Carbon mitigation in the dry reforming of methane

Thesis presented for the award of doctor of philosophy (PhD)

By

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Abstract

Dry reforming of methane is a technique to produce syngas from biogas or CO\textsubscript{2}-rich natural gas at high temperatures, generally over a Ni or Co catalyst. Syngas produced by dry reforming has a H\textsubscript{2}/CO ratio around 1, which makes it CO-rich, and therefore suitable for the production of pure CO or Gas-to-Liquid processes. Up to date, large-scale application of dry reforming has been limited, with the main barriers to industrial deployment being the highly endothermic reaction pathway that requires high operating temperatures to reach acceptable conversion levels in the presence of alumina-supported nickel catalysts and the formation of high-strength carbon whiskers catalysed by nickel crystallites, which are destructive to catalyst pellets. A thermodynamic analysis of the reaction pathway is first performed while relaxing the conventional assumption that graphite is the phase of carbon that forms. The effect of catalyst dispersion and the precursors to coking are identified, and the effect of sintering on carbon deposition is therefore better understood. Optimized temperature-pressure-time trajectories for the reactor operation show that pressure must be gradually increased with time on stream to avoid the carbon limits as the catalyst sinters.

In parallel, two catalyst systems are developed and tested: Supported molybdenum and nickel-molybdenum nitrides are synthesized and characterized. The nitrides are observed to perform well in terms of carbon resistance due to enhanced CO\textsubscript{2} adsorption by the support, but to deactivate within 7 hours on stream, with a phase transition to an oxide/carbide phase that provides terminal activity. In comparison, the tested trimetallic Ni-Co-Ru catalysts have both a higher activity (>90% conversion) and an excellent stability, but exhibit a slightly higher carbon formation rate. Synergetic effects in the Ni-Co system stabilize the active phase by a hydrogen spill-over effect and coking is reduced by the oxophilicity of Co. Higher activity is exhibited by Ni-rich catalysts, and Ru is shown to improve the reducibility and coke resistance by 51% at the expense of activity.

Experimental work in catalysis confirms the identified trade-off between activity, stability and ease of activation. Eventually, a combination of catalyst design and operating conditions optimization brings the process one step closer to industrial application by resolving this important limitation associated with dry reforming.


Declaration

This thesis is based on a joint research project between the University of Limerick and the American University of Beirut. I declare that the work in this thesis is my original research and that it has not been submitted anywhere for any award. In part of Chapter 1, I use research material from an article I co-authored with Mr. Jad Touma (AUB) with whom I shared the literature review and discussion tasks for the catalyst design section; and in Chapter 3, my optimization algorithm uses an artificial neural network model developed by Mr. Mazen Azzam (PhD candidate, University of Limerick). Where other sources of information have been used, they have been duly acknowledged.

Nicolas Aramouni

14/07/2020
This thesis is dedicated to my grandfather, Georges Tabbal (1914-2011), a firm believer in the value of education who dedicated his life to pharmacy and the teaching of natural sciences.

His legacy of humbleness, resilience and commitment to the pursuit of knowledge lives on.

May this dedication immortalize his memory.
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Chapter 1: Dry reforming of methane: chemistry, catalysis and industrial outlook

1.1: Syngas and its production

Syngas is a mixture of H$_2$ and CO that can be produced in varying ratios depending on the application and the production process. It is used as an intermediate in the production of many bulk chemicals such as methanol (Aasberg-Petersen et al., 2016), ammonia (Noelker, 2010), pure hydrogen (Roostrup-Nielsen, 2002) and liquid fuels (Navas-Anguita et al., 2019). Theoretically, syngas production through the reforming process involves a reaction between a hydrocarbon and an oxidant, and the majority of industrial reforming processes use methane or natural gas as feedstock. The main competitor to natural gas reforming in terms of global syngas production is coal gasification as shown in Figure 1-1, but a shift towards natural gas is predicted (Khan, 2019), although many believe coal will lead the syngas market in the upcoming 5-year period (2020). End-products in the syngas value chain consist in majority of ammonia for fertilizer manufacturing, methanol and liquid fuels through gas-to-liquid (GTL) and Fischer-Tropsch synthesis (Figure 1-2). The worldwide syngas production for the year 2020 is estimated at 245557 MWth (Thermal megawatts) with a cumulative annual growth rate of 10.5% forecasted, and is estimated to reach 406860 MWth by 2025. A strong increase in the demand for syngas derivatives is expected to occur in 2020 due to the COVID-19 pandemic creating an increased need for sanitation, hygiene and pharmaceutical/medical products (2020).

There are six basic types of reforming processes (Gangadharan et al., 2012), but syngas production on an industrial scale has been traditionally dominated by steam methane reforming (SMR). The main reactions in the steam reformer are the (1) steam reforming reaction, (2) reverse water-gas shift reaction, and (3) methanation reaction (Xu and Froment, 1989). During the process, natural gas at high pressure (20-30 bars) and high temperatures (inlet 450-650°C and outlet 800-950°C) (Roostrup-Nielsen, 2002) reacts with steam (steam/methane ratio between 1-5) in heated packed beds (tubular catalytic reactors) typically inside a furnace (Dybkjær, 1995). Typical industrial catalysts for steam reforming are 16-20% NiO supported on alumina or calcium aluminate, shaped into pellets of 3/8” to 5/8” in size that are reduced to yield Ni as active phase in-situ.

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \rightleftharpoons \text{CO} + 3\text{H}_2 \\
\text{CO} + \text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + \text{H}_2 \\
\text{CH}_4 + 2\text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + 4\text{H}_2
\end{align*}
\]

$\Delta H_{298}^\circ = 206.1 \text{ kJ/mol}$

$\Delta H_{298}^\circ = -41.15 \text{ kJ/mol}$

$\Delta H_{298}^\circ = 165 \text{ kJ/mol}$
Figure 1-1: Syngas feedstock distribution (Khan, 2019)

Figure 1-2: Syngas end-product distribution (Khan, 2019)
SMR produces syngas with an H₂/CO ratio of 3, which can be further increased by the use of downstream shift reactors, in which steam is added to the syngas. The water-gas shift reaction produces extra H₂ and converts the produced CO into CO₂ which is separated. This mature technology is attractive when hydrogen-rich syngas or pure hydrogen is to be produced at large scale, such as in the synthesis of ammonia. The expected H₂/CO ratio for the steam reforming reaction is 3:1, but the actual ratio at the outlet of the reformer is slightly lower due to the consumption of hydrogen by the reverse water-gas shift reaction. To account for the reverse water-gas shift reaction when using syngas as a precursor for the synthesis of other intermediate chemicals or end products such as methanol or dimethyl ether, a stoichiometric module, generally denoted as M, is used to assess the syngas composition.

![Haldor-Topsoe’s TITAN RC-67 steam reforming catalyst](image)

Rostrup-Nielsen and Christiansen (Rostrup-Nielsen and Christiansen, 2011) derived the module M for methanol synthesis from a simple stoichiometric calculation as an example, assuming a total completion of the reverse water-gas shift reaction. Assuming initial amounts of a, b and c for CO, CO₂ and hydrogen respectively, the final amounts of hydrogen and carbon monoxide are c-b and a+b. Hence the module M is equal to

\[ M = \frac{H_2 - CO_2}{CO + CO_2} \]

A list of stoichiometric modules for different processes is given by Rostrup-Nielsen in (Rostrup-Nielsen, 2002), and a list of target H₂/CO ratios for different syngas end uses is shown in Table 1-1 (Hernandez and Martin, 2018).

<table>
<thead>
<tr>
<th>Desired target process</th>
<th>Optimal H₂/CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>2.5</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 1-1 Optimal syngas ratio for different end products
Fischer and Tropsch, back in 1928, were the first to conduct studies on the reforming reactions driven by the need to secure alternatives sources for the chemical and petrochemical industries. They have studied the dry (CO\textsubscript{2}) reforming of methane (DRM) over various metals (cobalt and nickel) for the synthesis of long-chain hydrocarbons (Fornasari, 1995). In 1930, the first tubular reformer using natural gas was installed by Standard Oil in Baton Rouge (Cavani, 1991). Nowadays, with the great improvements in catalysts and the availability of enhanced materials for the manufacturing of reforming reactors, the production of syngas became strongly flexible and adaptable to the nature and scale of any process that uses syngas as an intermediate (Ahmadpour and Taghizadeh, 2015, Al-Sobhi and Elkanem, 2015, Hu, 2010). In applications where lower H\textsubscript{2}/CO ratios are needed, steam reforming becomes less attractive due to its high capital and energy costs, in addition to the production of excess hydrogen that adds complexity to downstream separation. CO\textsubscript{2} (dry) reforming, auto-thermal reforming (ATR) and catalytic partial oxidation (CPO) are the most common processes being explored and utilized for syngas productions with different H\textsubscript{2}/CO ratios. All these processes suffer from the same deactivation mechanisms and high process costs (Hu, 2010): typical Ni/Alumina catalysts employed in most reforming processes are limited by transport resistances (low effectiveness parameters), susceptibility to poisoning by sulfur and heavy metals, sintering and coking (Sehested, 2006). The choice of the suitable technology depends on many parameters including the scale of the operation and the desired product stoichiometry (Nahar, 2013).

Autothermal reforming is the most competitive process to steam reforming on an industrial scale when a lower H\textsubscript{2}/CO ratio is needed. Autothermal reforming is a modern technique used to produce syngas with a lower H\textsubscript{2}/CO ratio than steam reforming but without the need for a heat source as the process is exothermic. It is carried out by mixing the hydrocarbon feedstock (methane), with steam and air or oxygen and burning the mixture (H\textsubscript{2}O/C and O/C ratios typically around 1-2 and 0.5-1 respectively (Chen et al., 2010)) in a specifically designed burner over a catalytic bed at high temperatures and pressures. ATR can be used as a standalone unit to produce syngas or as a secondary reformer to complete the conversion of a partially reacted gas from a steam reformer (primary reformer) (Dybkjær, 1995), which allows the production of syngas with H\textsubscript{2}/CO close to 2. Typical reactor outlet conditions for autothermal syngas are a pressure of around 50 bar and temperatures around 950-1100\degree C (Zahedinezhad et al., 2009, Rice, 2007, Dybkjær, 1995). Generally, reformers are set up as part of a larger process train (methanol or ammonia synthesis) to allow for better heat integration (Figure 1-4, Figure 1-5).
The autothermal reforming process can be divided into two steps: the first step is the substoichiometric combustion of methane or other hydrocarbons in the burner and combustion section of the reformer, also known as partial oxidation.

$$\text{CH}_4 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{CO} + 2\text{H}_2 \quad \Delta H_{298K} = -36 \text{ kJ/mol}$$

The second step in the autothermal reforming process is the equilibration of the combusted gas over a catalytic bed, through which reforming, oxidation, water-gas shift and carbon formation reactions occur (Rostrup-Nielsen, 1993),

$$\text{CO} + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{CO}_2 \quad \Delta H_{298K} = -286 \text{ kJ/mol}$$

$$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{H}_2\text{O} \quad \Delta H_{298K} = 244 \text{ kJ/mol}$$
An overview of conventional and non-conventional reforming techniques are summarized by Alves et al. (Alves et al., 2013) in their overview of hydrogen production technologies from biogas in fuel cell applications.

1.2: Dry reforming

1.2.1: Chemistry

The dry reforming of methane (DRM) converts methane and carbon dioxide, identified as the world’s most abundant greenhouse gases (GHG) (Intergovernmental Panel on Climate, 2014), to syngas with a H₂/CO molar ratio close to 1 (Lercher et al., 1999, Rostrup-Nielsen, 1984). Despite the common claim that this process has the potentials to mitigate the environmental challenges associated with GHG emissions and to convert biogas and natural gas to syngas (Lunsford, 2000, Bradford and Vannice, 1999, Lucrédio et al., 2012), its positive environmental impact is limited (Mortensen and Dybkjær, 2015).

Still, the lower H₂/CO ratio syngas produced is convenient for the production of hydrocarbons via Fischer-Tropsch synthesis (Ross, 2005, Gallego et al., 2008, Inderwildi et al., 2008), in addition to the synthesis of oxygenated chemicals (Wurzel et al., 2000, Olsbye et al., 1997). The main reaction governing DRM is:

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

Being an extremely endothermic reaction (Brungs et al., 2000, Wang et al., 1996), DRM requires high operating temperatures, usually in the range of 900-1273 K, to achieve the desirable conversion levels. The reaction is favored at low pressures as dictated by stoichiometry. The positive effects of high reaction temperatures, low pressures and high CO₂/CH₄ molar ratios on the conversion levels were investigated and confirmed in several studies (Nikoo and Amin, 2011, Li et al., 2008, Luyben, 2014).

DRM is not however considered an industrially mature process. The highly endothermic reaction, coupled with rapid carbon formation eventually leads to catalyst deactivation, which has hindered its large scale commercialization (Navarro et al., 2006, Lavoie, 2014, Ginsburg et al., 2005, Bradford and Vannice, 1996, Pakhare and Spivey, 2014).

1.2.2: Industrial experience

So far, there has been limited success in producing commercial quantities of CO-rich syngas from dry reforming, mostly due to the severe carbon formation. Practically, a H₂/CO ratio below 1.3 is hardly reachable because a minimum amount of steam needs to be co-fed with CO₂ to avoid carbon formation (1998). Full-scale monotube pilot plant tests performed in Texas on a sulfur passivated Nickel catalyst have shown that the absence of steam as co-feed (purely dry reforming) quickly causes carbon buildup at the inlet of the bed, where the hydrocarbon partial pressure is elevated, from cracking reactions that occur on the catalyst (Mortensen and Dybkjær, 2015). Steam reforming of CO₂-rich natural gas is a similar challenge that has been the subject of considerable research efforts (Mortensen and Dybkjær, 2015, Jafarbegloo et al., 2015, Freitas and Guirardello, 2014, Simakov et al., 2015).

The earliest reforming process that produces a H₂/CO close to 1 successfully and economically is the SPARG process developed by Haldor-Topsoe AS (Roussiere, 2013).
In this process analogous to steam reforming, a nickel catalyst is partially poisoned by feeding a H₂S/H₂ mixture continuously so that small ensembles on the surface of the Ni metal particles are delimited by S atoms. This ‘ensemble control’ theory developed by Rostrup-Nielsen (Rostrup-Nielsen and Alstrup, 1988) allows the reforming reactions to take place while inhibiting carbon formation, even in conditions where the thermodynamics are favorable for coke formation (Rostrup-Nielsen and Alstrup, 1988). Steam and CO₂ are co-fed with methane to produce syngas with H₂/CO ratio ranging from 0.7 to 1.9 depending on the ratio and reactor conditions.

The Calcor process by Caloric Anlagenbau GmbH is the most successful industrial application of dry reforming to date. This process has been developed for on-site production of pure CO for the production of many chemicals including phosgene to compensate for the limited transportation availability of CO due to its toxicity. It is commercialized as small prefabricated plants that produce 40–800 Nm³/h of CO with a purity of 99.5% or higher. Two versions of the process are developed:

- In the Calcor Standard process, natural gas or LPG is first desulphurized by mixing with H₂ and flowing over a bed of ZnO where the hydrogenated sulphur compounds are removed by adsorption. The cleaned gas is then preheated and mixed with CO₂, then is sent to reformer tubes inside a fired furnace. The reformer uses a mixture of catalysts with different activities and shapes, and operates barely above atmospheric pressure to reduce reforming severity and avoid carbon. The produced syngas is cooled down, compressed and sent to an absorber tower where CO₂ is removed by absorption with monoethanolamine (MEA), methyldiethanolamine (MDEA), or other amines. Flue gas leaving the furnace is also sent to an auxiliary absorber to remove CO₂. The rich amine phases from both absorbers are mixed together and sent to a stripper to recover the CO₂ which is sent to a dephlegmator (flash drum) to remove condensate and is used in the reformer again. The cleaned syngas (now composed of roughly 70% CO and 30% H₂) is sent to a membrane or cryogenic purification process to produce pure CO.
The Calcor Economy is a simplified variant of the Calcor Standard process in which the CO₂ recovery section is omitted. It is used when an external CO₂ source is available. Instead of absorption with amines, the product syngas is instead compressed and sent to a two-stage membrane separation process to extract CO. The tail gas from the first membrane stage, which is rich in H₂ and CH₄ from reformer slip-through (unreacted methane that made it through the catalytic bed), is sent to the furnace burner. CO-rich tail gas from the second membrane stage is recycled to the separation process to increase CO recovery.
In the throughput ranges in which it is available, the Calcor processes become cost-efficient at CO capacities above 200 Nm$^3$/h, with production costs ranging between 0.2 and 0.4 USD/Nm$^3$ CO (using the 2001 value of the US dollar) depending on the choice of process layout and purification technology. Economies of scale in larger plants are not achieved due to the high compression cost and low reformer severity limiting throughput (1998).

Recently, Linde Engineering started developing a dry reforming process for commercial production. They developed two catalysts based on nickel and cobalt and proved their success under typical reactor conditions in the pilot reformer facility in Pullach (Germany). The process under development necessitates the use of steam as co-feed with CO$_2$ to avoid the formation of coke, at the risk of oxidizing the catalyst. Linde’s two catalysts have been shown to remain active for 1000 hours on stream (Tullo, 2016), and the group is in the process of upscaling the catalyst for commercial production.
1.2.3: Integrating the dry reformer: process developments

As the dry reforming technology is getting closer to large scale commercialization, current process engineering research is focused on assessing the technical and economic feasibility of integrating the dry reformer in larger process to improve energy efficiency, cost and environmental impact in the production of end-products.

The first integration possibility is the production of syngas via 2-step reforming with DRM replacing either the steam reformer or the autothermal reformer. The absence or low quantity of steam required in the dry reformer results in a smaller reactor volume required for the same hydrocarbon throughput, and lower energy requirements as steam generation is minimized. Hernandez et al (Hernández and Martín, 2016) noted that partial oxidation is not desirable to combine with DRM as all the methane has to be partially oxidized to yield high H₂/CO ratio, and this would leave the CO₂ unreacted. Gangadharan et al. (Gangadharan et al., 2012) compared the economic and environmental performance of a steam reforming process and a two-step steam/dry reforming process for a feed of 1850 kmol/h of methane. In their combined steam/dry reforming process, the natural gas is first cleared of acid gases and H₂S by absorption with diethanolamine, then goes through a steam reformer. The raw syngas produced is then sent to a CO₂ membrane where the CO₂ is removed, then the syngas is dewatered in a flash drum before being mixed with the CO₂ removed in the membrane to go through a final dry reforming step. The capital cost of the combined steam/dry reforming process was found to be about 10% higher than that of the steam reforming process. The environmental impact of the was assessed through the Waste Reduction algorithm (WAR) developed by the US EPA, that assesses quantitatively the environmental impact based on four main impact categories: human toxicity, ecological toxicity, regional atmospheric impact and global atmospheric impact (Young and Cabezas, 1999). The environmental impact of both processes was comparable, with only a marginally lower global warming potential for the combined SRM/DRM process. It was identified that a better catalyst that could operate efficiently...
at lower temperatures would improve the environmental impact of the combined process by decreasing the heat requirement.

