials is presented, and the results compared to the un-doped materials. A discussion regarding the effect of Yb doping is included after the characterisation of the materials. Dry reforming activity analysis of the set of doped catalysts is presented and the results are discussed in comparison to the undoped catalyst, before the carbon deposition occurring on the spent materials is explored.
5.1 Introduction

It has been well documented that the lanthanides (which are referred to as the rare earth elements when grouped with scandium and yttrium) are highly reactive, whilst also having the tendency to remain stable under increased temperatures\(^1\). Although the above properties have been widely exploited for catalytic behaviour in organic synthesis reactions, these elements have only been sparingly studied as catalysts / components of catalysts for industrial reactions; mainly due to concerns about their low commercial availability and subsequent high cost.

Research efforts in using lanthanides for industrial catalytic application in the last 20 years have included studies into the effects of lanthanide oxides as both supports for active phases, and more recently as low concentration dopants which may enhance a catalytic materials activity or stability. Such target reactions for research into the effect of lanthanide addition to catalysts have included oxidative coupling of methane to hydrocarbons\(^2\), propane steam reforming\(^3\), steam reforming of methane\(^4\), and more recently the dry reforming of methane\(^5\).

Choudhary and Rane first studied the rare earth oxides La\(_2\)O\(_3\), CeO\(_2\), Sm\(_2\)O\(_3\), Eu\(_2\)O\(_3\), and Yb\(_2\)O\(_3\) as catalyst supports in the oxidative coupling of methane to \(C_2\)-hydrocarbons\(^6\). They found that the order of activity and selectivity decreased over the set La\(_2\)O\(_3\) > Sm\(_2\)O\(_3\) > Eu\(_2\)O\(_3\) > Yb\(_2\)O\(_3\) > CeO\(_2\), where the acidity / basicity of the support influenced the activity / selectivity of the material; although this relationship was complex. Rare earth oxides have
also been studied as supports in the steam reforming reaction (reaction 1.4). Natesakhamat et al. studied the influence of low concentrations of lanthanides added to a Ni/Al₂O₃ catalyst for use in the propane steam reforming reaction and reported that the addition of only 2% w/w of the lanthanide dopant (La, Ce or Yb), resulted in slightly improved activity, stability and coke resistance across these materials³.

For the dry reforming of methane rare earth oxides have received some attention as support materials for active phases, although these supports have tended to have relatively low surface area, and suffered from rapid deactivation from carbon deposition⁷. Gronchi et al. found that when Rh was deposited across La₂O₃ supports, CH₄ and CO₂ conversion could be increased to 42% and 68% respectively (when 1.5%Rh/La₂O₃ was used at 550°C with a total gas flow of 80 sccm)⁸. This result was an increase of 5% and 12% conversion respectively over the previously reported SiO₂ supported Rh material. Although these results showed promise for activity enhancement, an increased CH₄:CO₂ input ratio was required to show significant improvements, and rapid deactivation through carbon deposition rendered the catalyst useless after short periods of time. Barroso-Quiroga et al. found that Ni supported on CeO₂ supports outperformed Ni supported on La₂O₃ in terms of initial CH₄ and CO₂ conversion, although deactivation over a short period of time still rendered the catalyst useless⁹. Therefore whilst rare earth oxides have been demonstrated to provide increased activity when used as catalyst supports in the dry reforming reaction they tend to deactivate rapidly due to this increased activity and the subsequent deposition of inactive carbon types across the materials.
The addition of lanthanides, as dopants, into materials capable of catalysing dry reforming of methane has recently been reported to enhance the activity and stability of these materials significantly. Su and Guo reported that the addition of lanthanides favoured a high metal dispersion across Ni/Al₂O₃ catalysts. This reportedly greatly improved their activity in the steam reforming reaction (which was apparently due to reduced Ni sintering / enhanced stability during the time-on-stream analysis). They also found that the formation of inactive NiO and spinel Ni (NiAl₂O₄) was suppressed by the addition of rare earth elements during preparation stages, where the heavy elements (Gd, Er and Dy) exhibited a more pronounced effect than the light ones (La, Pr, Nd).

However it has been reported that the addition of a larger concentration of similar lanthanide dopants has a negative effect on the ability of certain materials to catalyse the reaction due to physical coating of active surfaces; which in turn reduces the surface area of the active metal upon which the reaction mechanism takes place. Daza et al. revealed that the optimum doping concentration of rare earth elements into previously reported active materials is very limited within only a few per cent w/w concentration.

Amin et al. investigated the influence of the full series of lanthanides as low concentration dopants in a Ni/γ-Al₂O₃ dry reforming catalyst. A summary of the results obtained from these studies is given in Table 5.1 and Figure 5.1. It can be seen from the data given in Table 5.1 that whilst the addition of all lanthanides did not considerably affect the morphology (in terms of surface area) of the Ni/γ-Al₂O₃ material, the various lanthanides showed unique conversion characteristics across the reaction period. In particular the addition of Yb was shown to greatly enhance both the CH₄ and CO₂ conversions over time.
within the 20 h of reaction period. The 2%Yb15%Ni/\(\gamma\)-Al\(_2\)O\(_3\) material showed a CH\(_4\) conversion of 77.4% and a CO\(_2\) conversion of 85.3% after 17 h of reaction (at 700°C, 5.2 x 10\(^{-4}\) GHSV), whilst the materials loaded with various other lanthanides showed conversions of only 52.9-65.8% and 63.2-75.9% respectively. Whilst the improved activity of the above mentioned material clearly resulted in a far greater carbon deposition across the material over time, the activity loss over the reaction period analysed was only minimal; which was greatly improved over the previously reported undoped (15%Ni/\(\gamma\)-Al\(_2\)O\(_3\)) catalyst.
Figure 5.1: Lanthanide doping effect of 2% w/w La on γ-Al₂O₃ on CH₄ conversion in the dry reforming reaction\textsuperscript{12}
Table 5.1: Lanthanide doping effect of 2% w/w La on γ-Al₂O₃ on surface area, CH₄ conversion, CO₂ conversion and carbon deposition in the dry reforming reaction

<table>
<thead>
<tr>
<th>Lanthanide Dopant</th>
<th>BET Surface Area (m²/g)</th>
<th>CH₄ conversion (% at 17h)</th>
<th>CO₂ conversion (% at 17h)</th>
<th>Carbon on Spent Catalyst (% weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>116</td>
<td>64.4</td>
<td>74.4</td>
<td>25.6</td>
</tr>
<tr>
<td>Pr</td>
<td>122</td>
<td>62.8</td>
<td>73.5</td>
<td>9.2</td>
</tr>
<tr>
<td>Nd</td>
<td>121</td>
<td>58.0</td>
<td>68.5</td>
<td>7.4</td>
</tr>
<tr>
<td>Sm</td>
<td>128</td>
<td>61.8</td>
<td>72.3</td>
<td>6.9</td>
</tr>
<tr>
<td>Eu</td>
<td>119</td>
<td>65.3</td>
<td>74.6</td>
<td>15.2</td>
</tr>
<tr>
<td>Gd</td>
<td>139</td>
<td>52.9</td>
<td>63.2</td>
<td>12.0</td>
</tr>
<tr>
<td>Tb</td>
<td>120</td>
<td>64.8</td>
<td>74.6</td>
<td>15.8</td>
</tr>
<tr>
<td>Dy</td>
<td>134</td>
<td>59.9</td>
<td>70.1</td>
<td>15.7</td>
</tr>
<tr>
<td>Ho</td>
<td>122</td>
<td>64.7</td>
<td>75.1</td>
<td>19.5</td>
</tr>
<tr>
<td>Er</td>
<td>118</td>
<td>65.8</td>
<td>75.0</td>
<td>11.6</td>
</tr>
<tr>
<td>Tm</td>
<td>121</td>
<td>65.5</td>
<td>75.9</td>
<td>11.5</td>
</tr>
<tr>
<td>Yb</td>
<td>124</td>
<td>77.4</td>
<td>85.3</td>
<td>56.0</td>
</tr>
</tbody>
</table>

Whilst the beneficial effects of doping of Yb in low concentrations were observed across the Ni/γ-Al₂O₃ materials, they were not explored in further detail in the above mentioned study. Also the aforementioned undoped materials are known to be of low activity and stability compared to Ni supported on aluminas and silicas with higher surface areas and advanced morphologies. For these reasons this chapter explores the effects of doping small concentrations of Yb on the higher surface area catalysts studied in the previous chapters (Ni Ni/MAI and Ni/SiO₂ SG materials). Results obtained on the characterisation
of Yb doped Ni/MAI and Ni/SiO₂ SG materials and catalytic studies conducted with these materials in terms of selectivity, stability and carbon formation across the dry reforming reaction are presented and discussed.