Tri-reforming of methane has been introduced as a technique to offer flexibility in the $\text{H}_2/\text{CO}$ ratio and to reduce the heat requirement of the reforming process by reacting methane with steam, oxygen and $\text{CO}_2$ so that steam reforming, dry reforming and oxidation reaction carry out. The exothermic oxidation reactions supply part of the heat to drive the endothermic reforming reactions, and the presence of $\text{O}_2$ and $\text{H}_2\text{O}$ decreases coking on catalyst at the risk of oxidizing it. Swirk et al. (Świrk et al., 2017) studied the tri-reforming process as a chemical energy storage, and found that the heat requirement is reduced especially if $\text{CO}_2$ can be used directly without requiring an amine absorption process. Maximum $\text{CO}_2$ emissions are avoided when methanol is produced from tri-reforming syngas. Farniaei et al. (Farniaei et al., 2014) proposed a thermally coupled tri-reformer and dry reformer in a two concentric-tube reactor: Tri-reforming in the outer annulus provides the heat required to drive the dry reforming reaction pathway inside the center tube (recuperative coupled reactor). Their simulation showed that it was possible to reach conversions of 93% in the tri-reformer and 63% in the dry reformer without the need for a heat source, while producing two syngas streams of different qualities.

Given the high CO content of the syngas produced by dry reforming, methanol and Fischer-Tropsch syntheses are the most potent options for integration of the dry reformer in process trains beyond the 2-step reforming process. For example, the syngas unit in a typical Fischer-Tropsch train is the most expensive investment in the process, constituting approximately 40% of the overall capital expenditure (Fazeli et al., 2018), and therefore integration of dry reforming in the syngas section of such processes can potentially produce strong savings on capital cost. Furthermore, the higher temperatures in the dry reformer constitute a high quality heat source, and the low water content in the reformed syngas can decrease the heat duty to condense moisture in syngas cleanup stages.

Hernandez et al. (Hernández and Martín, 2016) studied the reforming of biogas to methanol via dry reforming or combined steam/dry reforming and optimized the process through a superstructure optimization technique. The authors optimized the superstructure in terms of an economic and an environmental objective function. The process model is formulated as a NLP problem and solved for both the economic and environmental objective functions. Both objective functions gave close economic and environmental objective results (cost and carbon footprint). Surprisingly, the optimization suggests that the dry reformer be operated at 1 bar, as this guarantees high conversion and no compression costs. This is because the objective function only considers operating expenses. A lower reactor pressure would imply a larger reactor due to lowered throughput. Economic optimization suggests the use of dry reforming without the addition of steam. This plant produces methanol at a cost of 1.75$/gal which is much higher than the current benchmark price of 0.9$/gal. CAPEX was estimated at 46 million dollars. Mondal et al. (Mondal et al., 2016) proposed another process study in which they assess the economics of methanol synthesis via syngas from dry reforming, and compared it with the traditional steam reforming to methanol process. Both the steam and dry reforming processes cool down the syngas after the reformers and send it to a flash drum.
to remove excess water. In the dry reformer, a higher temperature change is required as the syngas is hotter, but the lower water content decreases the latent heat duty for the cooler. The economic assessment was performed for 5000 MTPD basis. At the same methanol production output, the dry reforming option was found to consume less methane and no water. However, there was an increase in electricity consumption by roughly 500% and no steam was internally generated, which necessitated the purchase of steam from external sources. The DRM process gave a lower production cost of 123$/MT of methanol (0.36 $/gal) versus 140 for SRM (0.41$/gal), and had a return on investment of 33% compared with 25% for SRM. Weisberg et al (Wiesberg et al., 2016) also compared two processes to produce methanol from CO₂: hydrogenation and bi-reforming (combined steam/dry reforming) on an economic and environmental basis. The bi-reforming concept proposed by the authors combines the reforming reactions and the water-gas shift reaction in the same reactor. Two vertical integration (supply chain) scenarios were considered: a backward-forward integration with the raw materials supplier and methanol consumer plant (no raw material nor product storage is required), and a scenario with only backwards integration which requires 30 days of methanol storage. In the bi-reforming pathway, the integrated scenario was assumed to be non-viable, so only the non-integrated scenario was assessed. Both assessed routes have reduced global warming potentials, and the CO₂ hydrogenation route was found to be more profitable. The reforming route was not able to reduce emissions.

In their study, Roh et al. (Roh et al., 2016) described a framework to guide the design of a CO₂ conversion process based on criteria of demand availability, CO₂ emission reduction feasibility and economic feasibility, in parallel with two executive strategies: product substitution or process substitution. As a case study, a conventional two-step reforming to methanol process is compared with a CO₂ based methanol production process (combined reforming) for a base case of 1500 MTPD of methanol. Combined reforming had a higher capital cost (42 MMS$) compared to the conventional two-step reforming (31MMS$) but lower operating cost, in addition to a lower CO₂ impact and was economically feasible, although flue gas CO₂ emissions were higher.

In terms of integration with Fischer-Tropsch synthesis, Hernandez et al (Hernandez and Martin, 2018) studied and optimized biogas valorization via tri-reforming for Fischer-Tropsch (FT) synthesis, both in the high temperature and low temperature pathways, with biogas being used to operate the burner in their study. The low temperature FT was found to be more profitable. Sensitivity analysis performed on the identification of certain streams as valuable products suggested that when methane-rich biogas can be considered as a sellable product, it should be completely substituted by FT outgas in the reformer burner. Production costs using this process were found to be higher than current fuel production costs, but lower than the final selling price at a production scale of 12MMm³/year of biogas.

A life cycle assessment and simulation of a biogas to FT + power generation plant was performed by Navas-Anguita et al. (Navas-Anguita et al., 2019). The process uses a dry reformer with a catalytic circulating bed coupled with a regenerator, which generates the heat required by the reaction by burning off the carbon formed on the catalyst (this might
be unrealistic due both to the fact the Ni catalyst oxidizes and that whisker carbon irreversibly damages the catalyst). Tail gas obtained after recovering C₁-C₄ gases and heavier fractions of the light FT stream, and fuel gas obtained as residue of the distillation of liquid FT products, are mixed and sent as fuel to the power generation cycle in a combined cycle to produce steam and power. Flue gases are treated with ammonia in a selective catalytic reduction (SCR) unit that reduces NOx.

The study concluded that methane leakage and heat demand in the biogas production were the main sources of impact on the environment. NO emissions in the biogas-to-liquid plant was also identified as a major contributor. The LCA was generally favorable in terms of energy performance, but worse in terms of global warming potential, acidification and eutrophication.

Finally, Fazeli et al. (Fazeli et al., 2018) studied the integration of captured CO₂ from a post-combustion flue gas stream into a Fischer-Tropsch process train both using steam reforming and autothermal reforming scenarios. In their study, steam produced in the FT reactor and leftover steam was used to produce power, and it was shown that the plant produces enough energy to run the CO₂ removal unit for all scenarios considered. The scenario where steam reforming is selected and the process optimized to maximize wax production consumed almost 100% of the produced power in the CO₂ separation unit. Still, in both scenarios, the process was a net carbon emitter.

Integration of the dry reformer therefore has a good potential to improve the economic and environmental performance of the methanol synthesis train compared to the conventional route, but the improvement is dependent on the scale, availability of raw materials and the choice of heat integration and post-reformer separation scenarios. Integration with Fischer-Tropsch can improve the energy efficiency of the process despite a limited economic advantage, but it is nevertheless an attractive scenario that can compete with conventional steam or 2-step reforming.

1.2.4: Thermodynamics, Reaction Mechanisms and Coke Formation

1.2.4.1: Thermodynamics

Compared to autothermal reforming (ATR) and steam reforming (SRM), the dry reforming of methane is the most endothermic reaction. This can be attributed to the fact that CO₂, the oxidizing agent used in DRM, is the most stable compared to oxygen and steam used in ATR and SRM respectively (Lavoie, 2014, Ginsburg et al., 2005, Bradford and Vannice, 1996, Pakhare and Spivey, 2014, James et al., 2011).

Although DRM is mainly governed by the reaction between CH₄ and CO₂, several other reactions can also occur during the process. Nikoo and Amin, (Nikoo and Amin, 2011) presented these different reactions shown in Table 1-2, their equilibrium constants as a function of temperature and carried out the corresponding thermodynamics analysis. The equilibrium composition of the reaction system was analyzed based on the Gibbs free energy minimization method.
The works of Bradford and Vannice (Bradford and Vannice, 1999), Wang et al. (Wang et al., 1996) and Istadi et al. (Istadi and Amin, 2006) also showed that dry reforming is thermodynamically favored at high temperatures.

Nikoo and Amin, (Nikoo and Amin, 2011) identified that methane decomposition (reaction 8 in Table 1-2), carbon monoxide disproportionation (i.e. Boudouard reaction) (reaction 9), hydrogenation of carbon dioxide (reaction 10), and hydrogenation of carbon monoxide (reaction 11) are the four reactions responsible for carbon formation during DRM. Among these reactions, it was found that only methane decomposition is favored at high temperatures, while the other three are favored when operating at reaction temperatures lower than 800 K. Furthermore, it was found that the Reverse Water Gas-Shift RWGS (reaction 2), which is the reaction that leads to a H2/CO ratio less than unity, is dependent on the equilibrium at a certain temperature range and is usually present during DRM.

On the other hand, Wang et al. (Wang et al., 1996) reported that the RWGS and Boudouard reaction will not occur at temperatures exceeding 1093 K, and that the Boudouard reaction and methane decomposition will be mostly responsible for the formation of carbon at temperatures ranging from 830 K to 973 K (Table 1-2).

Zhang et al. (Zhang et al., 2007) reported an increase of the equilibrium constants of methane decomposition and RWGS with temperature and its decrease for the Boudouard reaction.

Concerning the remaining reactions shown in Table 1-2, the oxidative coupling of methane (reaction 3 and 4) were found to be only possible at very high temperatures.
Similarly, the dehydrogenation of ethane (reaction 5) is also favored at high temperatures. On the other hand, the reverse of reaction 6 and 7 are more favored at high temperatures. Conversely, reactions 12, 13 and 14 are favored at any temperature range and reaction 15 is dependent on equilibrium limitations. Finally, due to their exothermic nature, reactions 16 and 17 have the possibility of occurring at temperatures lower than 800 K.

1.2.4.2: Reaction Mechanisms

The mechanism of methane dry reforming on conventional catalyst (metallic particles supported on a metal oxide support) is detailed by Papadopoulou et al. (Papadopoulou et al., 2012b). It can be summarized in four steps as follows:

1. Dissociative adsorption of methane: although the dissociation energy of CH$_x$-H bonds is dependent on the surface properties, it is generally agreed that the dissociation of methane on the catalyst is the rate determining step. Each partially dissociated CH$_x$ species adsorbs preferentially on a site which completes its tetravalency, with CH$_3$ adsorbing on top of metal atoms while CH$_2$ adsorbs between two metal atoms (bridged adsorption). Step sites are more active for methane adsorption and dissociation than close-packed surfaces.

2. Dissociative adsorption of CO$_2$: The surface structure and defects also affect the adsorption and dissociation of CO$_2$, which can occur in three ways: C-only coordination, C and O coordination (Carbon and one oxygen adsorb on the catalyst surface and leave one oxygen atom exposed), or O-only coordination, with both oxygen atoms bonding with the surface metal. The latter two coordination geometries are more favorable towards dry reforming. This step is generally considered fast. CO$_2$ tends to adsorb on the metal-support interface. The presence of Lewis base sites on the support enhances CO$_2$ adsorption: CO$_2$ bending upon adsorption lowers the LUMO of the carbon atom, which facilitates Lewis base attack (electron pair donation to CO$_2$) (Alvarez et al., 2017).

3. Hydroxyl groups formation: Little work is done on the surface reaction mechanisms for dry reforming as compared to steam reforming. However, it is known that the water-gas shift reaction is at quasi-equilibrium, meaning that the surface reactions that are related to it are quite fast. Most developed models predict hydrogen migration from the active metal particle to the support where it forms hydroxyl groups at temperatures below 1073 K.

4. Intermediates oxidation and desorption: Surface oxygen on the metal particle reacts with S-CH$_x$ groups to form S-CH$_x$O or S-CO. Some authors consider the S-CH$_x$O groups to be precursors to CO formation while others assert that adsorbed CO$_2$ forms carbonates that are reduced to CO by carbon on the metal. Other authors claim that S-CO is formed directly without a formate S-CH$_x$O intermediate. Just as for steam reforming, there is no clear consensus about the details of the reaction mechanism on the surface of the catalyst, and the impact of the catalyst nature and operating conditions is also very important. However, in many cases, the formation and/or decomposition of formates S-CH$_x$O to CO and hydrogen is considered the rate determining step, especially knowing that the desorption of CO and hydrogen is fast.
Figure 1-9: Reaction steps for the dry reforming of methane (Papadopoulou et al., 2012a): (a) Dissociative adsorption of CO$_2$ on the metal and metal-support interface respectively. (b) Fast desorption of CO and hydrogen. (c) Formation of surface hydroxyls and oxygen spillover. (d) Surface hydroxyls and oxygen species oxidize hydrogen depleted S-CH$_x$ species and formation of CO and H$_2$.

Other reaction mechanisms have been observed (Mora-Briseño et al., 2019). Generally, catalytic reaction pathways are described by either Langmuir-Hinshelwood-Hougen-Watson mechanism where both reactants adsorb and react on the surface) or Eley-Rideal mechanism (where one reactant adsorbs and reacts with the other in the gas phase). The Mars-van Krevelen mechanism (where the catalyst oxidizes by reaction with a reactant then reduces by reacting with the other reactant, operating in a redox cycle) can also occur on transition metal oxides, and has been observed to drive the dry reforming reaction in transition metal carbides (Alexander and Hargreaves, 2010) and certain spinel structures (Wong et al., 2017). The oxidation-carburization redox cycle for molybdenum carbide is shown below as an example.

\[
\text{Mo}_2\text{C} + 5\text{CO}_2 \rightarrow \text{MoO}_2 + 6\text{CO}
\]
\[
\text{MoO}_2 + 5\text{CH}_4 \rightarrow \text{Mo}_2\text{C} + 4\text{CO} + 10\text{H}_2
\]

1.2.4.3: Coke formation:
Coke deposition on the reforming catalyst is expected due to the high operating temperatures, which raises the molecular energy enough to cleave the C-H bonds in methane. It is therefore desirable to understand the conditions of carbon formation and minimize it. The majority of catalysts used in the reforming industry consist of supported nickel, usually on aluminum oxides. The main problem with these catalysts is that they also catalyze carbon formation reactions (Rostrup-Nielsen, 1993, Bartholomew, 2001), resulting in loss of catalyst activity. Predicting the likelihood of carbon deposition at given operating conditions from purely theoretical calculations can be tricky since the surface phenomena occurring on the nickel crystals cause substantial deviations from theoretical carbon deposition thermodynamics with the assumption of graphite properties (Bartholomew, 2001). Carbon is formed in three main forms: pyrolytic coke, whiskers and gum; where coke and whiskers are more commonly formed at high temperatures and gum is formed at lower temperatures. Pyrolytic coke is generally formed when heavier hydrocarbons are exposed to high temperatures, while gum is formed as a CH$_x$ layer or a few layers of graphene which encapsulate the catalyst (Sehested, 2006). Ni (100) and Ni
(110) are more active than Ni (111) for methane cracking (Hu and Ruckenstein, 2004) and are therefore more likely to catalyze carbon growth.

At high temperatures above 650°C (Rostrup-Nielsen, 1993), especially in the presence of heavy hydrocarbons that undergo pyrolysis and steam cracking, ethylene produced by the decomposition of higher hydrocarbons causes a deposition of pyrolytic coke on the catalyst particles, completely encapsulating the catalyst pellets and causing a loss in activity and an increase in pressure drop across the reformer. At low temperatures and low steam to carbon ratios, carbon formed by surface reactions adsorbs on the catalyst particle and polymerizes forming gum-like carbon that blocks the catalytic activity of the particle (Rostrup-Nielsen, 2002). This type of carbon deposition is also very important in prereformer treating relatively heavy feeds (naphtha) since they operate at lower temperatures, in the range of 350-650°C. Gum carbon can consist of layers of graphite or thin films of hydrocarbons deposited on the catalyst (Munch, 2007). The loss of catalyst activity alters the reaction profile within the reformer and therefore modifies the temperature profile due to strong heat effects of the reactions involved. However, there are different carbon species that can form based on the thermodynamic conditions and catalyst properties, and therefore there is no unique description for carbon species on a catalyst. A classification of surface carbon species has also been developed based on TPH studies (Papadopoulou et al., 2012a): $C_\alpha$ denotes surface carbide that can be hydrogenated below 323K, $C_\beta$ (or amorphous carbon) can be hydrogenated between 373 and 573K, while $C_\gamma$ (graphitic carbon) is only hydrogenated above 673K.

The most notorious type of carbon deposition on nickel catalysts in reformers is, however, the filamentous carbon growth known as whisker carbon. It occurs at higher temperatures, low water content and is greatly influenced by the presence of aromatics (Bartholomew, 2001). The growth of high-strength carbon whiskers on catalyst pellets is especially severe in aged catalysts that have suffered extensive sintering (Sehested, 2006), and can lead to catalyst destruction, pellet breakage and loss of active metal. The mechanism of whisker growth has been studied by many authors (Alstrup, 1988, Alstrup et al., 1998, Baker et al., 1972, Borowiecki, 1982) and can be roughly summarized as the formation of adsorbed carbon from the Boudouard reaction, methane dissociation reaction and other decomposition reactions on the metal particle, followed by dissolution and diffusion of carbon throughout the metal particle to the whisker formation site on the unexposed metal-support interface (Rostrup-Nielsen, 1993) and whisker growth. The growing high strength carbon fiber pushes out fragments of the active nickel particle as it grows, and once the fiber reaches the pores of the particle, it can break it. Whisker carbon can even cause the catalyst pellets to break, potentially with catastrophic consequences ranging from increased pressure drop and loss of activity to reactor blockage in steam reformers, and hot spots/hot bands that can lead to reactor failure (Rostrup-Nielsen, 2002, Rostrup-Nielsen, 1993, Annesini et al., 2007, Munch, 2007).

The driving force for carbon diffusion through the metal crystal has been discussed extensively (Alstrup, 1988, Alstrup et al., 1998, Lobo et al., 1972, Rostrup-Nielsen and Trimm, 1977b, Baker et al., 1972). Baker et al. (Baker et al., 1972) proposed a mechanism for whisker carbon formation with diffusion through nickel crystals as the rate determining step, and postulated that the driving force for carbon diffusion was a
temperature gradient caused by the dissociation of acetylene on the catalyst surface (Alstrup et al., 1998). They also confirmed the diffusion of carbon through the metal particle to be rate limiting (Baker et al., 1973) by comparing activation energies for whisker carbon growth to carbon diffusion through different metals including nickel, and finding that they were equal. Lobo et al. (Lobo et al., 1972) proposed independently a similar mechanism to that of Baker et al. Rostrup-Nielsen and Trimm (Rostrup-Nielsen and Trimm, 1977b) discussed that the temperature gradient does not explain the diffusion of carbon issued from the endothermic dissociation of methane. They proposed a simpler alternative in which the driving force for diffusion is a carbon concentration gradient. Alstrup (Alstrup, 1988) proposed a corrected mechanism in which the rate limiting step is the formation of a metal carbide during the induction period on the surface of the crystal where carbon decomposition occurs, causing a restructuring of the metal particle. During the steady state carbon growth period, carbon diffuses through the carbide and a constant carbon gradient is maintained. This mechanism is in partial agreement with the mechanism proposed by Rostrup-Nielsen (Rostrup-Nielsen and Trimm, 1977a). Alstrup also noted that the metal particles in typical catalysts are usually well exposed thermally, which makes the thermal gradient model by Baker et al. (Baker et al., 1973) unlikely except for large metal particles which might not be in good thermal contact with the reaction medium. The deformation and restructuring of the metal particle with carbon formation has been observed by Alstrup et al (Alstrup et al., 1998), who noted that the nickel particle becomes pear shaped with a conical feature that is longer at higher temperatures, and concluded the graphite planes may be exerting friction forces strong enough to deform the metal particle into this shape. More recent studies by Abild-Pedersen et al. (Abild-Pedersen et al., 2006) and observations by Bengaard et al. (Bengaard et al., 2002) led to the formulation of a novel mechanism in which the step sites on the metal surface play a significant role in the nucleation and growth of graphene layers on the surface. These graphene layers are not stable when under a critical diameter, which is consistent with the observation that small active metal particles do not catalyze the formation of whisker carbon (Helveg et al., 2011). However, High Resolution Transmission Electron Microscopy (HRTEM) measurements concluded that surface diffusion of carbon was more likely than bulk transport.

Many authors noted that the thermodynamics of carbon formation on nickel catalysts deviated from the graphite thermodynamics, which brings into question the validity of the graphite assumption for carbon deposition on supported nickel catalysts used in most thermodynamic analyses. Dent et al. (Dent et al., 1945-1946) concluded that the equilibrium constants for CO and CH₄ decomposition had smaller equilibrium constants than graphite. Rostrup-Nielsen (Rostrup-Nielsen, 1993) and Alstrup et al. (Alstrup et al., 1998) made similar observations. Alstrup (Alstrup, 1988) studied the formation of carbon filaments on Ni, Ni-Cu and Ni-Fe catalysts and found deviations from graphite deposition thermodynamics that are dependent on particle size, irrespective of the (non-noble) active metal. In the same study, the author combined his finding to those of Rostrup-Nielsen (Rostrup-Nielsen, 1972) and proposed an expression for the deviation from the Gibbs free energy of graphite in function of the size of the largest particle catalyzing filament growth:
\[ \Delta G_{c}^{\text{dev}} \text{ (kJ/mol)} = 2.6 + 93/d \text{ (nm)} \]

With \( d \) being the diameter of the largest metal particle catalyzing filament growth in nm.

The mechanism of carbon formation in dry reforming of methane as summarized by Papadopoulou et al. (Papadopoulou et al., 2012a) corresponds closely to the mechanism discussed by Rostrup-Nielsen, Trimm, Alstrup and other authors who investigated carbon formation in steam reforming. The mechanism of carbon formation on nickel catalysts in most reforming technologies is the same, with the exception of the combustion zone in autothermal reformers where the main carbon type formed is soot.

An interesting observation made by Annesini et al. (Annesini et al., 2007) in their study of steam/CO\(_2\) reforming is that the presence of CO\(_2\), even in small amounts (2\%) can drastically affect the carbon limits. At temperatures below 1000°K, the increasing presence of CO\(_2\) in the gas increases the required steam/carbon ratio to avoid carbon deposition, while the opposite effect is observed at temperatures higher than 1000K.

Rostrup-Nielsen (Rostrup-Nielsen, 1993) proposed a mathematical formula to predict the likeliness of carbon formation in the steam reformer that takes into account the deviation from graphite equilibrium caused by the whisker structure, by means of evaluating the equilibrium carbon activity \( a_{c}^{\text{eq}} \):

\[ a_{c}^{\text{eq}} = K_{c} \frac{P_{\text{CH}_4}}{P_{\text{H}_2}} \]

In which \( K_{c} \) is the equilibrium constant for the methane decomposition reaction that takes into account the thermodynamic deviation from ideal graphite structure. A carbon activity lower than 1 is a safe design criterion to minimize carbon formation in the reformer. Bengaard et al. [43] observed that carbon layers formed on catalyst surfaces are thermodynamically stable above approximately 80 atoms in diameter, and therefore larger crystals are more prone to carbon deposition (Mortensen and Dybkjær, 2015, Rostrup-Nielsen, 2002, Borowiecki, 1982). It is then intuitive that a higher dispersion of nickel in the support phase will decrease carbon deposition on the catalyst since they retard the nucleation of carbon whiskers. A combination of high dispersion catalysts and correct operating conditions should maximize the initiation period and avoid the loss of catalyst due to coke formation.

A potential research prospect is the development of corrected thermodynamic studies of carbon formation taking into account the deviation from graphite thermodynamics proposed by Rostrup-Nielsen for nickel catalysts that would allow for better knowledge of the risk of carbon formation, especially towards the end of service of the catalyst batch suffering from sintering. Chapters 2 and 3 of this thesis explore this topic.

1.2.5: Catalysis in dry reforming

Noble and transition metal based catalysts were extensively investigated to promote the endothermic dry reforming of methane reaction. The activity and stability of these heterogeneous catalysts, the conversion rates of methane and carbon dioxide to synthetic
gas, the resulting H₂/CO molar ratio, in addition to the morphology and the amount of the carbon deposited throughout the process, were found to be directly related to various parameters determined by the selection of the active metals, supports and promoters (Usman et al., 2015). Many recent reviews have explored the topic of catalyst design, focusing on structured catalysts (Muraleedharan Nair and Kaliaguine, 2016), noble metals (Pakhare and Spivey, 2014) and process parameters (Usman et al., 2015). The effect of active metals, promoters and supports was explored in our previous work (Abdel Karim Aramouni et al., 2018) and are summarized here.

1.2.5.1: Effect of Active Metal

A- Monometallic catalysts

Due to their low cost, availability and high catalytic activity, nickel and other non-noble metal catalysts were widely used in the dry reforming of methane (Fidalgo et al., 2011, Castro Luna and Iriarte, 2008, Quincoces et al., 2002, Therdthianwong et al., 2008, Hao et al., 2009, Cheng et al., 2006, Zeng et al., 2012, Hao et al., 2008, Wu et al., 2014). However, despite their apparent convenience for industrial applications (Asencios and Assaf, 2013, Zhang and Verykios, 1996), the high coke formation associated with the use of these catalysts generally leads to their deactivation and constitute a major operational drawback (Ashcroft et al., 1991, Hou et al., 2006b). Ni has been the most used transition metal due to its activity and low cost (Adamu et al., 2020, Afzal et al., 2020, Albarazi et al., 2013, Bai et al., 2014).

Of the other transition metals, Co (Wong et al., 2017, El Hassan et al., 2016, Zhang et al., 2014) has had the most success as a monometallic active metal. Cu and Fe are also transition metals that are active for DRM but are almost exclusively employed in bimetallic catalysts. Unlike Ni, Co has a low stability and is prone to deactivation by oxidation. Chen et al (Chen et al., 2020) noted that the Co deactivation mechanism depends on loading: low Co loadings deactivate by oxidation while high loadings deactivate by coking, which was attributed to the presence of large Co (111) facets in cobalt particles at high loading, which promotes the formation of surface clusters from surface carbon species.

Noble metals have extensively been tested as single active metals with good success. Hou et al. (Hou et al., 2006a) used the impregnation method to prepare different types of catalysts in order to compare the coke deposition resistance, activity and stability of noble and non-noble based catalysts. 10 wt. % Nickel and cobalt with Ru, Rh, Pt, Pd, Ir (5 wt. %) supported on α-Al₂O₃, in addition to Rh (5 wt. %) on a meso-porous alumina support were prepared and tested. All noble metals showed no carbon deposition, except Pd which led to a carbon deposition of 4.9 mg coke/ g cat h. It was also found that the carbon deposition under Ni and Co catalysts were considerably high, 24 mg coke/ g cat.h and 49.4 mg coke/ g cat.h respectively, a factor repeatedly related to the poor resistance of these non-noble based catalysts to carbon formation (Ferreira-Aparicio et al., 1999, Safariani et al., 2009, Shi and Zhang, 2012, Özkara-Aydınoğlu et al., 2009, El Hassan
et al., 2016, Khani et al., 2016). These numbers strongly reflect the superior coke resistance ability of noble metal catalysts compared to their non-noble counterparts. The high coke resistance of noble catalysts was also confirmed by other studies (Ferreira-Aparicio et al., 1999, Safariamin et al., 2009, Shi and Zhang, 2012, Özkara-Aydınoğlu et al., 2009). The difference in performance can be attributed to the ability of noble metals, unlike their non-noble counterparts, to disperse on their support and retain a small particle size. In addition, they tend to reduce the amount of coke formed during reaction and alter its type, as carbon is insoluble in noble metals. Still, the practical use of these catalysts has been severely hindered by their elevated cost and limited availability (Zhang and Verykios, 1996, Crisafulli et al., 2002). The order of activity for noble and transition metals for dry reforming is Rh>Ru>Ir>Ni, Pt, Pd> Co> Fe, Cu (Gurav et al., 2012).

It is worth mentioning that, despite the higher coke formation witnessed under nickel and cobalt catalysts compared to the noble metal ones, the non-noble based catalysts achieved higher initial conversion rates than all other catalysts, except with Rh, thus reflecting the considerable catalytic activity of transition metal catalysts, especially supported nickel. However, under different support and reaction conditions, the catalytic activity of noble metal based catalysts was found to be higher than those of Ni and Co (Hao et al., 2008, Ghelamallah and Granger, 2014, El Hassan et al., 2016). Nevertheless, despite the higher coke formation associated with non-noble metals, maintaining a high dispersion of these metal particles can delay the catalyst’s deactivation time, thus paving the way for prolonged catalysts stability up to 320 and 600 hours (Zhang et al., 2006, Zeng et al., 2012).

Titanium has shown questionable performance in a catalyst formulation, be it as an active metal or oxide support (Liu et al., 2009, Steinhauer et al., 2009, Wang and Ruckenstein, 2000, Ballarini et al., 2005). Although Takanabe et al (Takanabe et al., 2005) found TiO₂ supported Ni-Co catalysts to be highly stable, the maximum methane conversion they obtained using these catalysts was approximately 50% at 1023 K, which is way below the equilibrium conversion. Usman et al (Usman et al., 2015) highlighted the good performance of TiO₂ as a support in maintaining dispersion and reducing carbon deposition rates. However, conversions obtained on titanium catalysts or catalysts supported on TiO₂ have shown quite low conversions even at high temperatures (Abdel Karim Aramouni et al., 2018).

**B- Bimetallic catalysts:**

Several approaches have been investigated in order to overcome deactivation issues. One solution is to create an alloy catalyst (usually bimetallic), where a noble or non-noble metal is added to another primary metal. This approach can potentially overcome the deactivation of non-noble catalysts caused by excessive coke formation and sintering, while simultaneously overcoming the high cost and unavailability of coke resistant noble catalysts. The addition of small amounts of noble metals (Rh, Ru, Ir, Pt, Pd, Au) or non-noble metals (Ni, Co, Cu, Fe) to conventionally non-noble based catalysts increase the dispersion of the metal, decrease the particle size and thus retain a good catalytic activity and stability (Crisafulli et al., 2002, Al-Fatesh et al., 2011, Horváth et al., 2011,
Bian et al (Bian et al., 2017) reviewed the design of bimetallic Ni-based catalysts with transition and noble metals. Three notable transition metal systems have been highlighted:

- **Ni-Fe system with redox properties:** No study has found Fe alone to be active for DRM so far, but it has extensively been studied in bimetallic Ni-Fe catalysts (Bian et al., 2017, de Lima and Assaf, 2006), which show good resistance to carbon formation. Most Ni-Fe structures derived from perovskites or spinel precursors. Fe-modified La-Ni perovskite showed a better coke resistance at the expense of activity when compared to La-Ni perovskite. The structure and promotion mechanism of Fe on Ni is still not well known, but a dealloying-realloying cycle has been documented (Kim et al., 2017). Theofanidis et al observed that the reaction on Ni-Fe catalysts carries via a Mars-Van Krevelen mechanism (Theofanidis et al., 2015): The Ni Fe alloy decomposes into Ni and Fe₃O₄ which is subsequently reduced back into a Ni-Fe alloy. The redox ability of Fe allows it to react with surface carbon species, thus lowering coking.

- **Ni-Cu system,** where partial substitution of Ni with Cu increases coke resistance. Preparation of Ni-Cu on SiO₂ prepared by the phyllosilicate route gives better metal support interaction than conventional methods (Wu et al., 2013). Cu competes with Ni for CH₄ adsorption and has lower methane dissociation kinetics. An excessive Cu loading therefore reduces the activity. Although evidence shows that an optimal Cu-Ni ratio reduces coking, there is still no clear explanation of the role of Cu. Sutthiumporn et al (Sutthiumporn et al., 2012) tested different transition metals (Bi, Co, Cr, Cu, Fe) in a LaNiO₃ perovskite partially substituted by Sr. The best performing catalysts were found to be the Cu and Fe modified perovskites, with the Cu catalyst having a higher initial activity and the Fe catalyst having the highest stability.

- **Ni-Co system with enhanced oxygen mobility:** The Ni-Co bimetallic system has been of particular interest due to its superior performance compared to other bimetallic transition metal catalysts (Zhang et al., 2007). The synergetic mechanism between Ni and Co has been linked to their alloying (Phan et al., 2018) and to their mutual stabilization. The works of Takanabe et al (Takanabe et al., 2005) showed that Ni, which is more active for CH₄ dissociation, deactivated by coking, while Co, which is more active towards CO₂ activation, deactivated by reoxidation. In a bimetallic Ni-Co catalyst, hydrogen spillover from Ni to Co prevents its oxidation, while the high oxygen affinity of Co contributes to C* oxidation by the reverse Boudouard reaction and reduces coking. Optimal Ni/Co ratio seems to be Ni-rich (Whang et al., 2017, Bian et al., 2017). Fan et al.(Fan et al., 2010) compared the methane conversion rates under Ni/MgO-ZrO₂, Co/MgO-ZrO₂ and Ni-Co/MgO-ZrO₂. It was reported that the bimetallic Ni-Co catalyst achieved the highest methane conversion. The increase in the catalytic activity of the bimetallic compound compared to the monometallic ones was attributed to the
synergic effect of Ni and Co, in addition to better metal dispersion and smaller particle size. Allo\onde a non-noble metal with a noble metal (Hou et al., 2006b, Arbag et al., 2010, Khani et al., 2016, Cheng et al., 2014, Frontera et al., 2009, Mahoney et al., 2014, Jóźwiak et al., 2005, Steinhauer et al., 2009) has been successfully shown to improve catalytic performance in terms of activity, reducibility and carbon formation resistance. leads to decreased carbon formation. DFT calculations by Foppa et al. (Foppa et al., 2016) showed that CO disproportionation is more likely to cause carbon formation on Ni, while CH₄ cracking is more likely to happen on Pt and Pd. Carbon species from CH₄ cracking are more active than those from Boudouard reaction and can be oxidized by CO₂, which may explain the better coke resistance of noble metals. Promotion with noble metal improves reducibility. For example, with Ni-Pt, reduction is facilitated by the initial reduction of adjacent Ni and Pt atoms forming an alloy, then reduction of the remaining Ni into a separate phase facilitated by H₂ spillover. Tomishige (Tomishige, 2004) noted that the reducibility of the catalyst determined the activity and resistance to coking. Ni is prone to oxidation which creates inactive surface Ni²⁺ coverage. The improved catalytic activity of Ni-noble metal alloys is also related to their observed ability to restructure based on the presence of adsorbates: In the presence of oxygen, Pt-Ni-Pt structure formed by annealing a Ni-Pt catalyst at high temperature rearranges into O/Ni-Pt-Pt structure (Li et al., 2015). This kind of surface restructuring is important in determining catalytic activity. El Hassan et al. (El Hassan et al., 2016) showed that by reducing metal sintering and by altering the type of coke formed during DRM reactions, noble metals are able to provide a superior catalytic activity and stability compared to their non-noble counterparts. They tested Co, Rh and Rh-Co catalysts supported on SBA-15 zeolites and observed a better stability in Rh and Rh-Co catalysts. High Resolution TEM imaging on spent catalysts showed that a significant amount of cobalt particles in Co₁₂/SBA-15 have migrated outside the pores, leading to the sintering of these nanoparticles and the formation of external particles ranging in size from 10 to 30 nm. The cobalt particles that remained inside the pores also suffered from sintering. On the other hand, doping the cobalt catalyst with Rh has severely reduced the migration of active metals to the pores’ exterior and reduced the size increase of the metal particles inside the pores. These results further support the claim that noble metals offer superior anti-sintering properties compared to non-noble ones (including nickel), thus leading to more stable catalysts. Arandiyan et al. (Arandiyan et al., 2013) compared the catalytic activity, stability and surface properties of different perovskite-type oxides catalysts doped with different noble metals used in the dry reforming of methane. Using the sol-gel method, the authors prepared perovskite catalysts La₀.₄M₀.₆Al₀.₂Ni₀.₈O₃ (M=noble metal) doped with Ir, Pd, Pt, Rh and Ru, in addition to LaAl₀.₂Ni₀.₈O₃. Following an activity performance test carried out on these catalysts, the authors concluded that CH₄ and CO₂ conversion were in the order, from the highest to the lowest, La₀.₄Rh₀.₆Al₀.₂Ni₀.₈O₃ > La₀.₄Ru₀.₆Al₀.₂Ni₀.₈O₃ > LaAl₀.₂Ni₀.₈O₃ > La₀.₄Ir₀.₆Al₀.₂Ni₀.₈O₃ > La₀.₄Pt₀.₆Al₀.₂Ni₀.₈O₃ > La₀.₄Pd₀.₆Al₀.₂Ni₀.₈O₃. These results were largely consistent with the findings of Hou et al. (Hou et al., 2006a), especially regarding the order of activity of noble metals (Rh>Ru>Ir>Pt>Pd). The
stability test showed that Rh and Ru catalysts were the most stable, while the Pd catalyst was the most prone to deactivation. The low stability of Pd and Pt supported catalysts was attributed to the sintering of the metal particles at high temperatures, while the superior ability of the other noble metals to eliminate coke deposition was attributed to their high dispersion and small particle size. The authors attributed the elimination of coke deposition on Rh promoted catalysts to the formation of Rh-Ni clusters having a Ni covered surface, thus enhancing the dispersion of the nickel particles and favoring the formation of more reactive intermediate carbonaceous species. These results were also confirmed by Matsui et al [48] and Tsyganok et al (Tsyganok, 2003).