5.2 Materials and Methods

5.2.1 Materials

Refer to section 2.1.1 for a list of materials used in catalyst preparation

5.2.2 Catalyst Preparation

5.2.2.1 Ytterbium Doped Nickel Mesoporous Alumina

Ni(10)/MAI materials containing 1-4% Yb were prepared as follows: Synthesis was similar to that of the Ni/MAI catalysts (refer to Chapter 3.2.1), with the exception of the calculated amount of Yb(NO₃)₂.5H₂O being added to solution at the same time as the Ni(NO₃)₂.6H₂O. In a typical synthesis of Yb(1)Ni(10)/MAI, 4.0 g of Pluronic P123 was dissolved in 30 ml of ethanol under stirring at room temperature, before 8.0 g of Al(OPr⁴)₃ was added to the solution. Nickel / ytterbium solution was made separately by dissolving 0.896 g of Ni(NO₃)₂.6H₂O and 0.065 g of Yb(NO₃)₃.5H₂O in 10 ml ethanol and 6 ml concentrated HNO₃. The latter solution was added to the P123 solution under vigorous stirring. The mixture was stirred for a further 2 h. The final slurry was transferred into a polypropylene bottle, closed and heated in an oven for 12 h at 90 °C. The temperature of the PP bottle was brought down to 50 °C and the bottle was uncapped overnight to permit
the remaining ethanol to evaporate. The obtained solid sample was ground to a fine powder and calcined using a specific pre-treatment cycle at 630°C for 2 h under static air. For the synthesis of Yb(x)Ni(10)/MAI materials with 2-4% Yb w/w, the same procedure was followed using a predetermined amount of ytterbium nitrate. For comparison to a sample with no Yb doping, a fresh Ni(10)/MAI sample was prepared without the addition of Yb.

5.2.2.2 Ytterbium Doped Nickel Silica

Ni(10)/SiO2 SG materials were fabricated with a further 1-4% Yb as follows: Synthesis was similar to that of the Ni/SiO2 SG catalysts (refer to Chapter 4.2.1), with the exception of the predetermined amount of Yb(NO3)2.5H2O being added to solution at the same time as the Ni(NO3)2.6H2O. In a typical synthesis of Yb(1)Ni(10)/SiO2 SG, 9.35g of tetraethyl orthosilicate (TEOS) was added dropwise to a mixture of 2g urea, 1.49g Ni(NO3)2.6H2O and 0.078g Yb(NO3)3.5H2O all dissolved in 10g of 0.1M HNO3 and 2.88g citric acid under constant stirring. The resulting solution was transferred to a sealed polypropylene bottle and heated to 80°C for 5 days in order to both decompose the urea and increase the pH of the gel solution. The temperature of the PP bottle was then reduced to 50°C and the bottle left uncapped for 1 week. The obtained solid sample was ground to a fine powder and calcined at 540°C for 2 h under static air. For synthesis of Yb(x)Ni(10)/SiO2 SG materials with 2-4% Yb w/w the same procedure was followed using a predetermined amount of ytterbium nitrate. For comparison to a sample with no Yb doping, a fresh Ni(10)/SiO2 SG sample was prepared without the addition of Yb.
5.2.3 Pre-Treatment of Ytterbium Doped Catalysts

The Yb doped Ni(10)/MAl and Ni(10)/SiO$_2$ SG catalysts were pre-treated under similar conditions as the undoped Ni/MAl and Ni/SiO$_2$ materials prior to reaction analysis (refer to Chapters 3.2.3 and 4.2.3). Reduction of the catalyst materials were performed in-situ immediately prior to the activity analysis, where subsequent to the loading of the pelletised material within the tubular reactor the temperature was raised to 700°C, and the catalysts were subject to a hydrogenated environment (5% H$_2$ purity 5, 95% He purity 5) for 2 h.

5.2.4 Catalyst Testing

The catalysts were analysed under standard catalyst testing conditions as outlined in section 2.2.2.

5.2.5 Characterisation / Analytical Methods

The freshly prepared materials were analysed by XRD and TPR prior to reduction; XRD, BET surface area analysis, TEM, and XPS methods after reduction; and XRD, TEM and TGA methods after activity analysis. These techniques are outlined in section 2.2.3.
5.3 Results and Discussion

5.3.1 Characterisation of Ytterbium Doped Ni/MAI and Ni/SiO₂ SG Materials

The powder X-ray diffraction patterns of the prepared ytterbium doped nickel loaded mesoporous-alumina (Yb(x)Ni(10)/MAI) and ytterbium doped nickel loaded silica sol-gel (Yb(x)Ni(10)/SiO₂ SG) catalysts before and after reduction (at 700 °C under flowing H₂), along with the corresponding undoped materials are presented in Figure 5.2 and 5.3 respectively.

In the XRD pattern for the Yb doped Ni(10)/MAI prior to reduction (Figure 5.2) peaks can be noted for the spinel (NiAl₂O₄) structure occurring at 37.0°, 45° and 65.0° 2θ representing the [311], [400] and [440] crystal planes respectively. Only minor peaks are observable showing the presence of NiO, but no crystalline Ni peaks can be seen (as expected prior to reduction), indicating most of the Ni was trapped within spinel form within the Yb doped Ni(10)/MAI materials even prior to reduction. The reduced Yb doped Ni(10)/MAI materials all showed similar spinel peaks, indicating that the environment / state in which the Ni was present in these materials was not altered significantly by the reduction process used.