Noble metals improve catalyst performance drastically, both as active metals and promoters, but their loading is very critical, with optimal concentrations usually low, and typically below 0.5% wt as promoters. Silver and gold are not as successful as the other noble metals: even on the excellent Mg-doped alumina support and at 800°C, a 2% Au catalyst yields only 0.8% CO₂ conversion and 0.3% methane conversion (Arbag et al., 2010). Furthermore, the synergetic effect observed in bimetallic formulations is not always apparent when using two noble metals. For example, Rh/Pt/La₂O₄ gives a better conversion than Rh-Pt/La₂O₄ (Ghelamallah and Granger, 2014).

Several studies have highlighted the importance of maintaining high dispersion and surface area, in addition to small metal particle size in order to achieve high catalytic activity, stability and avoid excessive carbon formation. More importantly, this factor has proved critical for both noble and non-noble based catalysts (Arandiyan et al., 2013, Liu et al., 2009, El Hassan et al., 2016, Tsyganok, 2003, Fan et al., 2010, Jiang et al., 2013, Alipour et al., 2014, Kim et al., 2000, Zhang et al., 2006). This amelioration of the catalytic performance and coke resistance is achieved by increasing the dispersion of the active metal particles and decreasing their size, enhancement of the catalyst reducibility, decreasing the rate of coke formation, altering the type of coke deposited on the catalyst’s surface, in addition to creating a synergic effect between the metals involved (Hou et al., 2006a, Al-Fatesh et al., 2011, García-Diéquez et al., 2010, El Hassan et al., 2016, Fan et al., 2010, Arbag et al., 2010, Jang et al., 2013, Tomishige et al., 2002b, Takanabe et al., 2005, Xu et al., 2009, Al-Fatesh, 2015, Tomishige et al., 2002a).

The presence of another metal as a support doping agent or as a support can have different effects based on the metal: noble metals such as Ru, Rh, Pt promoting nickel or cobalt can improve the catalyst activity and stability, but other metals, especially Ca, Mn and Sn (Castro Luna and Iriarte, 2008) are poisons to the catalyst, causing a large decrease in activity and increased carbon formation. Potassium in small amounts causes a decrease in activity but also a decreased carbon formation rate. However, manganese and potassium do not poison noble metals as much as nickel, and Yttrium has even shown to improve the activity of palladium catalysts (Shi and Zhang, 2012).

The addition of mixed rare earth metals (MREs) to cobalt/alumina catalysts enhances the coke resistance and increases the ratio of active carbon deposited on the catalyst (Zeng et al., 2012) . It is also observed that the addition of MRE oxides causes an increase in CO₂ conversion that is higher than the increase in methane conversion, meaning that the MREs in the amounts used promote the reverse water-gas shift reaction. Iridium based catalysts
also promote the reverse water gas shift reaction and therefore exhibit a CO₂ conversion higher than that of methane (Wang et al., 2017), while platinum based catalysts seem to inhibit this reaction, showing a much larger methane conversion (Tomishige et al., 2002a).

Alloy catalysts are not restricted to transition metal or noble - non noble bimetallic catalysts. Several studies have developed alloy catalysts based on two noble metals (Ghelamallah and Granger, 2014, Du et al., 2013) or trimetallic catalysts (Wu et al., 2014, Fan et al., 2015).

Du et al. (Du et al., 2013) investigated the catalytic performance of Pt, Ru and Pt-Ru catalysts supported on γ-Al₂O₃. After carrying out the methane reforming reaction for 1 hour at 700, 800 and 900 °C, the authors showed that the Pt-Ru/γ-Al₂O₃ bimetallic catalyst exhibited superior catalytic activity and selectivity (lower CO/H₂ molar ratio) compared to its corresponding monometallic ones under all the investigated reaction temperatures. Moreover, the authors tested the stability of the Pt-Ru/γ-Al₂O₃ for 500 hours at 800 °C. At the end of the test, the authors measured the conversion of CH₄ and CO₂ at 94% and 96% respectively. Moreover, the author found that this catalyst led to a molar ratio of CO/H₂ close to 1, thus indicating that the side reactions accompanying the dry reforming of methane reaction were limited to a large extent. Additionally, the spent catalysts were subjected to a thermo-gravimetric (TG) test to investigate the carbon deposited on their surfaces. It was shown that the mass loss for the bimetallic catalyst occurred at lower temperature ranges than the monometallic ones. Consequently, the Pt-Ru/γ-Al₂O₃ catalyst will be able to generate more active carbon species during the reaction, thus enhancing its stability compared to the other catalysts. Finally, the authors attributed the enhanced catalytic performance and stability of Pt-Ru/γ-Al₂O₃ to the anti-agglomeration of the active bimetallic particles.

On the other hand, Wu et al. (Wu et al., 2014) investigated the effects of adding small amounts of Au and Pt to Ni (4 wt. %) catalyst supported on Al₂O₃ and Al₂O₃-10 wt. %MOₓ (M = Ce or Mg) oxides. It was concluded that the addition of 0.2 wt. % of Au and Pt to Ni catalyst leads to the formation of bimetallic and trimetallic catalysts having a superior catalytic activity and stability as compared to monometallics. This was attributed to the formation of nanosized nickel particles that synergistically interact with Au and Pt.

C- Trimetallic catalysts

Trimetallic catalyst formulations do not always follow the same trends that are shown when comparing monometallic catalysts with bimetallic catalysts: Synergetic effects are less noticeable and sometimes even hindered as in the case of the Ni-Pt-Au /Al₂O₃ system (Wu et al., 2014) where the Ni-Pt catalyst showed a slightly better conversion than the Ni-Au-Pt catalyst in some cases. The use of more than one noble metal in a trimetallic formulation is therefore not always desirable both due to economic barriers and low technical advantage. Furthermore, due to the already intricate interactions between three metallic species yielding generally good catalyst properties, the effect of the support
material is less apparent in trimetallic catalysts. It appears there potential to use two non-noble metals promoted by a noble metal in a trimetallic catalyst. Part of this thesis will explore the Ni-Co-Ru trimetallic system in detail (Chapters 3 and 4).

Al Fatesh (Al-Fatesh, 2015) prepared Sr-doped Ni, Co, and Ni-Co catalysts supported on γ-Al₂O₃ by the impregnation method and concluded that the bimetallic Ni-Co catalysts offered a better catalytic activity and stability compared to the monometallic ones. This was ascribed to the interaction of the two species. The highest catalytic activity was experienced under Ni-Co, followed by 5Ni5CoSr₀.₂₅, 5Ni5CoSr₀.₇₅, 5Ni5CoSr₀.₅, 10Co, 5Ni5CoSr₁ and finally 10 Ni. Moreover, Sr promoted bimetallic catalysts exhibited higher stability (small decrease of methane conversion) and smaller amounts of coke deposition compared to the other catalysts, at the expense of a lower activity. The optimal Sr loading that balanced carbon formation reduction and activity loss was 0.75%. The enhancement offered by the Sr promoters was attributed to their high basicity and better metal-support interaction, thus reducing the sintering of active metal particles.

D- Perovskites

Perovskite-type catalysts were also investigated for the dry reforming of methane (Arandiyan et al., 2013, de Caprariis et al., 2016, Valderrama et al., 2013, Sutthiumporn et al., 2012). Perovskites are peculiar catalysts because they are often precursors to the final catalytically active structure. They consist of bimetallic oxides that have the formula ABO₃ or A₂BO₄, and that can accommodate a large spectrum of metals at A or B sites without modification to the crystal structure. The most common perovskite catalyst precursor for dry reforming is LaNiO₃. Partial substitution of A and B sites is therefore facile and allows the design of easily tunable catalysts. Transition metals generally occupy B sites while metals such as La, Sr and Ce are mostly located at A sites. Perovskite catalysts are actually precursors that transform in situ after reduction to their active form. For instance, LaNiO₃ perovskite synthesized by Batiot-Dupeyrat (Batit-Dupeyrat et al., 2003) was observed to transform into Ni/La₂O₃ after reduction, as Ni left the B-sites and formed particles on the perovskite surface.

Substitution at the A sites modifies the surface basicity and enhances oxygen mobility which enhances carbon resistance and activity (Moradi and Rahmanzadeh, 2012, Gallego et al., 2009), while substitution at the B site can affect metal-support interaction (if the substituted metal is irreducible), and introduces synergetic effects in case a reducible metal is used (de Caprariis et al., 2016).

Despite the interesting catalytic properties of perovskites, they have low surface areas and porosity that is generally not altered by partial substitution of A and/or B site metals. Recent studies have therefore attempted to improve the surface area by creating nanosized perovskite particles that are dispersed on a high area support (Nguyen et al., 2002, Wang et al., 2013).
Figure 1-10: Lattice structure of a perovskite, taken from (Zhu and Thomas, 2009). The red circle represents substitution of an A-site cation.

De Caprariis et al. (de Caprariis et al., 2016) investigated methane dry reforming under three ternary perovskite type oxides with Ba and Zr in the A site and using noble metals Rh, Ru and Pt as active species (B site). Performing the DRM reaction at atmospheric pressure and under reaction temperatures ranging from 850 to 1150 K, the authors showed that BaZr_{0.8649}Rh_{0.1351}O_3 displayed the highest catalytic activity followed by BaZr_{0.8649}Ru_{0.1351}O_3 then BaZr_{0.9272}Pt_{0.0728}O_3. The higher activity of Rh and Ru based catalysts compared to BaZrPtO_3 was connected to their higher reducible nature. Moreover, the low carbon formation rates witnessed under Rh and Ru perovskites at 0.0019 and 0.0027 g coke/g cat h respectively, compared to the Pt perovskite at 0.0094 g coke/g cat h, justified the lack of deactivation witnessed under the Rh and Ru catalysts after a 65-hour long stability test and the 10% drop of activity for the Pt catalyst after the same duration.

Valderrama et al (Valderrama et al., 2013) produced La_{1-x}Sr_xCoO_3 perovskites as catalyst precursors for DRM. The authors concluded that despite the extreme reaction conditions, the catalysts led to high activity and stability due to the formation of nano-sized Co^0 particles over the SrO and La_2O_3 phases which were highly dispersed in the La_2O_2CO_3_SrO solid matrix. Moreover, the Sr promoter has also proved its ability to stabilize the cobalt metallic particles.

**E- Miscellaneous active phases**

Apart from the conventional noble/non-noble metals and perovskites commonly studied as dry reforming catalysts, a number of less common catalytic materials have been tested. Those consist of mixed rare earth oxides (mixed oxides containing rare earth elements such as Ho, La, Ce and others), bimetallic Ni-actinide oxides, chemical looping catalysts (oxygen carriers that undergo sequential redox reactions in a process that convert CH_4 and CO_2 into syngas and CO: they have shown potential in successfully producing syngas
with low coke formation as they utilize surface carbon as an intermediate) and interstitial alloys.

- Zeng et al. (Zeng et al., 2012) were able to enhance the catalytic activity and stability of non-noble Co/γAl₂O₃ catalyst via the addition of mixed rare earth (MRE) oxides promoters. The addition of these promoters offered a beneficial synergetic effect that decreased the size of Co₃O₄ particles and increased the interaction between the cobalt species and its support, which lead to an increase in the anti-sintering ability of the metallic cobalt particles. Additionally, these promoters increased the ratio of active carbon and improved the anti-coking performance of the catalyst.

- Ferreira at al (Ferreira and Branco, 2020) tested Ni-actinide (thorium and uranium) bimetallic oxides in the dry reforming of methane. The catalysts performed well, with Thorium giving a good activity and stability but slightly higher carbon formation than with uranium. The very low carbon content in Ni-U oxide catalyst was attributed to the ability of uranium to change oxidation states, which gives it good redox properties that help oxidize surface carbon.

- Chemical looping catalysts for dry reforming operate in a reaction mechanism vaguely similar to the Mars-Van Krevelen mechanism to produce syngas with a H₂/CO ratio of 2 which is appropriate for Gas-to-Liquid applications using the Fischer-Tropsch process. The major difference is that the reduction and oxidation steps are performed sequentially by switching the reactant feed, and not continuously during reaction. The chemical looping catalyst is first exposed to the methane stream to which it donates lattice oxygen via the reaction:

$$\text{CH}_4 + \text{MeO}_x \rightarrow \text{CO} + 2\text{H}_2 + \text{MeO}_{x-1}$$

The exhausted carrier is then exposed to CO₂ to replenish it with oxygen and produce CO via the reaction:

$$\text{CO}_2 + \text{MeO}_{x-1} \rightarrow \text{CO} + \text{MeO}_x$$

This catalyst system is resistant to carbon formation as the surface carbon produced by the Boudouard reaction is gasified during the CO₂ treatment phase. Generally, developing a chemical looping catalyst with good oxygen exchange rate and coke resistance necessitates rare earth metals or lanthanides. Transition metals supported on reducible metal oxides such as Ceria are potent chemical looping catalysts (Guerrero-Caballero et al., 2019). Kim et al. (Kim et al., 2020b) synthesized Ni-Fe-Al catalysts for chemical looping dry reforming of methane, in which NiFe₂O₄/Al₂O₃ gives high conversion and shows a lower sintering than Ni/Al₂O₃. Wong et al. (Wong et al., 2017) tested cobalt aluminate as a chemical looping catalyst that also showed high activity and low carbon formation.

- Interstitial alloys are a family of compounds in which a small atom occupies part or all the interstitial spaces in a metal crystal. They have unique properties that have found applications in a wide variety of fields including biomedical imaging (Yang et al., 2015), coatings (Hintermann, 1981) and catalysis (Spivey and...
Dooley, 2006). The best known interstitial alloys for dry reforming catalysts are carbides, with molybdenum carbide being the best performing (Lavoie, 2014, Brungs et al., 1999, Claridge et al., 1998, Roohi et al., 2016). Claridge et al. (Claridge et al., 1998) found the activity of molybdenum and tungsten carbides to be comparable to Iridium and Ruthenium due to the close electronic similarities. Yao et al. (Yao et al., 2016) noted that pressures higher than atmospheric were necessary to prevent the oxidation of molybdenum carbide by CO$_2$. The use of nitrides as catalysts for dry reforming has only been reported by Cao et al. (Cao et al., 2017) who used boron nitride as a support for Ni catalysts encapsulated in mesoporous silica, and Fu et al (Fu et al., 2017), who compared the activity of bulk Mo$_2$N, NiMo$_3$N and CoMo$_3$N in the dry reforming of methane. The nitrides synthesized in their work showed low surface area, and a high activity in bimetallic nitrides. Mo$_2$N was shown to poorly adsorb CH$_4$ and CO$_2$ at the reaction temperature, which caused its low activity. Co-Mo and Ni-Mo nitrides performed much better, with a higher coking potential for NiMo$_3$N due to its higher CH$_4$ adsorption potential.

- Single-atom catalysts are attractive candidates for the dry reforming process due to their extremely high dispersions, often reaching atomic scale. They are often supported on hydroxyapatite, which has been identified as a potent support for single-atom catalysts (Boukha et al., 2007). The synthesis method is critical to achieve atomic dispersion. The strong electrostatic adsorption method has been classically used in single-atom catalysis. Recently, other methods such as the polyvinylpyrrolidone-assisted method were proposed as alternatives with better performance (Akri et al., 2020). The advantage of single-atom Ni catalysts is that they catalyze only the first C-H bond decomposition, and therefore do not catalyze carbon formation. They are however, relatively unstable and tend to agglomerate at high temperatures (Akri et al., 2019).

1.2.5.2: Effect of the Support Selection

Designing a highly active, stable and coke resistant catalyst for the dry reforming of methane should take into consideration the effect of the support selection on the overall catalytic performance. An appropriate selection of the support must exploit its textural and chemical properties, such as surface area, pores characteristics, thermal stability, redox properties, oxygen storage capacity and surface basicity, to enhance the metal-support interaction, increase the dispersion of active metal particles, prevent their sintering, facilitate the reduction of the catalyst, in addition to reducing or eliminating the formation of carbonaceous species. Supports can be generally classified as reducible metal oxides, irreducible metal oxides, and structured supports.

A- Reducible metal oxides

This family of supports consists of metal oxides that can take multiple oxide forms and have a low formation energy for energy vacancies (Tosoni et al., 2018), with the most
famous being CeO$_2$ and TiO$_2$. There seems to be a disagreement in the literature about the identity of ZrO$_2$, which has been described as not reducible by some authors due to its high oxygen vacancy formation energy (Tosoni et al., 2018), while others deem it reducible (Kim et al., 2020a) or having an intermediate behavior (Helali et al., 2017). The ability of the metal cation to change its oxidation state provides a high availability of surface oxygen, which is essential for good catalytic activity both in conventional and chemical looping dry reforming, and for eliminating carbon formation. Yet, the reactivity of reducible oxides as supports makes them prone to deactivation by sintering.