Elemental Ni [111], Ni [200] and Ni [220] peaks can clearly be seen in the Ni(10)/MAI material and the materials with higher Yb doping after reduction (Yb(3)Ni(10)/MAI and Yb(4)Ni(10)/MAI) at 44.5°, 51.9° and 76.4° 2θ respectively, but are not observed in the samples with low concentration of Yb doping (Yb(1)Ni(10)/MAI and Yb(2)Ni(10)/MAI).
Further noted was a small shoulder at 32.9° 2θ representing the Yb [111] plane, which was slightly more prominent in the samples with lower Yb loading. This is unusual based on the very low loading of Yb in the Yb(1)Ni(10)/MAI and Yb(2)Ni(10)/MAI materials, and the fact that the Yb peak size was observed to be reduced in size over a higher loading. All Yb doped MAI materials showed shoulders around 67.0° 2θ from the formation of γ-Al₂O₃ throughout the bulk of the support structure.
Figure 5.2: XRD of Yb doped Ni(10)/MAI and undoped Ni(10)/MAI materials
Analysis of the Yb doped Ni(10)/SiO₂ SG material (Figure 5.3) showed NiO peaks occurring in the calcined sample at 37.3°, 43.4° and 62.9° 2θ from the [101], [012] and [110] crystal planes. The presence of NiO can also be noted in the sample with the lowest Yb loading (Yb(1)Ni(10)/SiO₂ SG), and in low concentrations in the Yb(4)Ni(10)/SiO₂ SG and undoped Ni(10)/SiO₂ SG materials, where broad peaks around 37.2° and 62.9° 2θ indicates the NiO [101] and [110] crystal planes existed in these samples. Crystalline Ni peaks became observable in all reduced samples at 44.5° due to the presence of Ni [111] crystal planes, with minor peaks at 51.8° and 76.3° 2θ from the Ni [200] and Ni [220] planes. Interesting to note is the difference in crystalline Ni peak area across the catalysts with varying Yb doping. Whilst all of the materials in the set contained the same concentration of Ni (10% w/w), the peak areas clearly increased in area from the Yb(1)Ni(10)/SiO₂ SG material to the Yb(2)Ni(10)/SiO₂ SG and again to Yb(3)Ni(10)/SiO₂ SG, where the peaks then reduced slightly in size (similar in area to the undoped sample) in the Yb(4)Ni(10)/SiO₂ SG material. This indicates that the amount of loaded Yb had an effect on the Ni species present in the samples, where at low (1 % wt) and higher (4 % wt) loading the Yb caused some weakly bound surface species of NiO to form, and at high Yb loading (3 - 4 % wt) spinel Ni species changed to crystalline Ni. An amorphous region is obvious in all samples from the disordered SiO₂ sol-gel support, with a broad hump centred around 22° 2θ. No Yb peaks are observable in any of the Yb doped samples.
Figure 5.3: XRD of Yb doped Ni(10)/SiO₂ SG and undoped Ni(10)/SiO₂ SG materials
Representative TEM images of the reduced Yb doped Ni(10)/MAI and Yb doped Ni(10)/SiO₂ SG are shown in Figures 5.4 and 5.5 respectively. The porous nature of the MAI support (Figure 5.4) was evident after reduction (at 700°C) for the samples analysed. The images reveal the small number of distinct Ni particles throughout the bulk of the support in the case of the materials loaded with less Yb (Yb(1)/Ni(10)/MAI and Yb(2)/Ni(10)/MAI); where the darker areas present were either from irregularities in the support material itself or areas throughout the support that consisted of high concentrations of well distributed Ni (Figure 5.4a). There were a slightly increased number of discernible Ni particles in the samples with higher loading of Yb (Yb(3)/Ni(10)/MAI and Yb(4)/Ni(10)/MAI) as seen in Figure 5.4b. These above mentioned observations are in contrast to the undoped catalyst which clearly shows a greater number of large, distinct Ni clusters (Figure 5.4c). Also there were no Ni clusters observable on the very outer surface of the support in the case of the materials doped with Yb, which was different to the appearance of Ni clusters attached to the outer edge of the support in the undoped Ni(10)/MAI (Figure 5.4c). These observations can be attributed to the large amount of Ni bound strongly throughout the support in spinel form (NiAl₂O₄) as outlined in the XRD analysis, rather than being deposited as free surface or crystalline Ni particles located within the pore structure during preparation.
Figure 5.4: TEM images of reduced Yb doped Ni/MAI; a) Yb(1)Ni(10)/MAI; b) Yb(4)Ni(10)/MAI; and c) undoped Ni(10)/MAI material
Figure 5.5 shows a TEM image obtained representing the reduced Yb doped Ni(10)/SiO2 SG samples (Figure 5.5a) and an image of the undoped Ni(10)/SiO2 SG material (Figure 5.5b). The highly porous, amorphous nature of the support can be observed in the presented TEM images. The appearance of distinct Ni particles was noted throughout the bulk of all samples with Yb doping (Figure 5.5a) and larger clusters in the case of the undoped (Ni(10)/SiO2 SG) sample (Figure 5.5b). However only a small number of Ni clusters were observed in the samples, which is in agreement with the lack of / small size of NiO peaks in the XRD analysis, indicating the inclusion of mainly crystalline Ni particles, most likely residing within the pore structure of the materials.
The average Ni\(^0\) particle diameter in the reduced Yb doped samples was calculated based on the peak broadening for the Ni [111] diffraction line at 44.4\(^\circ\) – 44.9\(^\circ\) in the XRD patterns obtained. Where these peaks were not clear in the XRD analysis the particle size was estimated through size distribution observations from TEM imaging (see Appendix C). The Ni particle size for both Yb doped Ni(10)/MAl and Ni(10)/SiO\(_2\) SG materials sets are presented in Tables 5.2 and 5.3 respectively. For the Yb doped Ni(10)/MAl materials (Table 5.2) it can be seen that the materials with Yb doping of all concentrations had lower average Ni particle sizes throughout the material than the undoped sample. In fact the materials doped with small amounts of Yb (Yb(1)Ni(10)/MAl and Yb(2)Ni(10)/MAl), showed Ni average Ni particle sizes of approximately 8.1 nm, whilst those loaded with a greater amount of Yb (Yb(3)Ni(10)/MAl and Yb(4)Ni(10)/MAl), showed a Ni particle size of around 7.45-7.5 nm.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ni(^0) Crystal Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(10)/MAl</td>
<td>10.10</td>
</tr>
<tr>
<td>Yb(1)Ni(10)/MAl</td>
<td>&lt;7.90*</td>
</tr>
<tr>
<td>Yb(2)Ni(10)/MAl</td>
<td>&lt;8.10*</td>
</tr>
<tr>
<td>Yb(3)Ni(10)/MAl</td>
<td>7.42</td>
</tr>
<tr>
<td>Yb(4)Ni(10)/MAl</td>
<td>7.47</td>
</tr>
</tbody>
</table>

*Calculated by TEM image particle distribution count

Table 5.2: Ni particle size of Yb doped Ni(10)/MAl and undoped Ni(10)/MAl materials
From Table 5.3 it can be observed that Yb doping during the Yb(x)Ni(10)/SiO₂ SG preparation also had an effect on the Ni particle size through the Ni(10)/SiO₂ SG materials, however these Ni clusters were only reduced in size (compared to the undoped material) when a small amount of Yb was added (in the case of Yb(1)Ni(10)/SiO₂ SG and Yb(2)Ni(10)/SiO₂ SG). It can be seen that the Ni⁰ particle size in the above mentioned materials was 7.85 and 10.07 nm respectively, compared to a larger 11.73 nm in the undoped Ni(10)/MAI material after reduction. When a greater concentration of Yb was added to the Ni(10)/SiO₂ SG material (in the case of Yb(3)Ni(10)/SiO₂ SG and Yb(4)Ni(10)/SiO₂ SG) the Ni particle size can be seen to have been 12.94 and 15.86 nm respectively, greater than those in the undoped material.

Table 5.3: Ni particle size of Yb doped Ni(10)/SiO₂ SG and undoped Ni(10)/SiO₂ SG materials

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ni⁰ Crystal Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(10)/SiO₂ SG</td>
<td>11.73</td>
</tr>
<tr>
<td>Yb(1)Ni(10)/SiO₂ SG</td>
<td>7.85</td>
</tr>
<tr>
<td>Yb(2)Ni(10)/SiO₂ SG</td>
<td>10.07</td>
</tr>
<tr>
<td>Yb(3)Ni(10)/SiO₂ SG</td>
<td>12.94</td>
</tr>
<tr>
<td>Yb(4)Ni(10)/SiO₂ SG</td>
<td>15.86</td>
</tr>
</tbody>
</table>
Figures 5.6 – 5.9 show the nitrogen adsorption / desorption isotherms and representative pore size distribution plots of the reduced Yb doped Ni(10)/MAI and Ni(10)/SiO₂ SG catalysts. The Ni(10)/MAI samples with Yb addition showed type IV adsorption curves characteristic of ordered mesoporous materials (Figure 5.6). The adsorption / desorption isotherms of the materials doped with 1, 3 and 4% Yb all showed a large increase in the relative pressure ($P/P_o$) from 0.75 to 0.9 due to the capillary condensation of nitrogen within the mesopores, where the steepness of this inflection step indicates that the mesopores within the sample were highly ordered and of regular size. The high $P/P_o$ value of the inflection step in the above samples indicates the inclusion of a number of pores within the micropore region. The undoped sample also showed a steep inflection step, although this occurred at a lower $P/P_o$ value indicating that there was a lower external surface area across this material and possibly less micropores present. The material loaded with 2% w/w Yb (Yb(2)Ni(10)/MAI) showed a different trend to the other Yb doped materials, in which a less steep inflection step indicated the inclusion of a wide range of pore sizes which are less ordered, resulting from a wide range of both mesopores and possibly the inclusion of some small macropores throughout the support structure.

The pore distribution plots for the Yb(1)Ni(10)/MAI and Yb(2)Ni(10)/MAI materials are shown in Figure 5.7 to give a direct comparison between the two main support morphologies resulting from the addition of Yb to Ni(10)/MAI. The Yb(1)Ni(10)/MAI sample showed a range of pores from less than 5 nm (micropores) to 45 nm in diameter. The majority of the pores within this sample can be observed to be around 18-19 nm in diameter. This is in contrast to the Yb(2)Ni(10)/MAI sample, which showed a large pore distribution consisting of pores in the mesoporous range (from 5 nm to 22 nm diameter) but with the inclusion of a number of macropores (with 50 nm – 60 nm diameter).
Interesting to note is the smaller average mesopore diameter in this material (of 8 – 9 nm diameter), where there is a large number of pores within this specific diameter range compared to the other Yb doped materials which show larger average mesopore diameter, although the latter materials showed a lack of macropores.
Figure 5.6: BET isotherm plots of Yb doped Ni(10)/MAI and undoped Ni(10)/MAI materials

Figure 5.7: Pore size distribution within Yb(1)Ni(10)/MAI and Yb(2)Ni(10)/MAI materials
Analysis of the nitrogen adsorption / desorption isotherms for the Yb doped Ni(10)/SiO$_2$ SG materials (Figure 5.8) showed that these materials produce type IV hybrid isotherms, consistent with mesoporous materials containing a range of pore sizes. The undoped sample (Ni(10)/SiO$_2$ SG) and the sample doped with 2% Yb (Yb(2)Ni(10)/SiO$_2$ SG) showed similar isotherm plots, with a steep inflection step occurring at high $P/P_0$ values, indicative of the more regular porosity of the support compared with the other samples. The samples doped with 3 and 4% Yb showed an inflection step occurring at a slightly lower $P/P_0$ value, with a 2 step desorption. These materials therefore contain wider range of larger pores with various sizes and a number of closed pores. The closed pores are expected where the increased Yb loading may block some of the pore channels. The Yb(1)Ni(10)/SiO$_2$ SG material showed a unique isotherm type, where a less steep inflection step occurring at a low $P/P_0$ value indicated an increased range of pore sizes throughout the structure, which itself has a reduced outer surface area.

The pore distribution plots for the Yb(1)Ni(10)/SiO$_2$ SG and Yb(2)Ni(10)/SiO$_2$ SG materials are shown in Figure 5.9 for comparison. The Yb(2)Ni(10)/SiO$_2$ SG material showed a large distribution of mesopores within the range of less than 5 nm – 45 nm, but no pores in the macropore region as in agreement with the above observations. The material with with 1% Yb loading (Yb(1)Ni(10)/SiO$_2$ SG) showed a far narrower pore distribution within the mesopore region, but also contained signs of a small amount of macropores; indicated by the broad band between 30 and 65 nm in the pore distribution plot. These observations are again in agreement with the isotherm plot observations in the section above.
Figure 5.8: BET isotherm plots of Yb doped Ni(10)/SiO₂ SG and undoped Ni(10)/SiO₂ SG materials

Figure 5.9: Pore size distribution within Yb(1)Ni(10)/SiO₂ SG and Yb(2)Ni(10)/SiO₂ SG materials
The specific surface area, average pore diameter, and total pore volume of the catalysts with increasing Yb loading determined using BET analysis are reported in Table 5.4 for the Yb doped Ni(10)/MAI materials, and in Table 5.5 for the Yb doped Ni(10)/SiO2 SG materials.

Table 5.4 reveals that the surface area of all Yb doped Ni(10)/MAI materials were significantly lower than undoped Ni(10)/MAI. This is expected where the total metal loading is greater across the materials doped with a greater concentration of Yb. Although interestingly the surface area decreased in the order Ni(10)/MAI > Yb(4)Ni(10)/MAI > Yb(3)Ni(10)/MAI > Yb(1)Ni(10)/MAI > Yb(2)Ni(10)/MAI. The average pore diameter and total pore volume of the materials doped with 3 and 4% Yb (Yb(3)Ni(10)/MAI and Yb(4)Ni(10)/MAI) were similar to that in the undoped material (Ni(10)/MAI), however the Yb(1)Ni(10)/MAI material showed an increased pore diameter / pore volume and the Yb(2)Ni(10)/MAI showed a decreased pore diameter / pore volume.
Table 5.4: BET surface area, average pore diameter and total pore volume of Yb doped Ni(10)/MAI and undoped Ni(10)/MAI materials

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET Surface Area (m²/g)</th>
<th>Pore Diameter (nm)</th>
<th>Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(10)/MAI</td>
<td>315</td>
<td>13.5</td>
<td>0.76</td>
</tr>
<tr>
<td>Yb(1)Ni(10)/MAI</td>
<td>212</td>
<td>17.1</td>
<td>0.91</td>
</tr>
<tr>
<td>Yb(2)Ni(10)/MAI</td>
<td>195</td>
<td>11.5</td>
<td>0.56</td>
</tr>
<tr>
<td>Yb(3)Ni(10)/MAI</td>
<td>233</td>
<td>13.5</td>
<td>0.76</td>
</tr>
<tr>
<td>Yb(4)Ni(10)/MAI</td>
<td>241</td>
<td>12.3</td>
<td>0.76</td>
</tr>
</tbody>
</table>

The data in Table 5.5 shows the surface area and pore properties of the Yb doped Ni(10)/SiO₂ SG materials. The lower surface area of the Yb(1)/Ni(10)/SiO₂ SG can be noted compared with the other Yb doped Ni(10)/MAI materials and the undoped sample. The doped Ni(10)/SiO₂ SG materials with 2, 3 and 4% Yb showed a similar surface area to the undoped (Ni(10)/SiO₂ SG) material. It is interesting that the doping of higher Yb amounts did not result in a significant decrease in surface area of the material (as with the trend observed in the Yb doped Ni(10)/MAI materials). This indicates that the addition of Yb to these materials (in concentrations of 2 - 4%) had a direct affect on support morphology. The average pore diameter of the Yb doped materials were all greater than the undoped (Ni(10)/SiO₂ SG) material, where they decreased across Yb(2)/Ni(10)/SiO₂ SG > Yb(1)/Ni(10)/SiO₂ SG > Yb(3)/Ni(10)/SiO₂ SG > Yb(4)/Ni(10)/SiO₂ SG. The total
The pore volume of these materials was slightly decreased compared with the undoped sample with the exception of the Yb(2)Ni(10)/SiO\textsubscript{2} SG material which showed similar pore volume to the Ni(10)/SiO\textsubscript{2} material.

Table 5.5: BET surface area, average pore diameter and total pore volume of Yb doped Ni(10)/SiO\textsubscript{2} SG and undoped Ni(10)/SiO\textsubscript{2} SG materials

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET Surface Area (m\textsuperscript{2}/g)</th>
<th>Pore Diameter (nm)</th>
<th>Pore Volume (cm\textsuperscript{3}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(10)/SiO\textsubscript{2} SG</td>
<td>274</td>
<td>9.5</td>
<td>1.11</td>
</tr>
<tr>
<td>Yb(1) Ni(10)/SiO\textsubscript{2} SG</td>
<td>214</td>
<td>15.9</td>
<td>0.85</td>
</tr>
<tr>
<td>Yb(2) Ni(10)/SiO\textsubscript{2} SG</td>
<td>230</td>
<td>18.8</td>
<td>1.09</td>
</tr>
<tr>
<td>Yb(3) Ni(10)/SiO\textsubscript{2} SG</td>
<td>279</td>
<td>11.4</td>
<td>0.79</td>
</tr>
<tr>
<td>Yb(4) Ni(10)/SiO\textsubscript{2} SG</td>
<td>277</td>
<td>11.2</td>
<td>0.83</td>
</tr>
</tbody>
</table>
TPR profiles of the non reduced Yb doped Ni(10)/MAI materials are presented in Figure 5.10. Analysis of the results shows that the main reduction peak for Ni in the Yb doped materials appeared at higher temperatures than that observed in the undoped (Ni(10)/MAI) material. This was clearly due to the presence of spinel Ni phase (NiAl$_2$O$_4$) in the Yb doped samples (as observed in XRD). Other aspects of the TPR profiles presented in Figure 5.10 of note include:

- The decreased $T_{\text{max}}$ reduction temp for the 3% w/w Yb (Yb(3)/Ni(10)/MAI), which did not fit the trend observed for the other materials doped with Yb

- A minor peak centered around 500 °C which is clearly evident in the sample loaded with 4% Yb (Yb(4)/Ni(10)/MAI), whilst a similar peak was not observed for the other Yb doped materials

Figure 5.10: TPR profiles of Yb doped Ni(10)/MAI and undoped Ni(10)/MAI materials
TPR profiles for the Yb doped Ni(10)/SiO₂ SG materials are presented in Figure 5.11. The reduction temperature of the highest peak in all samples share a common $T_{\text{max}}$ value of around 640-700 °C, which is much lower than the $T_{\text{max}}$ obtained in the Yb doped Ni(10)/MAI samples, but still represents species with a high Ni-support interaction.

With a low Yb loading (in the case of Yb(1)/Ni(10)/SiO₂ SG and Yb(2)/Ni(10)/SiO₂ SG), there was only one reduction peak; which occurred centered around a temperature of 620-630 °C. The higher loaded of the aforementioned materials shows signs of a small portion of the Ni being reduced at slightly lower temperatures as the lower temperature area of the peak forms a sloping shoulder. Those materials doped with a greater amount of Yb (Yb(3)/Ni(10)/SiO₂ SG and Yb(4)/Ni(10)/SiO₂ SG) show Ni residing in two separate forms, with two main overlapping reduction peaks present. In the case of the Yb(4)/Ni(10)/SiO₂ SG material this is most likely the existence of Ni species similar to those appearing in the Yb(2)/Ni(10)/SiO₂ SG sample within the lower temperature shoulder. The material doped with 3% w/w Yb (Yb(3)/Ni(10)/SiO₂ SG) shows a unique Ni phase for this analysis; where the majority of the Ni particles within this sample exist in an environment that is more readily reduced compared to the higher temperature peak common to all samples analysed (as shown by the greater area of the peak with the lower $T_{\text{max}}$). The above mentioned peak is centered around a $T_{\text{max}}$ of 400 °C, which indicates the presence of Ni particles loosely bound to the support. The peak appears at a slightly increased $T_{\text{max}}$ compared to the peak in the undoped Ni(10)/SiO₂ SG material (as a result from weakly bound surface species in the Ni(10)/SiO₂ SG material – see pages 164-165). The above observations and the lack of NiO peaks in the XRD analysis together indicate that the above species are most likely Ni species that existed in the larger pores of the
Yb(3)/Ni(10)/SiO$_2$ SG material; and hence had some interaction with the support, but not to the same degree as those species which cause the peak with the higher $T_{\text{max}}$ in this material.