Wang and Ruckenstein (Wang and Ruckenstein, 2000) tested 0.5%Rh supported on reducible oxides and compared them to irreducible oxide supports. Initial activities for reducible oxide supports ranked in the following order: Ta$_2$O$_5$ >> TiO$_2$ >> ZrO$_2$ > Nb$_2$O$_5$ > CeO$_2$, and changed after 50 hours on stream to ZrO$_2$ > Ta$_2$O$_5$ > CeO$_2$ >> TiO$_2$ >> Nb$_2$O$_5$. The authors attributed the deactivation of Y$_2$O$_3$ and Ta$_2$O$_5$ to metal sintering, while the high stability exhibited by MgO and La$_2$O$_3$ was attributed to the strong metal-support interaction created by the production of LaRhO$_3$ and MgRh$_2$O$_4$ compounds.

The catalytic activity and stability of Ni-Pd bimetallic catalysts supported on ZrO$_2$-La$_2$O$_3$, La$_2$O$_3$, ZrO$_2$, SiO$_2$, Al$_2$O$_3$ and TiO$_2$ were investigated by Steinhauer et al. (Steinhauer et al., 2009). Carrying out the DRM reaction at 500, 600 and 700˚C for 2 hours each, the authors showed that the effect of the support was not prominent at low temperatures. However, the difference in conversion rates and H$_2$, CO yields increased at high temperatures. The catalytic activity of the catalysts decreased in the following trend according to the supports ZrO$_2$-La$_2$O$_3$, La$_2$O$_3$ > ZrO$_2$ > SiO$_2$ > Al$_2$O$_3$ > TiO$_2$. This varying catalytic performance was mainly attributed to differences in metal-support interaction and metal dispersion level. Moreover, the authors attributed the reduced activity of Al$_2$O$_3$ and TiO$_2$ supported catalysts to the blockage of active sites. The poor performance of TiO$_2$ and the beneficial effect of composite supports were in agreement with the findings of Zhang et al. (Zhang et al., 2015). The latter (Zhang et al. (Zhang et al., 2015)) investigated the effect of SiO$_2$, TiO$_2$, Al$_2$O$_3$, MgO-modified Al$_2$O$_3$, ZrO$_2$ and MgO supports on the catalytic performance of Ni based catalysts at 750 °C in a packed bed. The poor catalytic performance of NiO/TiO$_2$ was attributed to its small surface area and the weak metal-support interaction, leading to the agglomeration of the NiO particles. As for NiO/ZrO$_2$, the authors justified its high initial activity to the weak metal-support interaction which may have facilitated the reduction of the catalyst. However, it was found that this property may subsequently lead to the quick deactivation of the catalyst by allowing the sintering of the metal particles. Finally, the authors ascribed the good catalytic performance of the MgO supported catalyst to the ability of MgO’s basic sites to enhance the chemisorption of the acidic CO$_2$ gas on the catalyst surface, thus reducing the carbon deposition and enhancing the catalyst’s anti-coking capabilities by the gasification of the formed carbonaceous species. Finally, the authors concluded that MgO-modified alumina can be considered as the most stable and active support; the performance of the tested catalysts decreased in the following order NiO/MA (Al$_2$O$_3$-MgO) > NiO/SiO$_2$ ≈ NiO/MgO > NiO/Al$_2$O$_3$ > NiO/ZrO$_2$ > NiO/TiO$_2$. 

30
Naeem et al (Naeem et al., 2013) compared the performance of Ni (5 wt. %) catalysts supported on γ-Al₂O₃ (S\text{BET} = 180 m²/g), CeO₂ and ZrO₂. These catalysts were prepared by the polyol method. The authors concluded that, owing to its advantageous combination of high thermal stability, redox potential, reducibility and surface acidity, the Ni-ZrO₂ catalyst provided the best catalytic performance. On the other hand, Ni-Ce₂O₃ was the least active catalyst and led to the highest coke formation. This was directly related to the low Ni dispersion % on its surface and its large Ni crystal size, favoring the formation of coke. Moreover, the authors showed that Ni-Al was the most coke resistant catalyst, a property resulting from the high metal dispersion on its surface, small Ni particle size, in addition to its basic surface allowing for the gasification of the carbonaceous species.

**B- Irreducible metal oxides**

Supports such as Al₂O₃, SiO₂ and MgO are classified as irreducible due to the high stability of their cation in its oxidation state. In general, a low oxidation state of the metal cation in the oxide and a high coordination number are associated with low reducibility. Irreducible oxides have a high band gap, electron affinity and high oxygen vacancy formation energy. They also can host localized electrons in the position of oxygen vacancy.

Alumina is a good support for DRM but under high temperatures transforms into the α phase which is less porous and has lower surface area. Much research has been aimed into stabilizing transition alumina phases (γ, θ or η) (Adamu et al., 2020).

Basic metal oxides, such as cerium or magnesium enhance the surface reactions and promote carbon gasification, adding to the stability of the catalyst. They are especially effective when used in moderate amounts (~10%) on an already potent support such as alumina (Zhang et al., 2007, Tsyganok, 2003, Alipour et al., 2014), which is less basic, with a point of zero charge at pH=8 approximately. Ceria shows a slightly better performance than magnesia when doping alumina(Wu et al., 2014). Another interesting observation concerning alkaline metal oxides doping alumina is that small amounts of CaO increase the catalyst activity and stability while larger CaO loadings have the opposite effect of increasing the carbon formation on the catalyst and decreasing the CO₂ conversion (Sengupta and Deo, 2015). Alumina doped with La proves to be a potent support for Ni catalysts, but not for Co catalysts (Xu et al., 2009).

Wang and Ruckenstein (Wang and Ruckenstein, 2000) compared the performance of 0.5 wt% Rh catalysts supported on reducible (CeO₂, Nb₂O₅, Ta₂O₅, TiO₂, and ZrO₂) and irreducible (γ-Al₂O₃, La₂O₃, MgO, SiO₂, and Y₂O₃) metal oxides. Under the same reaction conditions, the conversions of CH₄ and CO₂ varied widely according to the support employed, thus reflecting the important influence of the support type on the catalytic activity and stability. Moreover, it can be noticed that the catalysts supported on irreducible oxides generally led to higher conversions and H₂/CO ratios than their reducible counterparts. After 0.5 hours on stream, the conversions rates, H₂ and CO yields obtained under the irreducible oxides decreased in the following order SiO₂ > MgO > γ-Al₂O₃ > Y₂O₃ > La₂O₃. However, due to the deactivation of the Rh/SiO₂ catalyst, 50 hours after the start of the reaction, the order changed to γ-Al₂O₃ > MgO > Y₂O₃ > SiO₂ > La₂O₃.
Additionally, although no chemical compounds were created between the alumina support and the rhodium metal, the authors attributed the stability of $\gamma$-Al$_2$O$_3$ and the lack of Rh sintering to the strong metal-support interaction.

In their work, Zhang et al (Zhang et al., 2015) attributed the high initial metal dispersion on SiO$_2$ to its large surface area. However, metal sintering resulting from the weak NiO-SiO$_2$ interaction occurred with time, leading to the subsequent deactivation of this catalyst. On the other hand, the strong interaction between NiO and alumina, resulting in the formation of the difficultly reduced NiAl$_2$O$_4$ spinel, led to the low metal dispersion in NiO/Al$_2$O$_3$. However, the MgO modification of alumina was found to be critical in increasing the metal dispersion in NiO/MgO-Al$_2$O$_3$. This was attributed to the ability of MgO to weaken the strong NiO-alumina interaction and facilitate the reduction of NiO. The authors concluded that the reaction between Mg$^{2+}$ and unsaturated Al$^{3+}$ ions on the catalyst surface has weakened the metal-support interaction, thus enhancing the dispersion of the metal particles on the support and lowering the reduction temperature.

On the contrary, studying the catalytic performance of supported Iridium (Ir) catalysts, Nakagawa et al. (Nakagawa et al., 1998) ranked the activity of the supported catalysts as follow TiO$_2$ ≥ ZrO$_2$ ≥ Y$_2$O$_3$ > La$_2$O$_3$ > MgO ≥ Al$_2$O$_3$ > SiO$_2$. The authors showed that carbon deposition was only present on Al$_2$O$_3$ and SiO$_2$ supported catalysts. The authors attributed the effects of the support to the activation of CO$_2$ with the metal oxides support. Moreover, the low stability of Al$_2$O$_3$ and SiO$_2$ supported catalysts was believed to be caused by the deposition of carbonaceous species on their surfaces.

Hongjing Wu et al. (Wu et al., 2014) investigated the performance of monometallic and trimetallic Ni based catalysts supported over Al$_2$O$_3$ and modified Al$_2$O$_3$. The sol-gel method was used to prepare the Al$_2$O$_3$ and Al$_2$O$_3$-10 wt% MO$_x$ (M = Ce or Mg) supports. It was found that the modified AlCe and AlMg supports have offered an important enhancement to the catalytic activity and stability compared to their unmodified counterpart. The authors reported that the strong metal-support interaction between NiO and CeO$_2$ species has enhanced the reducibility of Ni-Al and prevented metal sintering. Moreover, the interaction of CeO$_2$ and Al$_2$O$_3$ to create CeAlO$_3$ was also found to be beneficial for the catalytic performance. This was attributed to the ability of CeAlO$_3$ species to prevent carbon formation via catalyzing CO$_2$ decomposition and thus creating active oxygen atoms necessary to oxidize the carbon derived from methane decomposition. As for the Ni-AlMg catalyst, the authors concluded that the metal-support interaction was enhanced after doping Al with MgO, thus allowing to retain a small Ni particle size and avoid metal sintering. Moreover, the authors concluded that the Ni-AlMg catalyst offered a superior coke resistance compared to Ni-Al due to the presence of basic MgO sites on the catalyst’s surface, thus enhancing CO$_2$ chemisorption and leading to a faster gasification of carbonaceous species. Interestingly, doping Al$_2$O$_3$ with MgO and CeO$_2$ did not enhance the catalytic activity or stability when trimetallic NiAuPt was employed due to good performance of the active metals combination. These results strongly reflect the dominant effect of metal selection on the catalytic performance compared to the effect of the support. Although doping Al$_2$O$_3$ with MgO and CeO$_2$ has
enhanced the catalytic activity of monometallic Nickel catalysts (Wu et al., 2014), different results were observed when operating under Rh catalysts (Feng et al., 2016).

Asmaa Drif et al. (Drif et al., 2015) investigated the catalytic activity and stability of monometallic Rh catalysts supported over alumina and various MₓOᵧ - Al₂O₃ oxides (M = Zr, Mg, Ni, Ce, La). For the DRM reaction, the highest hydrogen yields were observed under Rh/NiO-Al₂O₃ > Rh/Al₂O₃ > Rh/MgO-Al₂O₃ > Rh/CeO₂-Al₂O₃ > Rh/ZrO₂-Al₂O₃ > Rh/La₂O₃-Al₂O₃. The authors attributed the superior catalytic performance of Rh/NiO-Al₂O₃ to the high dispersion of Rh over the catalyst’s surface and the formation of NiAl₂O₄ spinel structure.

C- Structured supports

Although many single-cation metal oxide supports such as γ-alumina perform well, it is apparent that mixed and/or structured supports have properties that make them more attractive to use as support materials. Zeolites are a highly potent group of materials to consider, and it is apparent that zeolites with a higher Si/Al ratio, which are more basic, give better performance (Moradi et al., 2016). Their good performance is linked to the confinement of active metal particles inside their well-structured pores, ensuring a higher resistance to sintering, in addition to their tunable basic character that decreases carbon deposition. Promoting a zeolite-supported catalyst with a noble metal does not have a noticeable effect on the conversion (Frontera et al., 2009), but gives a higher stability to the active metal particles inside the pores (El Hassan et al., 2016).

Several studies have investigated the DRM reaction under mesoporous zeolites such as SBA-15 and ZSM-5 (El Hassan et al., 2016, Zhang et al., 2006, Sarkar et al., 2012, Moradi et al., 2016, Huang et al., 2012, Huang et al., 2011). Zhang et al. (Zhang et al., 2006) synthesized a highly stable Ni catalyst supported on SBA-15 zeolite with nickel loadings ranging from 2.5 to 20% wt. Higher conversions were obtained at high temperatures, and the catalysts having a Ni loading larger than 10% yielded similar conversion rates at high temperatures. The authors were able to overcome the deactivation of nickel catalysts and maintain a conversion of CH₄ and CO₂ close to 90% for 600 hours by limiting the sintering of Ni and ensuring its high dispersion through exploiting the confinement effect and porosity of the SBA-15 support. The authors noted, however, that the deactivation rate for CH₄ and CO₂ conversions were different, which suggested that two active centers exist for the activation of CH₄ and CO₂ as expected. The size of Ni particles did not significantly increase before the reaction and after 710 hours, thus indicating that Ni was confined to the pores of the support and did not sinter throughout the reaction. Moreover, it was concluded that coke formation and not nickel sintering led to the deactivation of the catalyst. The loss of surface area and reduction in pore size were attributed to coke formation.

El Hassan et al. (El Hassan et al., 2016) compared the catalytic activity and stability of Co catalyst supported on SiO₂ and SBA-15. It was found that Co/SBA-15 exhibited higher catalytic activity and stability than Co/SiO₂. This was attributed once again to the occlusion of the cobalt particles inside the mesoporous of the zeolite support.
The use of a mesoporous support offers similar advantages to ZSM-5 and SBA-15 zeolites in terms of confinement effect. Adamu et al. (Adamu et al., 2020) compared Ni/Ce-yAl2O3 and Ni/Ce-mesoAl2O3 (Ce-doped mesoporous alumina support), and showed that the mesoporous support was more stable despite having a weaker metal-support interaction. There was a tradeoff between higher activity on the Ce-Al2O3 support and higher stability on the mesoporous support.

Apart from the choice and loading of active metal, the preparation method of the catalyst also plays an important role in achieving satisfactory dispersion and good metal-support interaction while minimizing the formation of spinel that is difficult to reduce. In general, catalysts synthesized by the sol-gel method give better results than those synthesized by impregnation, which in turn perform better than catalysts synthesized by co-precipitation (Hao et al., 2009, Li et al., 2010, Rahemi et al., 2013). For multimetallic catalysts prepared by impregnation, the order of impregnation also plays a role in determining the catalyst performance, with sequential impregnation being more advantageous than co-impregnation (Tomishige et al., 2002a). The results of Jozwiak et al. (Jóźwiak et al., 2005) for Rh-Ni/SiO2 catalysts show that the choice of noble metal precursor for incipient wetness impregnation does not greatly affect the performance of the catalyst, mostly due to the uncontrolled nucleation of metal particles on the support taking place during solvent evaporation and not during impregnation. This is not the case for other methods such as strong electrostatic adsorption or deposition-precipitation. Nitrate salt precursors are however advantageous to use over sulfates or chlorides (at least for non-noble metals) because the nitrate counter ion easily decomposes into gaseous NO2 and does not leave nonvolatile contaminants in the final product (2009). The use of nickel nitrate as a Ni precursor gives a higher dispersion on alumina when compare to other precursors (Chen I., 1988). The works of Chen et al on the synthesis of Ni/alumina catalysts (Chen I., 1988) have shown that calcination temperatures and heating rates affect the Ni particle size much more below 673K and 10 K/min, but the effect is milder above these values. Increasing the amount of water during impregnation increases the Ni particle size slightly, which infers that incipient wetness impregnation method can lead to better dispersion. Furthermore, a Ni loading higher than 20 wt % causes the particle size to increase more severely than smaller loadings.

Table 1-3 summarizes the properties of each type of support and active metal and highlights the effect of their combinations. A typical, well-performing catalyst is proposed as an example for each combination.

<table>
<thead>
<tr>
<th>METAL</th>
<th>Monometalic</th>
<th>Bimetallic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-Noble</td>
<td>Noble</td>
<td>Non-Noble</td>
</tr>
<tr>
<td>Mixed</td>
<td>Noble</td>
<td></td>
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</tbody>
</table>
For any catalyst to have a potential in industrial applications, many parameters must be met: It is desirable for the synthesis method to be quick, require a minimal number of steps and amount of solvent and employ inexpensive precursors. The catalyst must be highly active, resistant to coking and durable, a parameter which is often overlooked:

<table>
<thead>
<tr>
<th>Support</th>
<th>Mesoporous</th>
<th>Composite</th>
<th>Irreducible Metal Oxides</th>
<th>Reducible Metal Oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td>- Good redox property and oxygen mobility improve sintering.</td>
<td>- Higher conversion rates can be achieved under noble metals on mesoporous supports.</td>
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<tr>
<td></td>
<td></td>
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<td>- High risk of sintering remains evident, deactivation occurs due to coking.</td>
<td>- Resistance of noble metals to coke deposition and sintering can counteract the weak metal-support interaction.</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Ni/ZrO₂</td>
<td>Ni/Al₂O₃</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>- Less prone to sintering than reducible metal oxides.</td>
<td>- Deactivation time can be extended by confining the non-noble metal particles inside the porous support.</td>
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<tr>
<td></td>
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<td></td>
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<td>- Coke formation rate will not be reduced. Co/Activated Carbon</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Ni/Al₂O₃</td>
<td>Rh/Al₂O₃</td>
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<td>Ni-Ce/Al₂O₃</td>
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<td>(no individual mesoporous support with two metals were studied to the knowledge of the authors) Ni-Co/SBA15</td>
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<td>Rh/Al₂O₃</td>
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<td></td>
<td>Ni-Mo/SBA15-La₂O₃</td>
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<td></td>
<td></td>
<td>Ni-Mo/SBA15-La₂O₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Rh on Perovskites</td>
</tr>
</tbody>
</table>

Synergic effect improves dispersion, but weak metal-support interaction. Poor performance. Only mixed RMO supports investigated Ni-ZrO₂/Al₂O₃. -Noble metal promoter improves reducibility -Irreducible oxide gives better activity than RMO Ni-Rh/Al₂O₃ -Excellent stability and activity due to support strength, noble metals and synergistic effect Pt-Ru/γ-Al₂O₃.
although it is highly interesting to synthesize catalysts that yield high conversions in laboratory experiments, a commercially viable catalyst must have the ability to retain its performance over a long period. Table 1-4 shows a selection of highly stable catalysts described in the literature.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Description</th>
<th>Time on stream (h)</th>
<th>Metal - Support - Promoter</th>
<th>CH4 Conversion %</th>
<th>CO2 Conversion %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Fan et al., 2015)</td>
<td>Co-O affinity accelerated the gasification of carbon intermediates</td>
<td>1000</td>
<td>Co$<em>{0.075}$Ni$</em>{1.425}$Mg$_{0.625}$O -- n/a -- n/a</td>
<td>69</td>
<td>75</td>
</tr>
<tr>
<td>(Zhang et al., 2006)</td>
<td>Ni stabilized by confinement in the pores of SBA-15</td>
<td>600</td>
<td>Ni -- SBA-15 -- n/a</td>
<td>90</td>
<td>89</td>
</tr>
<tr>
<td>(Du et al., 2013)</td>
<td>Bimetallic particles suppress sintering, Formation of active amorphous carbon species</td>
<td>500</td>
<td>Pt-Ru -- γAl$_2$O$_3$ -- n/a</td>
<td>94</td>
<td>96</td>
</tr>
<tr>
<td>(Zeng et al., 2012)</td>
<td>MRE promotion decreases the size of Co$_3$O$_4$ particles, increases the metal-support interaction and reduces coking</td>
<td>320</td>
<td>Co -- γ-Al$_2$O$_3$ -- MRE</td>
<td>75</td>
<td>90</td>
</tr>
<tr>
<td>(Chen et al., 2013)</td>
<td>CeAlO$_3$ phase suppressed coke without reducing activity and inhibited the growth of graphitic carbon</td>
<td>250</td>
<td>Ni -- γ-Al$_2$O$_3$ -- CeO$_2$</td>
<td>79</td>
<td>88</td>
</tr>
<tr>
<td>(Jang et al., 2013)</td>
<td>Strong interaction between Ni and MgO stabilizes Ni</td>
<td>200</td>
<td>Ni--MgO -- Ce$<em>{0.2}$Zr$</em>{0.2}$O$_2$ -- n/a</td>
<td>95</td>
<td>96</td>
</tr>
<tr>
<td>(Wang et al., 2017)</td>
<td>- Pr$<em>3$O$</em>{11}$ doping of CeO$_2$ matrix lead to better metal-support interaction, avoids Ir aggregation . improved oxygen storage capacity reduces coke</td>
<td>200</td>
<td>Ir -- Ce$<em>{0.5}$Pr$</em>{0.5}$O$_2$ -- n/a</td>
<td>56</td>
<td>75</td>
</tr>
</tbody>
</table>
(de Araújo Moreira et al., 2020) Small particle size of Rh prevents coking.

<table>
<thead>
<tr>
<th>Catalyst Design</th>
<th>Active Component</th>
<th>Stability</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>184</td>
<td>Rh—Al₂O₃—n/a</td>
<td>61</td>
<td>55</td>
</tr>
</tbody>
</table>

(Kim et al., 2019) Exsolving of Ru from perovskite structure increases active sites.

<table>
<thead>
<tr>
<th>Catalyst Design</th>
<th>Active Component</th>
<th>Stability</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>Sr₀.₉₂Y₀.₀₈Ti₀.₉₀Ru₀.₁O₃₋ₓ</td>
<td>80.07</td>
<td>85.81</td>
</tr>
</tbody>
</table>

(Rego de Vasconcelos et al., 2020) Hydroxyapatite retains a good Ni dispersion (10-20nm).

<table>
<thead>
<tr>
<th>Catalyst Design</th>
<th>Active Component</th>
<th>Stability</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>Ni—Hydroxyapatite·Ca</td>
<td>66</td>
<td>73</td>
</tr>
</tbody>
</table>

### 1.2.6: Catalyst Durability-Activity Tradeoff

Industrial applications require active and durable catalysts. It is shown that active catalysts require a fine dispersion and good surface oxygen mobility, which comes at the expense of higher sintering risk. Furthermore, a good metal-support interaction, crucial quality for a catalyst resistant against sintering, is often accompanied by the formation of a spinel structure that is difficult to reduce, leading to less active catalysts. The catalyst designer has then to find a compromise that gives a catalyst with an acceptable performance.

Table 1-1 shows CO₂ and methane conversions reached by the most durable catalysts considered in this study. The durability is designated by the time on stream, irrespective of the composition or operating temperature. The general trend is indeed a lower conversion obtained for the most stable catalysts, showing effectively the trade-off between activity and stability.

![Figure 1-11: Conversion versus time on stream for multiple catalysts](image-url)
1.3: Conclusion
Dry reforming of methane is not an industrially mature process given the operational constraints exhibited by the various catalysts involved. As several studies have shown, satisfactory catalytic activity and stability are dictated in large part by active metal dispersion, adhesion to support and resistance to sintering, but also by low carbon formation. While a good catalyst cannot fully eliminate the formation of coke, it can favor the formation of more reactive intermediate carbonaceous species over that of the destructive Carbon Gamma type (Cγ).

The rapid deactivation and high coke formation associated with non-noble based monometallic catalysts, coupled with the expensive price of the more coke resistant and stable noble monometallic ones, dictate that new and innovative approaches must be investigated to overcome these limitations. Consequently, an economically potent catalyst is expected to be based on an inexpensive non-noble metal, while adding a small yet influential amount of noble and/or other non-noble metals to enhance its catalytic properties, as bimetals have shown better performance. Additionally, trimetallic catalysts can also lead to similar outcomes. Nevertheless, despite their superior performance, noble-noble bimetallic catalysts are not viable candidates due to price and scarcity concerns.

For a given active metal, choosing an appropriate support can enhance the metal-support interaction, thus leading to a reduction of metal sintering, while too strong a metal-support interaction comes at the expense of catalyst reducibility, thus leading to lower catalytic activity. In that case, an adequate doping of the support with another species can ensure that the metal-support interaction is strong enough to avoid metal sintering, and weak enough to ensure low reduction temperatures (MgO doping of NiO/Al₂O₃). Additionally, the anti-coking abilities of the catalyst can be enhanced by the presence of basic sites on the catalyst’s surface or by doping the support with species that can catalyze CO₂ decomposition. Finally, Ce, Zr or MRE doping can also lead to better metal-support interaction and enhanced anti-coking capabilities. Moreover, mesoporous and composite can perform better than reducible and irreducible metal oxides due to their peculiar properties.

Although these general guidelines for the influence of supports and promoters are generally valid, different studies have reported varying degrees of success for a given support or promoter. This can be attributed to the fact that the influence of a given support or promoter, and thus the validity of the aforementioned factors, is extremely dependent on the active metal species involved. This confirms the dominant influence of metal selection on the overall catalytic performance. Moreover, accurately defining an optimum choice of active metal, support and promoter cannot be achieved separately, given the intertwining influence of all these components, as summarized in Figure 1-12.
Future research in catalyst design should investigate the alloying and synergetic effect of nickel and cobalt with the excellent promoting effect of Rh or Ru in trace amounts in a trimetallic Ni-Co-Ru or Ni-Co-Rh catalyst. Alternatively, a cheaper catalyst with strong potential would confine Ni and Co particles in the mesopores of SBA15 zeolite. No such combinations have been reported in literature so far. Another interesting field of study would be to exploit interstitial alloys (carbides, nitrides etc) as diffusion barriers that have catalytic activity, to hinder the rate determining step in whisker growth.

1.4: Outlook
This chapter is an introductory survey of the literature on syngas, reforming and catalyst design for dry reforming laying the foundations for the upcoming thesis chapters. The effect of metal particle size and sintering on carbon formation was identified, and the graphitic carbon assumption widely made in thermodynamic studies of the reforming process has been shown to be questionable. In addition, a review of the catalysis literature summarized the main catalyst design parameters and their effects. The data shows that a combination of the Ni-Co active metal system with a noble metal dopant has a promising potential that has not been explored. The nature of the carbon whisker formation mechanism suggests that a catalytically active diffusion barrier may constitute a carbon-resistant catalyst as well.

The identified research gaps mentioned above will be guide the structure of the thesis: Chapters 2 and 3 will study the thermodynamics of the dry reforming process while relaxing the assumption of graphitic carbon to produce more realistic thermodynamic predictions, and couple the corrected thermodynamic results to a sintering model to understand and optimize the dynamic thermodynamic equilibrium in a dry reformer under catalyst sintering.
Chapter 4 explores transition metal nitrides (Mo and Ni-Mo) as interstitial alloy catalysts for the dry reforming process.

Finally, Chapters 5 and 6 study the trimetallic Ni-Co-Ru system to assess the effect of support properties, Ni/Co ratio and the role of the Ru promoter on the performance and coke resistance of this catalyst.

Appendix 1 describes a multi-scale, non-isothermal steady-state model for a dry reforming packed bed reactor. Its purpose is to provide realistic reactor and pellet profiles taking into account internal and external transport limitations to optimize reactor design and scale-up. Work using this code was unfortunately not possible in the given timeframe with the latest work disruptions brought in 2020.

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Chapter 2: Thermodynamic Analysis of Methane Dry Reforming: Effect of the Catalyst Particle Size on Carbon Formation
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Abstract: The effect of catalyst particle size on thermodynamic equilibrium of methane dry reforming and carbon formation has been studied through the Gibbs free energy minimization method taking into account the deviation of carbon formed from graphite Gibbs energy and its dependence on catalyst particle size. Methane and CO₂ conversions are maximized at 1-2 bars and temperatures above 1200K, and a molar H₂/CO ratio of 1 is obtained at 1100-1200K and 5-10 bar. Carbon formation was found to increase with particle diameter, and carbon presence was noticed at conditions of high pressure/low temperature and high temperature/low pressure. Optimal operating conditions were found to be close to carbon limits, highlighting the need for active metal particle size to be less than 5-6 nm to minimize coking. CO was identified as the precursor for carbon at low temperature, while CH₄ was found to be the main precursor at high temperature.

Keywords: Dry Reforming, Methane, CO₂, Syngas, Ni Catalyst

Nomenclature:
- yᵢ: mole fraction of i in the gas phase
- µᵢ: Chemical potential of species i, J/mol
- ΔGᵢ: Graphite deviation Gibbs energy, J/mol
- d: particle diameter, nm
- aⱼ: Moles of element i per moles of species j
- bᵢ: Initial moles of species i
- T: Temperature, K
- Φᵢ: fugacity coefficient of species i

G¹: Total Gibbs free energy, J/mol
nᵢ: Moles of species i
ΔGᵢ: Standard Gibbs energy of formation (298 K), J/mol
fᵢ: Partial fugacity of species i (Pa)
fᵢ: Standard state fugacity of species i
R: Universal gas constant, 8.314 J/mol.K
P: Pressure, Pa


2.1: Introduction

The ongoing depletion of fossil fuels is driving the world to search for alternative, sustainable and renewable sources of energy (Muneer T, 2003) to meet its ever increasing energy demand (Li, 2005). Furthermore, global warming and environmental consequences from the continuously growing economies, in addition to environmental regulations, require new energy sources to produce less pollutants such as SO\(_x\), NO\(_x\) and greenhouse gases. In parallel, the population growth has caused waste to be generated at a higher rate (Usman et al., 2015) and frequently mismanaged (Noor et al., 2013, Massoud and Merehbi, 2016). Landfill is a widely used method of municipal solid waste disposal, especially in developing countries such as Lebanon (Massoud and Merehbi, 2016), and large amounts of greenhouse gases, especially carbon dioxide and methane, are produced in landfills.

Hydrogen is a promising alternative fuel due to its high efficiency and clean combustion (Farshchi Tabrizi et al., 2015). It is also attractive as a renewable energy source since it can be produced from biomass, water and solar energy (Cau et al., 2014). Steam reforming has been the most common process to produce hydrogen from hydrocarbon feedstock, especially methane from natural gas, through further processing of the syngas product, essentially composed of hydrogen, carbon monoxide, CO\(_2\) and water. Traditionally, ammonia synthesis has been the primary consumer of syngas (Rostrup-Nielsen, 1993). However, more recent developments in the field of hydrocarbon reforming allowed for a better control of syngas composition, making it a very desirable feedstock for gas to liquid applications. Recently, it has been of interest to use biogas from landfills or anaerobic digestors as a feedstock for syngas production through the dry reforming process, both due to the expected syngas H\(_2\)/CO ratio being close to unity, which is suitable for gas-to-liquid applications and Fischer-Tropsch synthesis (Bereketidou and Goula, 2012, Hu and Ruckenstein, 2004), and due to the possibility of recycling two greenhouse gases, methane and CO\(_2\), into useful products.

The main reactions governing the process are as follows:

\[
\begin{align*}
\text{CH}_4 + \text{CO}_2 &= 2\text{CO} + 2\text{H}_2 \quad (\Delta H_{298K} = +247 \text{ kJ/mol}) \quad \text{(main reaction)} \\
\text{CO} + \text{H}_2\text{O} &= \text{CO}_2 + \text{H}_2 \quad (\Delta H_{298K} = -41.5 \text{ kJ/mol}) \quad \text{(water-gas shift)} \\
\text{CH}_4 + \text{H}_2\text{O} &= \text{CO} + 3\text{H}_2 \quad (\Delta H_{298K} = 206 \text{ kJ/mol}) \quad \text{(steam reforming)}
\end{align*}
\]

In addition to the carbon formation reactions

\[
\begin{align*}
2\text{CO} &= \text{CO}_2 + \text{C} \quad (\Delta H_{298K} = -171 \text{ kJ/mol}) \quad \text{(Boudouard reaction)} \\
\text{CH}_4 &= \text{C} + 2\text{H}_2 \quad (\Delta H_{298K} = 75 \text{ kJ/mol}) \quad \text{(Methane cracking)}
\end{align*}
\]

For more comprehensive set of possible reaction see the work of Nikoo and Amin (Nikoo and Amin, 2011).
The industrial application of the dry reforming process, however, has been heavily hindered by the performance of catalysts (Navarro et al., 2006, Lavoie, 2014, Ginsburg et al., 2005, Bradford and Vannice, 1996, Pakhare and Spivey, 2014). Traditional, nickel-based catalysts used in reforming technologies are cheap and active, but are prone to deactivation by sintering and carbon deposition (Sehested, 2006). This problem is more severe in the case of dry reforming, where the endothermic nature of the reaction requires high operating temperatures. The increased presence of carbon in the feed gas as compared to steam reforming or dry reforming, in addition to the elevated temperatures, causes a significant amount of carbon to form on the catalyst, leading to quick deactivation (Chein et al., 2015). Sintering of the nickel particles during operation leads to a loss of dispersion, ultimately leading to catalyst deactivation and increased carbon formation (Bengaard et al., 2002): Carbon layers that grow from nuclei on step sites on the nickel particle are stable above 80 atoms in diameter (approximately 6 nm), meaning that larger particles are more likely to yield carbon. Noble metals, such as ruthenium or rhodium, are less prone to coking and have a high dispersion (Khani et al., 2016, Hou et al., 2006), but are very expensive and hence their use is limited.

It is imperative to model the reactions and carbon formation in order to decide on the optimal operating conditions for the reforming process. The first indication to the feasibility of the process is a thermodynamic evaluation of the equilibrium conditions to estimate the expected conversion and carbon formation. This can be done through the computation of the equilibrium constants based on standard ∆H and ∆G values (Simakov et al., 2015, Annesini et al., 2007), entropy maximization calculations (de Souza et al., 2014) or Gibbs energy minimization routines (Solsvik et al., 2016, Farshchi Tabrizi et al., 2015, Nikoo and Amin, 2011, Li et al., 2008, Amin and Yaw, 2007, Challiwala et al., 2017, Atashi et al., 2016, Jafarbegloo et al., 2015). The Gibbs minimization method has been widely used due to its simplicity and its ability to compute equilibrium compositions even for systems where the reaction pathways are not known. Challiwala et al (Challiwala et al., 2017) noted that many studies assumed the gas phase behaved as an ideal gas, while the group’s work, amongst others cited above, use non-ideal equations of state to model the non-ideal gas-phase such as the Peng-Robinson and Soave-Redlich-Kwong equations of state.

The majority of thermodynamic studies in reforming have accounted for carbon formation tendencies with the assumption that the carbon species formed is graphite, which has a zero standard Gibbs energy of formation and negligible dependence of fugacity on operating conditions, (Nikoo and Amin, 2011, Challiwala et al., 2017, Noureldin et al., 2014), with the exception of Atashi et al (Atashi et al., 2016) and Ayodele et al (Ayodele and Cheng, 2015) who have ignored carbon formation within the dry reforming process in their simulations, and Nematollahi et al (Nematollahi et al., 2012) who incorporated the activity of graphite into their model. However, practical experience has shown that three general types of carbonaceous species can be distinguished on a used reforming catalyst based on temperature programmed hydrogenation (TPH) studies (Papadopoulou et al., 2012): Cα refers to surface carbide that can be hydrogenated below 323K, Cβ (or amorphous carbon) can be hydrogenated between 373 and 573K, while Cγ (graphitic carbon) is only hydrogenated above 673K.
Electron microscopy imaging shows that filamentous carbon ‘whiskers’ often grow from nickel and non-noble active metal particles, and many studies have noted that carbon filaments, and carbon deposits on reforming catalysts in general, deviate from graphite thermodynamics. Whisker carbon is the most dangerous form of carbon growing on a catalyst due to its high strength. Whisker growth can cause pore damage and detachment of active metal particles from the support, leading to dusting and increased pressure drop, hot bands and eventually plant shutdown (Rostrup-Nielsen, 2002). It has been observed that the Boudouard reaction and methane cracking reactions have lower equilibrium constants than graphite formation (Dent et al., 1945-1946, Rostrup-Nielsen, 1993, Alstrup et al., 1998).

Alstrup (Alstrup, 1988) studied the formation of carbon filaments on Ni, Ni-Cu and Ni-Fe catalysts and found deviations from graphite deposition thermodynamics that are dependent on particle size, irrespective of the (non-noble) active metal. In the same study, the author combined his finding to those of Rostrup-Nielsen (Rostrup-Nielsen, 1972) and proposed an expression for the deviation from the Gibbs free energy of graphite in function of the size of the largest particle catalyzing filament growth: \( \Delta G_c^{\text{dev}} \) (kJ/mol) = 2.6 + 93/d (nm).

To the knowledge of the authors, such a deviation has not been considered in a thermodynamic analysis of a reforming process prior to this work. The practical implications of this deviation are twofold: On one hand, there is some uncertainty around the present carbon limits calculated in thermodynamic studies. On the other hand, the carbon limits in a reformer are a function of the catalyst particle size: in other terms, the age of the bed, and consequently the severity of sintering in the catalyst batch, affects the carbon limits and it is then possible to define dynamic carbon limits from a semi-empirical approach. By incorporating the deviation parameter, this study shows the impact of non-graphite behavior and bed aging on the main parameters of the dry reforming process. The intricate reaction mechanism on the catalyst surface, in addition to the added complexity of modeling carbon whisker formation on a catalyst particle makes it very difficult to use a set of chemical reactions as a basis for thermodynamic equilibrium (Kalai, 2015). The Gibbs energy minimization method was chosen to model the chemical equilibrium of the process while incorporating the deviation Gibbs energy into the model while avoiding the difficulties of working with multiphase chemical reactions where the thermodynamic and kinetic constants are not well-defined.