The larger area under the peak with the higher $T_{\text{max}}$ compared with the smaller area in the lower $T_{\text{max}}$ peak in the Yb doped materials (with the exception of the Yb(3)/Ni(10)/SiO$_2$ SG) indicates the majority of the Ni particles are located deep within the smaller pores of the support (and not as loosely bound surface particles or species located within the larger pores of the support) with strong metal-support interaction, but can be nevertheless reduced at 700$^\circ$C.

Therefore the following Ni phases could be observed in the Yb doped Ni(10)/SiO$_2$ samples:

- Loosely bound surface species; in a small amount in the undoped sample,

- Species with a slightly higher metal-support interaction found within the larger pores of the support; in large concentration in the Yb(3)/Ni(10)/SiO$_2$ SG material and somewhat in the Yb(2)/Ni(10)/SiO$_2$ SG and Yb(4)/Ni(10)/SiO$_2$ SG materials, and

- Species with a stronger metal-support interaction than those mentioned above; most likely as Ni species located deep within the smaller sized pores in all samples.
XPS analysis of the reduced Yb doped Ni catalysts were conducted and the results obtained are presented in terms of Ni profiles in Figures 5.12 and 5.13 for the Yb doped Ni(10)/MAI and Ni(10)/SiO2 SG materials respectively.

Figure 5.12 shows the characteristic Ni peaks occurring in the range of 844-870 eV in the XPS profiles for the Yb doped Ni(10)/MAI materials. The binding energy of the Ni 2p3/2 remained constant within the range of 856.8-857.6 eV across the samples. The slight shift in these peak binding energies indicated a different binding strength of elemental Ni across the materials with different Yb loading. Whilst the binding energy for the Ni peak was 856.8 eV for the undoped Ni(10)/MAI material (a), it shifted to a higher binding energy (
up to 857.6 eV) in the Yb doped materials representing a stronger Ni-support interaction. A third Ni peak appeared in the materials with 1 - 4 wt % Yb (b-d), but was not observable in the material loaded with 4 wt % Yb (e). This peak represents the strongly bound spinel Ni (NiAl₂O₄) species, which were evident in the XRD analysis (see page 161-163). Whilst this structure was also observed in the Yb(4)Ni(10)/MA1 material, crystalline Ni was observed in increased amounts, indicating instead that this observed structure was instead a spinel Yb (where the added Yb replaced the Ni in the spinel phase). The small area in the third XPS Ni peak in the Yb(3)Ni(10)/MA1 is further indicative of this conclusion, where crystalline Ni was also observed in the XRD analysis within this material, however not all of the spinel Ni species would have been replaced by Yb (and hence a small amount remained as NiAl₂O₄).
Figure 5.12 Binding energy peaks for Ni range from XPS analysis of: a) Ni(10)/MAI; b) Yb(1)Ni(10)/MAI; c) Yb(2)Ni(10)/MAI; d) Yb(3)Ni(10)/MAI; and e) Yb(4)Ni(10)/MAI materials.
Figure 5.13 shows the characteristic XPS Ni peaks occurring in the range of 844-870 eV in the XPS profiles for the Yb doped Ni(10)/SiO$_2$ SG materials. The binding energy of the Ni$_{2p3/2}$ peak in the undoped material (Ni(10)/SiO$_2$ SG) was 856.5 eV (a), whereas the binding energy shifted to 856.8 eV with the Yb doped Ni(10)/SiO$_2$ SG materials. This slight shift in binding energies indicated the slightly increased Ni-support interaction in the materials with Yb doping. The binding energies of the main peak remained similar across all concentrations of Yb (b-e), further indicating that the amount of Yb doping had no further effect on the Ni-support interaction in the materials.
Figure 5.13: Binding energy peaks for Ni range from XPS analysis of; a)Ni(10)/SiO$_2$ SG; b)Yb(1)Ni(10)/SiO$_2$ SG; c) Yb(2)Ni(10)/SiO$_2$ SG; d) Yb(3)Ni(10)/SiO$_2$ SG; and e)Yb(4)Ni(10)/SiO$_2$ SG materials.
5.3.2 Discussion of Role of Yb as Dopant Based on Characterisation Data Obtained

The influence of Yb doping on the structure of the Ni(10)/MAI and Ni(10)/SiO₂ SG materials is most likely due to a ‘seeding effect’ of Ni particle growth preferentially on the surface of the Yb over the support. This is based on the following:

- The Yb doped Ni(10)/MAI materials showed a decreased Ni particle size with the addition of Yb (see page 169), yet the total Ni concentration in these materials remained constant (10 % wt). Therefore there was an increased Ni dispersion in these materials, in which Yb was directly involved. On this point a highly-bound spinel Ni (Ni₃Al₂O₆) phase became evident in the Ni(10)/MAI even with a low concentration of Yb, where this phase transition is known to occur across increased surface area supports with small active particle sizes (increased dispersions).

- The binding energies in the Ni peaks of XPS analysis (see pages 182-184) increased for Yb doped Ni(10)/MAI materials. This indicates a direct increase of Ni-support interaction, which is most likely attributed to a direct interaction of Yb with the support, and hence Ni with the Yb.

- Pore structure was lost at higher concentrations of Yb doping in all materials (with constant Ni concentration), in terms of decreased pore sizes and volumes (see pages 171-175). This can be attributed to the agglomeration of Yb particles.
throughout the supports, which in turn resulted in a greater nucleation of Ni
directly within the pores of the material.

Slightly different trends were observed across the Yb doped Ni(10)/SiO₂ SG material,
where low concentrations of Yb initially resulted in a decreased Ni particle size (over the
undoped material) (see page 170), yet increased concentrations of Yb resulted in larger Ni
particles. Also the Ni peak XPS binding energies only very slightly increase with Yb
loading (see pages 185-186). This would suggest that the Yb particles had less of an
interaction with the SiO₂ SG support than the MAI material, where the addition of low
concentrations of Yb still initially ‘seeded’ Ni nucleation, but higher concentrations
resulted in some Yb interacting instead directly with the Ni particles. A similar trend has
been previously noted, where Daza et al. observed that an increased doping concentration
of Ce into a Ni/Mg-Al material resulted in a coating of the active sites by the lanthanide,
producing larger Ni particles¹⁶.

5.4 Catalyst testing results

The influence of Yb doping on Ni(10)/MAI and Ni(10)/SiO₂ SG catalysts in the dry
reforming reaction was investigated. Catalytic activity was measured in terms of direct
conversion of reactant gases (refer to Chapter 2.2.4.2) and H₂:CO product ratio (refer to
Chapter 2.2.4.3). Stability was evaluated in terms of loss of activity over the reaction
period. Post run analysis of spent catalyst materials included XRD analysis, TEM imaging,
and TGA characterisation techniques in an attempt to understand activity, stability, and
specific carbon deposition. A material containing 10 % wt Yb supported on mesoporous
alumina (Yb(10)/MAl) was tested and found to have no activity in the dry reforming reaction, hence Yb doping was expected to have no direct influence on the results obtained with the Yb doped Ni based catalysts studied.

5.4.1 Yb doped NiMAl

Figures 5.14 and 5.16 show the CH₄ and CO₂ conversion percentages respectively for the Yb doped Ni(10)/MAl catalyst materials and the undoped Ni(10)/MAl catalyst over a reaction time of 900 mins at a temperature of 700°C and a total GHSV of 52000 mL h⁻¹ g⁻¹. The conversion of each reactant gas was greatly enhanced over the reaction period tested for the Yb doped Ni(10)/MAl materials compared to the undoped (Ni(10)/MAl) material. There was also a general increase in overall activity of the catalysts with increasing Yb loading concentration with the exception of the Yb(2)Ni(10)/MAl material, which showed a very similar conversion profile to that of the Yb(1)Ni(10)/MAl sample. The aforementioned difference in trend is most likely due to the lower surface area (and likely lower resulting Ni dispersion), decreased pore volume, and/or decreased average pore size of the Yb(2)Ni(10)/MAl material compared to the other Yb doped Ni(10)/MAl materials tested. All Yb doped Ni(10)/MAl catalysts also showed a superior stability over the reaction period compared to the undoped (Ni(10)/MAl) material as outlined in Table 5.6, where it can be seen that the average activity loss was less than 1.51% as opposed to the 8.48% loss over the 15 h reaction period respectively. In fact the catalyst with the highest loading of Yb (Yb(4)Ni(10)/MAl) can be observed to have no activity loss across the whole time-on-stream analysis. This indicates that both the methane decomposition (reaction 1.7) and the Boudard reaction (reaction 1.8) occur at a similar rate across the above mentioned material, where the carbon species being deposited on the surface of the
material are utilised and do not build up on (and inhibit) the active Ni particles during the reaction. The increased stability of the Yb doped Ni(10)/MAI materials could be related to the increased stability of the Ni particles which are less likely to sinter when trapped within the highly stable spinel (NiAl₂O₄) form, but gradually reduced to well distributed active Ni particles.¹⁷
Figure 5.14: CH$_4$ conversion % over Yb doped Ni(10)/MAI and undoped Ni(10)/MAI materials at 700 °C, 5.2 x 10$^4$ mL·h$^{-1}$·g$_{cat}^{-1}$ GHSV gas flow, for 900 mins reaction period.

Figure 5.15: CO$_2$ conversion % over Yb doped Ni(10)/MAI and undoped Ni(10)/MAI materials at 700 °C, 5.2 x 10$^4$ mL·h$^{-1}$·g$_{cat}^{-1}$ GHSV gas flow, for 900 mins reaction period.
Table 5.6: Loss of CH₄ and CO₂ conversion over time across Yb doped Ni/MAl and undoped Ni(10)/MAl catalysts after 900 mins time on stream

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CH₄ Activity Loss (%)</th>
<th>CO₂ Activity Loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(10)/MAl</td>
<td>8.48</td>
<td>5.80</td>
</tr>
<tr>
<td>Yb(1)Ni(10)/MAl</td>
<td>0.27</td>
<td>0.38</td>
</tr>
<tr>
<td>Yb(2)Ni(10)/MAl</td>
<td>1.51</td>
<td>1.23</td>
</tr>
<tr>
<td>Yb(3)Ni(10)/MAl</td>
<td>0.38</td>
<td>0.33</td>
</tr>
<tr>
<td>Yb(4)Ni(10)/MAl</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 5.16 shows the average H₂:CO product ratio across the set of Yb doped Ni(10)/MAl catalysts and the undoped Ni(10)/MAl material for the 900 min reaction period (tested under the conditions listed in Chapter 2.2.4). All Yb doped materials far outperformed the undoped catalyst (Ni(10)/MAl); where in particular the catalyst with the highest loading of Yb (Yb(4)Ni(10)/MAl) catalysed the production of H₂ and CO at a ratio very close to unity. This strengthens the conclusions drawn in the activity analysis section, that the material allows for the production of mainly active forms of carbon (which are able to be readily utilised in the Boudard reaction), which in turn would also limit the degree of the reverse water gas shift reaction (reaction 1.2).
Figures 5.17 and 5.18 show the CH₄ and CO₂ conversion percentages for the Yb doped Ni(10)/SiO₂ SG catalyst materials and the undoped Ni(10)/SiO₂ SG catalyst over identical reaction conditions used in the analysis of the doped Ni(10)/MAI materials; that is a reaction time of 900 mins at a temperature of 700°C and a total GHSV of 52000 mL h⁻¹ g⁻¹. The Yb doped catalysts only slightly outperformed the undoped (Ni(10)/SiO₂ SG) material in terms of initial conversion (and all showed similar conversion percentages) of both CH₄ and CO₂, however the Yb dopant clearly leads to a slightly improved stability for these materials over the Ni(10)/SiO₂ SG material.

Table 5.7 outlines the loss of activity in terms of CH₄ and CO₂ conversion drop over the 15 h on-stream for the Yb doped Ni(10)/SiO₂ SG and undoped Ni(10)/SiO₂ SG catalysts. It
can be noted that whilst the undoped (Ni(10)/SiO₂ SG) catalyst lost 5.33% of activity (in terms of CH₄ conversion) over the testing period, the Yb doped materials lost substantially less activity (between 0.35 – 1.88% conversion). From the activity test and stability analysis of the materials it can be seen that the catalyst doped with the smallest concentration of Yb (Yb(1)Ni(10)/SiO₂ SG) slightly outperformed the materials doped with various other concentrations in terms of both activity and stability over time. This is interesting to note, where the opposite trend was noted with the Yb doped Ni(10)/MAI materials (with the material doped with the higher concentration of Yb outperforming those with less). This is also interesting based on the BET surface area results which show this material has a substantially lower surface area than the undoped (Ni(10)/SiO₂ SG) catalyst, (and those doped with various other concentrations of Yb.) The size of the Ni particles (as observed in XRD analysis) may explain this slightly enhanced activity, where they are observed to be smaller (7.85 nm) than in the other materials studied (10.07-15.86 nm). Whilst this is not expected to show a direct increase in activity for dry reforming catalysis, it may result in the formation of more active forms of carbon (which are deposited during the reaction period), and hence the rate of the Boudard reaction (reaction 1.8) was increased. Subsequently there is very little loss of conversion of either CH₄ or CO₂ over time in the Yb(1)Ni(10)/SiO₂ catalyst.
Figure 5.17: CH₄ conversion % over Yb doped Ni(10)/SiO₂ SG and undoped Ni(10)/SiO₂ SG materials at 700 °C, 5.2 x 10⁴ mL h⁻¹ g⁻¹ GHSV gas flow, for 900 mins reaction period.

Figure 5.18: CO₂ conversion % over Yb doped Ni(10)/SiO₂ SG and undoped Ni(10)/SiO₂ SG materials at 700 °C, 5.2 x 10⁴ mL h⁻¹ g⁻¹ GHSV gas flow, for 900 mins reaction period.
Figure 5.19 shows the H$_2$CO ratios obtained for the Yb doped Ni(10)/SiO$_2$ SG and undoped Ni(10)/SiO$_2$ SG catalyst materials. There is only a slight improvement on the product ratio for the Yb doped materials over the undoped (Ni(10)/SiO$_2$ SG) catalyst, but this is significant considering that the value is approaching unity; which is desired in industry for downstream applications$^{19}$. The Yb(1)Ni(10)/SiO$_2$ SG material slightly outperformed the materials loaded with other concentrations of Yb, where the H$_2$:CO ratio is 0.95 which confirms the observations made in the activity analysis section above.
Figures 5.20 and 5.21 show a comparison of the powder XRD analysis of the best and worst performed Yb doped materials for each catalyst type; that is the spent Ni(10)/MAl materials doped with 2 and 4% Yb w/w; spent Ni(10)/SiO₂ SG materials doped with 1 and 4% w/w Yb; and the spent undoped materials.

Diffraction peaks representing γ-Al₂O₃ were present in the spent undoped Ni(10)/MAl material (as discussed on pages 161-163) (Figure 5.20). Diffraction peaks for spinel Ni (NiAl₂O₄) are still present in both the spent Yb loaded Ni(10)/MAl samples, with peaks occurring at 37.2°, 45.4° and 65.8° 2θ. Crystalline Ni remains over the reaction period in the undoped catalyst (Ni(10)/MAI) and the materials with higher Yb loading (Yb(4)Ni(10)/MAI), indicated by the peaks at 44.5° and 51.9° 2θ from the [111] and [200]
Ni planes respectively. In the spent material with low Yb loading (Yb(1)Ni(10)/MAI) the presence of NiO can be observed even after the full 15 h time-on-stream indicated by the large peak at 43.3° 2θ. This is interesting based on the XRD analysis of the material prior to reduction (see pages 161-163), where only minor NiO peaks were observed. The above results indicate that some of the Ni species which are trapped within the spinel structure (NiAl₂O₄) prior to reaction may be reduced during time on stream, and subsequently would migrate to become active surface species with less metal-support interaction during catalysis.

Graphitic carbon (Cᵣ) can be observed only on the spent material with a high Yb loading (Yb(4)Ni(10)/MAI), however the [002] peak occurring at 26.2° 2θ is only very small, indicating a very low concentration of inactive carbon build up over time. Interestingly the Yb(4)Ni(10)/MAI spent sample shows an amorphous region from 20-35° 2θ, which is most likely a result of a high concentration of amorphous carbon types (Cₐ) deposited during the reaction across the material.
Figure 5.20 shows the XRD patterns for the spent Ni(10)/SiO2 SG, Yb(1)Ni(10)/SiO2 SG and Yb(4) Ni(10)/SiO2 SG materials. Whilst there are strong crystalline Ni peaks in the undoped material (Ni(10)/SiO2 SG), occurring at 44.5 and 51.9° 2θ, representing the [111] and [200] Ni crystal planes, the spent samples with Yb loading (Yb(1)Ni(10)/SiO2 SG and Yb(4) Ni(10)/SiO2 SG) show only very small peaks for this phase in comparison.