2.2: Modeling
The Gibbs energy minimization problem is treated as an optimization problem, with the objective being to minimize the total Gibbs energy of a system that can contain CH\(_4\), CO\(_2\), CO, H\(_2\), H\(_2\)O and solid carbon, subject to atomic species conservation constraints. The pressure and temperature are fixed, as it is assumed that the reaction takes place in a heated reactor.
2.2.1: Objective Function

In a given multicomponent system, the total Gibbs energy is given by:

\[ G^T = \sum_{i=1}^{N} n_i \left( \Delta G_{f,i}^0 + RT \ln \frac{f_i}{f_i^0} \right) \]  

(1)

With the chemical potential, \( \mu_i \), defined as:

\[ \mu_i = \Delta G_{f,i}^0 + RT \ln \frac{f_i}{f_i^0} \]  

(2)

\[ G^T = \sum_{i=1}^{N} n_i \mu_i \]  

(3)

The partial fugacity and standard state fugacities for every component is given respectively by:

\[ \overline{f}_i = y_i \phi_i P \]  

(4)

and \( f_i^0 = P_0 = 0.1 \text{ MPa} \)

The fugacity coefficient \( \Phi_i \) can be obtained from the equation of state modeling the gas phase (Atashi et al., 2016, J.M. Smith, 2005).

Solid carbon is expected to form during the reaction, and its Gibbs energy (kJ/mol) is given by:

\[ G_C = n_C \left( \Delta G_{f,\text{Graphite}} + \Delta G_{\text{dev}}^C \right) \]  

(5)

With \( \Delta G_{\text{dev}}^C = 2.6 + 93/d \) being the particle-size dependent deviation parameter

The total Gibbs energy of the reactive system is then the sum of the gas and solid phase Gibbs energies, assuming that the solid phase is only pure carbon:

\[ G^T = \sum_{i=1}^{N-1} n_i \left( \Delta G_{f,i}^0 + RT \ln \frac{f_i}{f_i^0} \right) + n_C \left( \Delta G_{f,\text{Graphite}} + \Delta G_{\text{dev}}^C \right) \]  

(6)

2.2.2: Constraints

The reactive system is assumed to contain only 6 potential compounds: CH\(_4\), CO\(_2\), CO, H\(_2\), H\(_2\)O and solid carbon. Thus we define

\[ n_f = [n_{\text{CH}_4} \ n_{\text{CO}_2} \ n_{\text{CO}} \ n_{\text{H}_2} \ n_{\text{H}_2\text{O}} \ n_{\text{C}}] \]  

as the vector containing the number of moles of each of the species at equilibrium, and \( n_0 \) is the vector containing the initial number of moles of each species.

We define matrix \( a \) such that \( a_{ij} \) is the number of moles of element \( i \) in a mole of species \( j \). Matrix \( a \) is a 3x6 matrix with rows representing C, H, and O respectively, and columns representing the species in vector \( n \) respectively, then

\[
a = \begin{bmatrix}
1 & 1 & 1 & 0 & 0 & 1 \\
4 & 0 & 0 & 2 & 2 & 0 \\
0 & 2 & 1 & 0 & 1 & 0
\end{bmatrix}
\]
Let \( b \) be a 3x1 vector containing the initial number of moles of each atomic species, then
\[
b = a \cdot n'_0
\]  
(7)

The atomic conservation of atomic species then dictates: \( a \cdot n'_f = b \)

Molar compositions should also be non-negative, and hence the problem statement becomes:
\[
\min G^T = \sum_{i=1}^{N-1} n_i \left( \Delta G^0_{f_i} + RT \ln \frac{f_i}{f'_i} \right) + n_C \left( \Delta G_{f,\text{graphite}} + 2.6 + \frac{93}{a} \right)
\]  
(8)

Subject to \( a \times n'_f = b \)

Where, \( n_0, n_f, d \geq 0 \)

This problem was solved in MATLAB using \textit{fmincon} with the interior-point algorithm for temperatures between 700 and 1000°C and pressures between 1 and 20 bars for various catalyst diameters. The temperature range was chosen based on the review of a large number of experimental and theoretical studies (Xu et al., 2009, Liu et al., 2009, Xiancai et al., 2005, Arbag et al., 2010, Barroso-Quiroga and Castro-Luna, 2010, Wu et al., 2013) on dry reforming of methane, where the most relevant temperature range was identified. Although reforming reactions are favored at lower pressures due to the increase in the total number of moles in the system through the reaction, it was chosen to model up to 20 bars for the same reasons for which steam reformers and autothermal reformers are operated at high pressures; a higher syngas throughput is obtained through higher pressures and therefore it is of interest to predict the performance of the reactor at these conditions. Catalyst particle diameters considered are in the range of 5 to 20 nm, as these values give a reasonable representation of sintering throughout the catalyst lifetime (Sehested, 2006). Although nickel particle sizes can go up to ~100 nm, the results discussed here are limited to the range of 5-20 nm, since they sufficiently highlight the trends observable. Furthermore, the model by Alstrup (Alstrup, 1988) for the deviation from graphite thermodinamics does not assume a unique particle size or a very narrow particle size distribution, but rather correlates the deviation to the diameter of the largest particle catalyzing carbon growth. Still, it is assumed that as a catalyst sinters, the particle size distribution changes and the upper bound on catalyst particle size increases.

2.3: Results

Parameters studied are the methane and CO\textsubscript{2} conversion, defined as
\[
X_i = \frac{n_{i,0} - n_{i,f}}{n_{i,0}} \times 100
\]  
(9)

in addition to the H\textsubscript{2}/CO ratio and the carbon formation, expressed as a molar percentage.
\[
C_s = \frac{n_{C,f}}{\sum N n_{i,f}} \times 100
\]  
(10)
The carbon limits are defined here as conditions of temperature and pressure where carbon deposition exceeds 0.1%. The initial molar composition of the reactive system is taken as 60% methane and 40% CO$_2$, as these values are an approximate representation of biogas composition. One must note that raw biogas also contains other gases such as H$_2$S, ammonia and water. The effect of these gases on the catalyst cannot be neglected, especially for hydrogen sulfide as they cause catalyst deactivation (Jablonski et al., 2015). The deactivated catalyst then fails to make the reactive system reach equilibrium, and hence removal of these pollutants is usually done before introduction of the raw material to the reforming reactor, even when using methane as a feedstock for reforming. We can then safely assume negligible levels of contaminants in the system. Furthermore, the modeling of these compounds in a Gibbs Free energy minimization study is not representative since it cannot account for their effect on the catalyst directly. One must note that the possibility of coupling a dry reformer to a biogas plant must be the subject of detailed economic studies, as the scale at which reforming processes achieve economies of scale is higher than the typical scale of a biogas plant.

Figure 2-1: Conversions, H$_2$/CO and solid carbon percentage as function of temperature and pressure for d=5 nm and molar CH$_4$/CO$_2$=1.5

2.3.1: Methane conversion
Figures 2-1, 2-2, 2-3, 2-5 and 2-6 show the results of the simulation in terms of methane and CO$_2$ conversions, H$_2$/CO ratio and carbon formation as function of temperature and pressure. As is the case for an endothermic reaction, methane conversion increases with temperature, with a decreasing slope at higher temperatures, where the conversion reaches its maximum around 1000°C and 1 bar. Lower pressures and high temperatures both favor the dry reforming reaction, as demonstrated by the increase in methane conversion with a decrease in pressure. A sharper increase in conversion is noticed at high temperature/low pressure, especially at low catalyst particle size. This jump is observed around the same P-T conditions at which the carbon limits are crossed, and therefore, the
conversion spike is associated with the methane decomposition reaction producing solid carbon. shows the evolution of methane and CO\textsubscript{2} conversion at 1000°C and 1 bar in function of the catalyst particle diameter. A positive relationship is noticed, which can be related to the methane decomposition reaction proceeding further as the catalyst particle grows. This observation is in agreement with the results obtained for carbon formation, where the amount of carbon formed at these conditions increases with particle size.

It is to note that the trend exhibited by methane conversion is in good agreement with other theoretical studies (Nikoo and Amin, 2011), although the conversion is lower. With CO\textsubscript{2} being the limiting reactant, it can be easily shown that the maximum conversion that can be attained by methane through the dry reforming reaction alone is 66.7\% for a 60/40 methane/CO\textsubscript{2} initial composition, meaning that the reaction reaches almost complete conversion above ~850°C and below ~8 bar. Methane conversions exceeding the theoretical maximum of 66.7\% are attributed to carbon formation.

The obtained model shows a good agreement with experimental measurements of methane conversion on a Ni/Al\textsubscript{2}O\textsubscript{3} catalyst with a nickel particle diameter of 23 nm at atmospheric pressure and CH\textsubscript{4}/CO\textsubscript{2} molar ratio of 0.5 (experimental conditions by Ocsachoque et al. (Ocsachoque et al., 2011)), as shown in Figure 2-7, and other nickel catalysts of varying diameters (Figure 2-8). The model slightly overestimates experimental data, which is expected due to transport and kinetic limitations in experimental catalytic tests. At the experimental conditions of the data in Figure 2-8, the model predicts a small increase in CH\textsubscript{4} conversion and a small increase in CO\textsubscript{2} conversion (-0.01\% and +0.03\% respectively) as the particle size increases. Experimental data shows minima in CH\textsubscript{4} and CO\textsubscript{2} conversions instead. This has been attributed by (Goula et al., 2015) to the effect of the different preparation methods used to synthesize each catalyst on its reducibility and activity. The catalyst of Ni particle size of 9mm in their work was prepared using incipient wetness impregnation and gave a sample which is more difficult to reduce, hence its lower activity.
2.3.2: CO\(_2\) conversion

The conversion of CO\(_2\) is generally higher than that of methane, especially at lower temperatures. Carbon dioxide being the limiting reactant explains the higher conversion, although this trend has been noticed experimentally (Xu et al., 2009, Lucrédio et al., 2012, Kim et al., 2000) and has been associated to the reverse water-gas shift reaction proceeding further at lower temperatures (Wang et al., 1996). The CO\(_2\) conversion is very weakly affected by the catalyst particle diameter, and is maximized at low pressures and high temperatures, and conversions above 99% can be reached above 1200 K.

No spike in conversion is observed in CO\(_2\) when the carbon limits are crossed, unlike in methane, meaning that methane dissociation is the main source of carbon formation at a CH\(_4\)/CO\(_2\) ratio of 1.5. However, it is reported (Bradford and Vannice, 1999) that CO disproportionation is the main contributor to carbon deposition. The difference between the present work and the literature is probably due to CO\(_2\) reaching a conversion close to 100% even outside the carbon limits.

Simulation results for an equimolar feed of methane and carbon dioxide (Figure 2-3) show that CO\(_2\) conversion does not increase in a sharper fashion at high temperatures. The methane spike is not observed, but no carbon is formed at higher temperatures, in perfect accordance with Bradford and Vannice (Bradford and Vannice, 1999). However, at lower temperatures, carbon deposition is increased as compared to the 60/40 methane/CO\(_2\) system where carbon dioxide is depleted essentially through the dry reforming reaction. Trends in methane and carbon dioxide conversion obtained are in good agreement with the literature (Sun et al., 2011) and experimental measurements (Figure 2-7, Figure 2-8).
Figure 2-3: Conversions, \( \text{H}_2/\text{CO} \) and solid carbon percentage as function of temperature and pressure for \( d=15 \) nm and molar \( \text{CH}_4/\text{CO}_2=1.0 \)

Figure 2-4: Methane and \( \text{CO}_2 \) conversions at 1000°C and 1 bar as a function of particle diameter for molar \( \text{CH}_4/\text{CO}_2 \) ratio of 1.5
2.3.3: H₂/CO ratio

Average H₂/CO ratio is slightly below unity for all catalyst particle sizes, with a convex relationship with respect to pressure that is less noticeable at smaller particle sizes. The minimum is reached at lower temperatures and moderate to high pressures (10-20 bars) while the maximum is generally reached at lower pressures and high temperatures. This pattern is explained by the mutual effect of the reverse water-gas shift reaction and the two main modes of carbon formation, through CH₄ or CO decomposition, reaching different extents at different conditions. At lower temperatures, the exothermic Boudouard reaction is favored over the methane decomposition reaction. Furthermore, the reverse water-gas shift reaction converts hydrogen into water, causing a decrease in the H₂/CO ratio. At higher temperatures, the reverse water-gas shift reaction is less favored, hence the increase in H₂ presence. Methane decomposition into carbon and hydrogen also causes the H₂/CO ratio to rise above unity at conditions of low pressure and high temperature. At catalyst diameters larger than 15 nm, the hydrogen/CO ratio becomes convex with respect to temperature as well. This trend can be explained by the effect of the exothermic Boudouard reaction yielding less carbon as temperature increases while the endothermic methane decomposition reaction only forms carbon at high temperatures. The behavior of the hydrogen/CO ratio is in agreement with Atashi et al (Atashi et al., 2016) except for temperatures above 1200K where a drop in the H₂/CO ratio was reported while in this work a monotonous trend was obtained.
Figure 2-6: Conversions, H₂/CO and solid carbon percentage as function of temperature and pressure for d=20nm and molar CH₄/CO₂=1.5

Figure 2-7: Comparison of simulation results with experimental measurements from (Ocsachoque et al., 2011) with d=23 nm and molar CH₄/CO₂=0.5 at P=1 bar.
2.3.4: Carbon formation

The patterns of carbon deposition noticed correspond exactly to theoretical predictions: the amount of carbon formed increases with catalyst particle size, especially above 6 nm which is the thermodynamic stability limit for carbon deposits on the catalyst, corresponding to the critical diameter of 80 atoms described by Bengaard (Bengaard et al., 2002) and confirmed by Kim et al (Kim et al., 2000). Table 2-1 shows this pattern corresponds to experimental results obtained by different groups. The behavior of carbon formation is observed to be similar to simulation results by Tsai and Wang (Tsai and Wang, 2008) but carbon mole fractions calculated are lower: carbon formation for an equimolar CH₄/CO₂ feed was found to reach a maximum of 7-8 mol% while the mole fractions obtained by (Tsai and Wang, 2008) went as high as 20 mol%.

Table 2-1: Experimental results for various nickel catalysts
*: after 5 hours on stream

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ni particle size nm</th>
<th>T°C</th>
<th>CH₄ mol.%</th>
<th>CO₂ mol.%</th>
<th>Carbon</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>8% Ni/Al₂O₃</td>
<td>14</td>
<td>860</td>
<td>71.5</td>
<td>96</td>
<td>0.18 g/gcat *</td>
<td>(Bereketidou and Goula, 2012)</td>
</tr>
<tr>
<td>8% Ni/20Ce-Al₂O₃</td>
<td>10</td>
<td>860</td>
<td>70.6</td>
<td>97.1</td>
<td>0.168 g/gcat *</td>
<td>(Bereketidou and Goula, 2012)</td>
</tr>
<tr>
<td>8% Ni/Al₂O₃ edf</td>
<td>6</td>
<td>800</td>
<td>72</td>
<td>94</td>
<td>0.96 wt%</td>
<td>(Goula et al., 2015)</td>
</tr>
<tr>
<td>8% Ni/Al₂O₃ wet</td>
<td>10</td>
<td>800</td>
<td>69</td>
<td>87</td>
<td>6.17 wt%</td>
<td>(Goula et al., 2015)</td>
</tr>
</tbody>
</table>
Carbon seems to form in two different modes: at low pressures and high temperatures, moderate amounts are formed especially on fine catalysts. Under these conditions, the main contributor to carbon deposition is methane, as its decomposition into hydrogen is endothermic and increases the total number of moles, hence the low pressure requirement. Furthermore, at d=15 nm, carbon forms at these conditions for CH₄/CO₂=1.5 but not for an equimolar system. In other words, the presence of methane is correlated to the formation of carbon at the conditions that favor methane decomposition. At low temperatures, solid carbon only forms at higher pressures, and the amount formed decreases with increasing temperature but is larger than high temperature coke. This trend is typical of CO as a precursor to carbon formation by the Boudouard reaction, as it is exothermic and decreases the total number of moles of gas, therefore requiring higher pressures from Le Chatelier’s principle. It can also be noticed that an increase in CO₂ concentration from 40% to 50% in the initial system causes an increase in the amount of carbon formed at low temperatures. Although the expected result is the reverse Boudouard reaction to be favored, the added CO₂ forms extra CO that reacts to give solid carbon.

Figure 2-9 shows the carbon limits beyond which solid carbon forms more than 0.1 mol% of the system. As the diameter of the metallic catalyst particle increases, carbon is expected to form in a wider region of temperature and pressure. At d= 15 nm, the two distinct regions of carbon presence overlap and carbon is then expected at high temperatures or high pressures.

The positive relationship between pressure and carbon formation is in agreement with the literature but this study noted that an increase in the CO₂ content of the initial system caused an increase in solid carbon at low pressures while Sun et al (Sun et al., 2011) found the opposite trend. Their work assumed graphite is the carbon phase formed, and attributed the beneficial effect of CO₂ addition to the promotion of the reverse Boudouard reaction. This work relaxes the graphite assumption, which explains the opposing trends. Upon increasing the CO₂/CH₄ ratio, the carbon limits at low temperature shift from delimiting two zones of carbon formation to delimiting one zone of carbon formation below a certain temperature. At the lower CO₂/CH₄ ratio, there is a range of low temperatures and moderate pressures that is in between the two main coking zones, where carbon formation is not expected, which justifies the difference observed.
The optimal operating conditions should guarantee a high conversion while remaining outside the carbon limits and maintaining a H₂/CO ratio close to unity. Conditions of both high temperatures and pressures (1200K, 10-15 bar) are not expected to yield carbon, but the methane conversion is not maximized and hydrogen/CO ratio is around 0.8. Equimolar H₂ and CO are obtained at approximately 1100-1200 K and 5-10 bar with satisfactory CH₄ and CO₂ conversion, but the risk of carbon formation is high since the carbon limits are close. From an industrial point of view, a fresh catalyst with high dispersion can tolerate such an operation but the catalyst has to be carefully monitored and replaced when the upper limit on particle size is around 10 nm. This study further highlights the requirement of having a stable catalyst that can resist sintering for long periods of time. From the catalyst designer’s perspective, this means that the catalyst should have a very strong active metal-support interaction (spinel structure), which in turn renders the catalyst more difficult to reduce at process startup, requiring higher temperatures and longer reduction times. The corrosive reducing environment and higher temperatures significantly reduce the reactor service life, which in turn increases the maintenance costs of the plant. An optimization study should then be performed to find the best balance between catalyst cost and maintenance cost of the reformer.