Interesting is the fact that there are also only very minor observable NiO peaks in the samples with Yb loading occurring at approximately 37.3° 2θ, indicating most of the Ni is neither in elemental (Ni₀) or simple oxide (NiO) form, but rather bound in a unique way within the support in these samples, obviously as a direct affect of the addition of Yb.
Whilst an excess of graphitic type carbon can be observed in the spent un-doped (Ni(10)/SiO₂ SG) sample; with a large peak occurring at 26.0° 2θ, only a small peak is observed at the same angle in the sample with 1% Yb (Yb(1)Ni(10)/SiO₂ SG), and an even smaller peak at the same angle in the sample with 4% Yb (Yb(4)Ni(10)/SiO₂ SG). This indicates there is less inactive carbon deposited overall on the surface of the Ni(10)/SiO₂ SG catalysts with increasing Yb loading during catalysis of the reaction.

Figure 5.21: Figure 4.10: XRD of spent Yb(1)Ni(10)/SiO₂ SG, Yb(4)Ni(10)/SiO₂ SG and Ni(10)/SiO₂ SG catalysts
Figures 5.22 and 5.23 show the TEM images for the spent Yb doped Ni(10)/MAI and Yb doped Ni(10)/SiO₂ materials. Figure 5.22a and 5.22b show an overview of the spent Yb(1)Ni(10)/MAI and Yb(2)Ni(10)/MAI catalysts. These images provide good evidence that there was very limited inactive carbon deposition across the catalyst material over the reaction period, as it can be seen that there is a distinct lack of graphitic carbon present across the image. The distinct morphology of the mesoporous support can be observed, with some small areas of greater density prominent as the Ni particles; which are still well distributed. Figure 5.22c and 5.22d show the spent Yb(3)Ni(10)/MAI and Yb(4)Ni(10)/MAI catalysts respectively. It can be seen that there is some observable graphitic carbon across these spent materials, appearing in the form of wormlike structures, although these structures are irregular in diameter (from 9 – 15 nm), and in only a small concentration. There are Ni particles observable as dense points still well distributed throughout the support. For comparison Figure 5.22e presents an overview of the spent undoped (Ni(10)/MAI) catalyst. It can be seen that there is a greater concentration of graphitic wormlike carbon which has grown from the surface of the material, and several of the Ni particles seem to have dislodged from the support; where they can be seen to be attached to the terminals of the carbon. This would account for the difference in stability between the undoped material and the Yb doped materials; where the Ni particles are more strongly bound to the support when Yb doping is present, maintaining a well distributed active phase across the reaction period, whereas a small percentage of the Ni particles in the undoped material are free to sinter and migrate during the time-on-stream, inherently leading to a loss of reactant conversion.
Figure 5.22: TEM images of spent; a) Yb(1)/Ni(10)/MAI; b) Yb(2)/Ni(10)/MAI; c) Yb(3)/Ni(10)/MAI; Yb(4)/Ni(10)/MAI; and e) undoped Ni(10)/MAI materials after 900 mins time on stream
Figure 5.23a shows the spent Yb(1)Ni(10)/SiO₂ SG material subsequent to dry reforming activity analysis listed in the activity analysis sections. The spent material can be seen to have maintained its high porosity and high distribution of Ni particles during the reaction period, indicating a high thermal stability and strong active particle-support interaction. A significant concentration of graphitic carbon can be observed in the form of wormlike nanotubes protruding from the surface of the support in the above mentioned material. The spent Yb(4)Ni(10)/SiO₂ SG catalyst is presented in Figure 5.23b. It can be seen that there is a decreased concentration of graphitic carbon nanotubes within this spent material which also appear to be less regular in diameter (between 10 – 30 nm) than across the Yb(1)Ni(10)/SiO₂ SG catalyst mentioned above. There are more distinct Ni particles which can be seen throughout the bulk of the support compared to the spent material with low Yb loading. The increase in observable Ni clusters may account for the increase in activity of the materials loaded with a greater concentration of Yb (as observed in the activity section of the chapter). There are several Ni particles that appear to have been separated from the support within this sample which could explain the slightly higher loss of activity over time. Although this is significant within the series of Yb doped materials with various concentrations of Yb added, all doped Ni(10)/SiO₂ SG samples far outperformed the undoped (Ni(10)/SiO₂ SG) catalyst.
The amount of carbon deposited on the spent catalysts during the activity test (see pages 188-197) was investigated using TGA. The rate of carbon deposition on the spent catalysts was determined from the total weight of inactive carbon species detected by TGA (above 450 °C) compared to the time-on-stream, per gram of catalyst and is listed in Tables 5.8 and 5.9 for the Yb doped Ni(10)/MAI and Ni(10)/SiO₂ SG materials. Table 5.8 reveals that the carbon deposition rate was similar across all Yb doped Ni(10)/SiO₂ SG catalysts and
the undoped Ni(10)/MAI during the 15 h on stream. These rates were very low, and
deemed to be less than $6.6 \times 10^{-4}$ in the materials loaded with 1 and 2 wt % Yb, where this
represented less than 1 % wt carbon formation over the full testing period.

Table 5.9 shows that the carbon formation in the Yb doped Ni(10)/SiO$_2$ materials was also
less over the 15 h reaction period compared with the undoped (Ni(10)/SiO$_2$ SG) material.
A decreased carbon deposition could also be noted in the materials with greater Yb
concentration (3 and 4 wt %). The carbon deposition rate in these materials was greater
than in the Yb doped Ni(10)/MAI materials, which is consistent with the increased acidity
of the support (see section 4.1)

Table 5.8: Rate of carbon formation over time across Yb doped Ni(10)/MAI and undoped Ni(10)/MAI catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Rate of C Formation ($g_{\text{carbon}}/g_{\text{cat}}/\text{Hr}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(10)/MAI</td>
<td>$6.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>Yb(1)Ni(10)/MAI</td>
<td>$&lt; 6.6 \times 10^{-4}$</td>
</tr>
<tr>
<td>Yb(2)Ni(10)/MAI</td>
<td>$&lt; 6.6 \times 10^{-4}$</td>
</tr>
<tr>
<td>Yb(3)Ni(10)/MAI</td>
<td>$6.7 \times 10^{-4}$</td>
</tr>
<tr>
<td>Yb(4)Ni(10)/MAI</td>
<td>$6.7 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
Table 5.9: Rate of carbon formation over time across Yb doped Ni(10)/SiO₂ SG and undoped Ni(10)/SiO₂ catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Rate of C Formation (g_{carbon}/g_{cat}/Hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(10)/SiO₂</td>
<td>2.4 x 10⁻²</td>
</tr>
<tr>
<td>Yb(1)Ni(10)/SiO₂ SG</td>
<td>1.2 x 10⁻²</td>
</tr>
<tr>
<td>Yb(2)Ni(10)/SiO₂ SG</td>
<td>1.6 x 10⁻²</td>
</tr>
<tr>
<td>Yb(3)Ni(10)/SiO₂ SG</td>
<td>8.5 x 10⁻³</td>
</tr>
<tr>
<td>Yb(4)Ni(10)/SiO₂ SG</td>
<td>4.4 x 10⁻³</td>
</tr>
</tbody>
</table>
5.5 References

(14) Booth, J. RMIT University - Personal Communication 2012.
This chapter concludes the research outlined in this Thesis by summarising all major findings within the work. The future of research in this area is discussed in terms of relevant questions which were outside the scope of the research but relevant to the materials presented, as well as the possible paths for the further optimisation of catalysts in the dry reforming reaction.
6.1 Summary of Findings

The potential renewable fuel source that biogas offers is of great importance, especially due to the rapid depletion of fossil fuels. The dry reforming reaction is capable of converting the primary components of biogas into useable products, but remains a non-viable option over large scales, as an effective catalyst has not been developed which shows a high enough activity and stability over time for economic practicality of the reaction. By catalysing the dry reforming reaction with more effective catalytic materials, research into this process is effectively driving towards the use of lower operating temperatures, whilst maintaining a high conversion of both CO₂ and CH₄ to high energy syngas with a product ratio close to unity. Research and development on catalysts for use in the dry reforming of methane is therefore critical in order for the efficient use of biogas in industry to be achieved.

The research presented in this thesis investigated the use of several new Nickel based materials for catalysing the dry reforming reaction. The following conclusions were drawn based on the results obtained from these investigations:

- Ni-incorporated mesoporous alumina (MAI) materials with different Ni loading (7, 10 and 15 wt %), prepared by a template assisted hydrothermal synthesis method, showed a small Ni particle size (9.8-18.6 nm) with a high distribution, both across the outer surface of the support and within the highly controlled pore structure.

- Ni/MAI materials showed a notable increase in activity and stability when catalysing the dry reforming reaction at relatively low reaction temperature (700°C). The most active
catalyst tested (Ni(10wt%)/MAI) also showed a very high stability over 200 h at 800°C compared to a Ni(10wt%)/γ-Al2O3 prepared using a wet-impregnation method which had a significant loss in activity after only ~4 hours of testing. The high stability of the Ni/MAI materials prepared by the template assisted method was most likely due to the Ni nanoparticles in these catalysts being highly stable towards migration / sintering under the reaction conditions used. The low susceptibility of the Ni nanoparticles in these catalysts to migration / sintering was related to a strong Ni-support interaction the ‘confinement effect’ of the mesoporous channels on the active metal particles. The Ni/MAI catalysts had significantly lower amounts of inactive carbon deposited compared to the catalyst prepared using the co-precipitation method.

- Ni-incorporated silica sol-gel (SiO2 SG) materials with various Ni loading (10, 20 and 30 wt %), prepared using in-situ deposition of Ni with the preparation of a sol-gel with increased pore size, showed a decreased Ni particle size (to less than 13.7 nm) with increased distribution over a similar material prepared by wet-impregnation / precipitation technique. This was most likely due to the increased surface area (from 238 m2/g up to 264 m2/g) and pore distribution within the SG materials, effectively trapping the Ni particles within the pores of the support.

- It was found that all Ni/SiO2 SG materials showed a comparable initial activity and very high stability over 15 h reaction period (700°C, 52000 mL.h⁻¹.g⁻¹ GHSV) compared to the Ni(10 wt %)/SiO2 prepared using a wet-impregnation method, which lost all ability to catalyse the reaction after a very short testing time (6 h). The high activity and stability of the Ni/SiO2 SG materials was most likely due to the increased resistance to sintering of the small, well dispersed Ni nanoparticles.
- Ni(10 wt %)/MAl and Ni(10 wt%)/SiO₂ SG materials with different Yb doping concentrations (1 – 4 wt %) were prepared by in-situ deposition of Yb and Ni to support preparation. Based on the characterisation results obtained it was proposed that the role of the added Yb was to ‘seed’ the nucleation of small, well dispersed Ni particles across the material, which indirectly showed an increased Ni-support interaction.

- The Yb doped materials showed a further increased conversion of CO₂ and CH₄ over the whole 15 h reaction time over un-doped materials, losing only 0 - 1.51% conversion of reactants in the Yb doped Ni/MAl materials, and 0.35 - 1.88% in the Yb doped Ni/SiO₂ SG materials over time. The further increased activity and stability of the Yb doped Ni/MAl materials were most likely due to the decreased Ni particle size and increased Ni-support interaction observed in these materials based on the characterisation results obtained, where strongly bound spinel Ni structures (NiAl₂O₄) formed in the materials. The increased stability of the Yb doped Ni/SiO₂ SG materials were most likely related to the slightly increased Ni-support interactions occurring within these catalysts, and the smaller active metal particle size observed in these materials. Both Yb doped Ni/MAl and Ni/SiO₂ materials showed a decreased inactive carbon deposition over time compared to the undoped materials.
6.2 Future Research

Considering the high activity and stability of the dry reforming catalysts found in this research the possibilities for further exploration into these new materials is numerous, including:

- Further research into the use of various dopants in Ni/MAI and Ni/SiO$_2$ SG materials, and the beneficial effects that these may have on activity and stability within the dry reforming reaction, including investigations into other ‘seeding’ elements which improve the distribution and Ni-support interaction of the materials, and

- Studies on active metals other than Ni being used on high surface area mesoporous alumina and silica sol-gel supports as catalysts.

Further, the interesting beneficial doping effects of the lanthanide Yb should be explored across various other previously reported materials that show promise as catalysts within the dry reforming reaction.

In general, whilst it is generally accepted that materials that have a high dispersion of small, well anchored active particles results in improved dry reforming catalytic ability, there are several areas which remain unclear and therefore need further investigation in understanding of the reaction, including:
• Effect of specific active metal particle sizes on carbon deposition type (and overall stability) in the catalysts,

• Effect of specific active metal crystal planes on carbon deposition type, and

• Effect of specific active metal-support interaction on carbon deposition type.

With the rapid development of novel materials preparation procedures and the improvement of characterisation techniques, the next decade should see a rapid expansion in the knowledge of the role of a catalytic material in such reactions as the dry reforming reaction. Optimisation of materials through an increased understanding of their role as catalysts should also result in the production of materials which show far increased conversion and stability in the reaction over those currently reported.
Appendix A

A1: Temperature Measurements of Reactor

Figure A1: Measurements of reactor internal temperature points
Table A1 outlines the measured temperatures at each of the points a-e outlined in the diagram above.

<table>
<thead>
<tr>
<th>Temperature at Point (°C)</th>
<th>Set Temperature (°C)</th>
<th>300</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>700</th>
<th>800</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>300</td>
<td>398</td>
<td>501</td>
<td>601</td>
<td>699</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>299</td>
<td>399</td>
<td>500</td>
<td>602</td>
<td>699</td>
<td>798</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>248</td>
<td>359</td>
<td>536</td>
<td>503</td>
<td>597</td>
<td>671</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>29</td>
<td>39</td>
<td>42</td>
<td>39</td>
<td>46</td>
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<tr>
<td>e</td>
<td>22</td>
<td>37</td>
<td>39</td>
<td>42</td>
<td>35</td>
<td>45</td>
<td></td>
</tr>
</tbody>
</table>

Table A1: Measurements of temperature at reactor internal points

From table A1 it can be seen that under a significant gas flow, when the temperature of the furnace is set to any temperature up to 800°C, the centre of the reactor held within the heating zone of the furnace sits within a minimum variation of the set temperature. This procedure proves that the designated temperature for an experimental analysis of the catalyst material reported in later chapters will be accurate. These measurements subsequently show that the temperature difference across a gradient bed of 20mm will be negligible for further analysis. The measurements towards the end of the reactor show that even under a high flow of gas there is sufficient cooling prior to analysis, even under highly elevated temperatures. The catalyst activity analysis system has been designed so that the only catalysis occurring in the system must be due to the catalyst bed, where no significant elevated temperatures allow further downstream catalysis to occur. It is well
known that stainless steel can catalyse the dry reforming reaction [refs], so therefore it is
of paramount importance that for a correct determination of catalytic activity across a
designed catalyst, there is negligible conversions of reactants occurring anywhere except
the catalyst bed under examination.
To ensure there was no self catalysis of the dry reforming reactants inside the blank
reactor, the thermocouple was removed prior to any further experimental analysis (due to
its stainless steel nature), and a primary blank analysis was carried out with a suitable flow
of reactants.

A2 Blank Dry Reforming Analysis

The reactor was set up as for a regular catalytic analysis; where it was loaded into the heat
zone of the furnace, with the exception that no catalyst material was loaded into the reactor
itself. Quartz wool plugs were still placed into the centre of the reactor where a regular
catalyst bed would sit, and quartz rods were loaded prior to the blank bed as to promote a
suitable mixing of reactant gases before reaching set temperature. CO₂ and CH₄ flow rates
were set at 25 sccm each channel, whilst He carrier was set at 50sccm as to deliver a 1:1:2
ratio of CO₂:CH₄:He across the blank reactor. Prior to analysis a bypass analysis of the
reactant gases was achieved by re-directing the gas mixture with the 4-way automatic
switch located prior to the reactor assembly. The temperature of the furnace was set to
various temperatures between 400 and 900°C, and the gases were allowed to pass through
the reactor at temperature for a period of 1 h at each set temperature prior to GC analysis.

Bypass analysis of the reactant gases showed peak areas of CO₂ and CH₄ of 7022559 and
5124859 units respectively as measured by the TCD detector and output by the Shimadzu
software. Figure A2 represents the individual peak areas of the gases measured at the set temperatures after being allowed to flow through the reactor for 1 h.

It can clearly be seen that there is no conversion of either CO₂ or CH₄ in the reactor when no catalyst is present, even at highly elevated temperature, meaning that for future catalyst activity analysis there is negligible conversion of reactants to products occurring anywhere but the catalyst bed. This ensures that maximum repeatability across all subsequent analysis gives a high accuracy of reported results with no interference.
Appendix B

Figure B1: TPR of pure NiO
Appendix C

Figure C1: Ni particle count from TEM images of Yb(1)/Ni(10)/MAI

Figure C2: Ni particle count from TEM images of Yb(2)/Ni(10)/MAI