2.4: Conclusion

The formation of carbon was found to be a dynamic phenomenon that is not only a function of temperature and pressure but also of the catalyst, with larger active metal particles yielding carbon at more moderate conditions. Though the impact of the catalyst on carbon formation has been demonstrated by countless experimental studies, this work offers a theoretical tool that accounts for the effect of sintering on reactor performance. Optimal process conditions were found to be dangerously close to the carbon limits, hence highlighting the need for a fine catalyst particle size, ideally below 5 nm, to avoid excessive carbon deposition. Conditions of very high temperature and low pressures were
found to yield moderate amounts of carbon mainly through methane decomposition, while conditions of low temperature and high pressure gave higher amounts of carbon through the Boudouard reaction.

2.5: Outlook
This work has provided an understanding of the thermodynamic equilibrium in the dry reformer in terms of temperature, pressure and active metal particle size. Two main points were drawn:

- Conditions of temperature and pressure that give high conversions were identified
- Carbon limits were shown to heavily depend on particle size

By developing an understanding of how the particle size changes with time (and temperature), it is then possible to predict how the carbon limits change with time on stream, and one can therefore perform a time-dependent optimization on the reformer to guarantee high conversion and no carbon formation. Chapter 3 describes the development of an optimization algorithm that couples a sintering model with the thermodynamic analysis developed in this chapter.

2.6: References


Chapter 3: Dynamic Optimization of Dry Reformer Under Catalyst Sintering Using Neural Networks

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Preamble:

This chapter constitutes an extension to Chapter 2, in which the thermodynamic analysis results are coupled with a time-dependent sintering model to optimize the operation of a dry reforming reactor. As the thermodynamic data is generated by an optimization algorithm, optimizing the reactor operation would involve a computationally expensive nested optimization. Computational complexity can be reduced by producing a smooth, derivable input-output model to represent thermodynamic data instead. Due to the complicated dependence of equilibrium results on input conditions and non-monotonous behavior, the use of artificial neural networks to model the data was found to be advantageous. Mr. Mazen Azzam has developed, optimized and validated the neural network model that I use in the coupled time-dependent optimization algorithm I developed. My contribution to the work includes the development of the optimization algorithm, its coupling with the sintering model, interpretation of the reformer results and write-up of the related sections of the manuscript.

Abstract: Artificial neural networks (ANN’s) have been used to optimize the performance of a dry reformer with catalyst sintering taken into account. In particular, we study the effects of temperature, pressure and catalyst diameter on the methane and CO2 conversions, as well the H2/CO ratio and the molar percentage of solid carbon deposited on the catalyst. The design of the ANN was automated using a genetic algorithm (GA) with indirect binary encoding and an objective function that uses the effective number of parameters provided by Bayesian regularization. Results show that an industrially-acceptable catalyst lifespan of two years for a dry reformer can be achieved by periodically optimizing temperatures and pressures to accommodate for the change in catalyst diameter caused by sintering [5-12 nm]. In particular, it was found that the reactor’s operation favors high temperatures of almost 1000 °C, while the pressure must
be gradually increased from 1 to 5 bars to remain as far as possible from carbon limits and ensure acceptable conversions and molar ratios in the syngas.

3.1: Introduction

The dry reforming of methane is a promising technology to convert the two main greenhouse gases – methane and carbon dioxide (Selvarajah et al., 2016) – into syngas which can produce useful chemicals. In the dry reforming process methane reacts with CO₂ as an oxidant to produce syngas with a H₂/CO ratio close to unity, which makes it suitable for the synthesis of alcohols in the Fischer-Tropsch process (Bereketidou and Goula, 2012, Hu and Ruckenstein, 2004). This technology is an attractive option to valorize biogas produced in anaerobic digesters or landfills, with the annual biogas production reaching 59.0 billion cubic meters in 2013 (Kummamuru, 2016), or natural gas combined with a CO₂ capture or gas cleanup technology such as absorption [1st ref] or membrane separation [2nd ref], highlighting the huge potential feedstock for the process. The dry reforming process is an attractive technique to utilize greenhouse gases captured by gas separation processes. The main reactions governing the process are as follows:

\[ CH_4 + CO_2 = 2CO + 2H_2 \ (\Delta H_{298K} = +247 \text{ kJ/mol}) \ (Main \ Reaction) \]

\[ CO + H_2O = CO_2 + H_2 \ (\Delta H_{298K} = -41.5 \text{ kJ/mol}) \ (Water-gas \ Shift) \]

\[ CH_4 + H_2O = CO + 3H_2 \ (\Delta H_{298K} = +206 \text{ kJ/mol}) \ (Steam \ Reforming) \]

In addition to the carbon formation reactions:

\[ 2CO = CO_2 + C \ (\Delta H_{298K} = -171 \text{ kJ/mol}) \ (Boudouard \ Reaction) \]

\[ CH_4 = C + 2H_2 \ (\Delta H_{298K} = +75 \text{ kJ/mol}) \ (Methane \ Cracking) \]

For a more comprehensive set of possible reactions see the work of Nikoo and Amin (Nikoo and Amin, 2011).

Despite its huge potential, dry reforming did not have any major industrial application, due to limitations concerning catalyst performance especially with carbon resistance (Abdullah et al., 2017, Navarro et al., 2006, Lavoie, 2014, Ginsburg et al., 2005, Bradford and Vannice, 1996, Pakhare and Spivey, 2014): supported nickel catalysts are the most widely used in industrial applications in reforming reactors, due to their low cost and good activity. Sehested (Sehested, 2006) outlined four main shortcomings of nickel catalysts, namely: limited effectiveness, susceptibility to poisoning by sulfur and other elements, carbon formation and sintering at higher temperatures. In dry reforming processes, carbon formation and sintering are particularly problematic since they are related: compared to the steam reforming reaction (Rostrup-Nielsen, 1984) and the autothermal reforming reactions (Rice, 2007), the dry reforming reaction is the most endothermic and therefore requires the highest operating temperature to achieve satisfactory conversion. The low concentration of steam and the higher temperatures, in addition to the increased mole fraction of carbon in the process gases (high concentration
of CO₂) cause an amount of carbon to build up on the catalyst. The literature is contradictory when it comes to describing carbon formation on nickel catalysts: experimentally, three general types of carbon have been observed. Pyrolytic carbon forms essentially during thermal degradation of heavier hydrocarbons (Abdullah et al., 2017), while encapsulating carbon occurs especially in the presence of aromatic compounds and blocks the surface of the catalyst, preventing access to the active sites and causing a decrease in activity. Whisker carbon is the most dangerous type of carbon growth (Helveg et al., 2011, Nikoo and Amin, 2011) due to its high strength which causes irreversible damage to the catalyst, including pellet breakage and detachment of active metal crystals. Its mechanism of formation has been the subject of numerous studies (Dent et al., 1945-1946, Rostrup-Nielsen, 1993, Alstrup et al., 1998) and can be associated to the solubility of carbon in the nickel lattice. Carbon deposits diffuse through the nickel crystal and accumulate at the nickel/support interface from which a strong fiber grows and pushes the nickel crystal out. Still, most modeling works have assumed carbon to behave like graphite for equilibrium calculations (Nikoo and Amin, 2011, Challiwala et al., 2017, Noureldin et al., 2014, Nematollahi et al., 2012). In a previous work (Abdel Karim Aramouni et al., 2017), we proposed a thermodynamic analysis for carbon formation derived from experimental measurements by Rostrup-Nielsen and Alstrup (Rostrup-Nielsen, 1972), (Alstrup, 1988). The diameter of the active metal particle has been found to affect the Gibbs energy of formation of carbonaceous species on the catalyst, with more carbon being formed on larger particles. Catalyst particles below the threshold value of 6 nm were found to accumulate very low amounts of carbon.

On the other hand, exposure of a supported catalyst to elevated temperatures over its service life causes it to suffer sintering, i.e. a loss of active surface area due to coalescence of the dispersed active metal particles (Bai et al., 2014), and thus an increase in active metal particle diameter over time. The temperature at which a material suffers from sintering is roughly dependent on its melting point, in addition to its Tamman and Huttig temperatures: At the Huttig temperature, atoms at crystal defects in the material experience mobility, while at the Tamman temperature, atoms in the bulk experience mobility. These temperatures for nickel are shown in Table 3-1.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point</td>
<td>1453 °C</td>
</tr>
<tr>
<td>Tamman Temperature</td>
<td>581 °C</td>
</tr>
<tr>
<td>Huttig Temperature</td>
<td>484 °C</td>
</tr>
</tbody>
</table>

Two main mechanisms describe the sintering of reforming catalysts (Sehested, 2003): at low temperatures, particle migration is the primary cause of sintering. The mobility of surface atoms and adatoms makes the center of the particle migrate on the catalyst surface, and collisions with other particles cause them to coalesce, and an increase in average particle diameter is exhibited. At higher temperatures, Ostwald ripening (atom migration)
is responsible for an increase in the sintering rate. In reforming catalysts, the presence of steam in the gas above the catalyst increases sintering rate due to the mobility of Ni$_2$-OH dimers on the catalyst surface (Sehested, 2004). Sintering in these processes is mostly due to particle migration except at temperatures above 700-750 °C where Ostwald ripening becomes significant.

In addition to the activity loss that sintering causes, the increase in catalyst particle size with time decreases the Gibbs energy of formation of carbonaceous species and therefore an increase in carbon formation is expected. In this work, we employed artificial neural networks (ANN’s) to model the dry reforming process, which is originally described by the Gibbs energy minimization method in (Abdel Karim Aramouni et al., 2017). Given a certain temperature, pressure and catalyst diameter, the model predicts the methane and CO$_2$ conversions, H$_2$/CO ratio and molar percentage of solid carbon deposited on the catalyst. This provides a faster method to estimate the outputs of the reactor. Next, we use the ANN model as an objective function to maximize the conversions and minimize carbon deposition and thus obtain optimal process conditions that change with the sintering of the catalyst.

### 3.2: Thermodynamic Model

The dependence of carbon Gibbs energy of formation on the particle diameter has been studied by Alstrup (Alstrup, 1988) and the deviation from graphite thermodynamics $\Delta G_{C}^{\text{dev}}$ is given by:

$$\Delta G_{C}^{\text{dev}} \text{ (kJ / mol)} = 2.6 + 93 / d$$  \tag{1}$$

with $d$ being the particle diameter in nm.

Equilibrium compositions for given temperature and pressure are obtained by minimizing the total Gibbs free energy $G^T$ of the multicomponent system subject to conservation of mass constraints. In a given system of $N$ chemical species, the total Gibbs energy $G^T$ is given by:

$$G^T = \sum_{i=1}^{N} n_i \left( \Delta G_{f,i}^0 + RT \ln \left( \bar{f}_i / f_{i,0} \right) \right)$$  \tag{2}$$

Where $\Delta G_{f,i}^0$ is the standard Gibbs energy of formation of species $i$, $\bar{f}_i$ is the partial molar fugacity of species $i$ at process conditions, $f_{i,0}$ is the standard state fugacity of species $i$, $n_i$ is the number of moles of species $i$, $R$ is the ideal gas constant, and $T$ is the absolute temperature at process conditions.

The Gibbs energy of solid carbon $G_C$ in this case is given by:

$$G_C = n_C \left( \Delta G_{f,i,\text{Graphite}}^0 + \Delta G_{C}^{\text{dev}} \right)$$  \tag{3}$$
The total Gibbs energy of the reactive system is then the sum of the gas and solid phase Gibbs energies, assuming that the solid phase is only pure carbon:

\[
G^T = \sum_{i=1}^{N-1} n_i \left( \Delta G_{fi}^0 + RT \ln \left( \frac{f_i}{f_{i,0}} \right) \right) + n_C \left( \Delta G_{f,Graphite}^0 + \Delta G_{C}^{dev} \right)
\]  

(4)

The problem statement becomes:

\[
\min_n \ G^T = \sum_{i=1}^{N-1} n_i \left( \Delta G_{fi}^0 + RT \ln \left( \frac{f_i}{f_{i,0}} \right) \right) + n_C \left( \Delta G_{f,Graphite}^0 + 2.6 + 93/d \right)
\]  

(5)

Details of the thermodynamic model and constraints are demonstrated in (Abdel Karim Aramouni et al., 2017). The problem is solved for temperatures between 700 and 1000 °C and pressures between 1 and 20 bars for various catalyst diameters. The temperature range was chosen based on the review of a large number of experimental and theoretical studies (Xu et al., 2009, Liu et al., 2009, Xiancai et al., 2005, Arbag et al., 2010, Barroso-Quiroga and Castro-Luna, 2010, Wu et al., 2013). The carbon limits are defined here as conditions of temperature and pressure where carbon content exceeds 0.1 mol %. The initial molar composition of the reactive system is taken as 60% methane and 40% CO₂, as these values are an approximate representation of biogas composition.

Parameters studied are the methane and CO₂ conversions, defined as:

\[
X_i = 100 \left( \frac{n_{i,0} - n_{i,F}}{n_{i,0}} \right)
\]  

(6)

Where \( X_i \) is the conversion of species \( i \), and \( n_{i,0}, n_{i,F} \) denote respectively the initial and final number of moles of species \( i \). In addition, other parameters considered were the molar H₂/CO ratio and the carbon formation, expressed as a molar percentage \( C_s \), and given by:

\[
C_s = 100 \left( \frac{n_{C,F}}{\sum_{i=1}^{N} n_{i,F}} \right)
\]  

(7)

3.3: Sintering Model

At lower temperatures and in the presence of steam, the relation between average particle diameter \( \bar{d} \) and time \( t \) is given in (Sehested, 2006) by:

\[
\frac{\bar{d}}{d_0} = \left( \frac{\text{const.} \cdot K_{(OH-dimer)} D_{(OH-dimer)} X_{Ni} \left( \frac{P_{H_2O}}{P_{H_2}^{0.5}} \right)^{\frac{1}{2}}}{(1-X_{Ni}) A_{carrier} \bar{d}_0^3 \cdot d_0^2 \cdot (d_0^2 + 1)} \right)^{1/7}
\]  

(8)

Where \( \bar{d}_0 \) is the initial particle diameter, \( K_{(OH-dimer)} \) is a temperature dependent constant, \( D_{(OH-dimer)} \) is the particle diffusion constant in the presence of water and hydrogen, \( X_{Ni} \)
is the mass fraction of nickel, $A_{carrier}$ is the support surface area; and $P_{H_2O}$, $P_{H_2}$ are respectively the partial pressures of steam and hydrogen in bar.

Sehested et al. (Sehested, 2003) have given another rate law in a previous paper where they do not consider the effect of steam and hydrogen pressure but provide numerical values for the constants in the model. For a steam/hydrogen ratio of 1:1 at atmospheric pressure, the fitted model was:

$$\frac{d\bar{a}}{d\bar{a}_0} = \left[ \frac{K}{A_{carrier}} \exp\left(-\frac{E_a}{RT}\right) \right]^{1/7} t + 1$$

(9)

Where $E_a$ is the activation energy and $K$ is a lumped parameter. In order to apply this simplified model to dry reforming conditions, it is necessary to adjust the value of $K$ in order to take into account the different $H_2O/H_2$ ratio.

By identification between the models in (Sehested, 2006) and (Sehested, 2003) to isolate the effect of hydrogen and steam on the sintering rate, the final model used for dry reforming sintering kinetics (valid up to 750°C) is:

$$\frac{d\bar{a}}{d\bar{a}_0} = \left[ \left( \frac{K_{2}}{A_{carrier}} \frac{P_{H_2O}}{P_{H_2}^{0.5}} \right) \exp\left(-\frac{E_a}{RT}\right) \right]^{1/7} t + 1$$

(10)

Where $K_{2} = e^{47.18/2} \text{ m}^2/\text{g.h.bar}^{0.5}$ and $E_a = 332 \text{ kJ/mol}$. The dependence of the model on the hydrogen and steam partial pressure is verified in (Sehested et al., 2006) and therefore the derived model can be considered valid.

3.4: Modeling Using Artificial Neural Networks and Genetic Algorithm

ANN’s are computational models loosely based on the mode of action of biological brains, capable of recognizing complex relationships between different parameters, and thus solving and modeling a large variety of problems. Feedforward Neural Networks (FNN’s) are a special type of ANN’s that possess a structural representation that can be perceived in a network form (Ojha et al., 2017) which makes it a universal function approximator, capable of handling any continuous function (Hornik, 1991). This powerful approximation ability has been recruited in a variety of applications, including clustering and classification, pattern recognition, regression, control, bioinformatics, signal processing, etc (Ojha et al., 2017).

In the chemical process industry, ANN’s have been applied successfully to complex process modeling, process control, and fault detection and diagnosis (Ayodele and Cheng, 2015). However, the use of ANN’s in the modeling of dry reforming processes is still limited in the literature. Amin and Istadi (Istadi and Amin, 2007) simulated the effects of feed ratio, total feed flow rate, discharge voltage and reactor wall temperature on reforming in a catalytic-dielectric barrier discharge plasma reactor, while Ayodele and Cheng (Ayodele and Cheng, 2015) investigated the effects of reactant feed ratio, reaction temperature, and reactant partial pressures. More recently, the effect of the catalyst metal
loading has been investigated by Hossain et al. (Hossain et al., 2016). So far, no work in the literature has used ANN’s to investigate the effect of the variation of catalyst diameter on the dry reforming process caused mainly by sintering, an issue that is inspected in this paper.

3.4.1: Structure of a FNN

A FNN is composed of computational units, known as neurons, arranged in layers with every neuron receiving a weighted sum of inputs from neurons in the previous layer (Figure 3-1). Mathematically, the output from a single neuron can be computed as (Ojha et al., 2017):

\[
y_{i,k} = \varphi_{i,k} \left( \sum_{j=1}^{n_{i,k}} w_{j,i,k}^k y_{j,k-1} + b_{i,k} \right)
\]

(11)

Figure 3-1: General structure of a FNN, with the computational model of a sample neuron. One hidden layer is shown, but the number of hidden layers generally increases with the complexity of the problem at hand.

Where \( y_{i,k} \) is the output of neuron \( i \) in layer \( k \), \( w_{j,i,k}^k \) is the weight of the connection between neuron \( j \) in layer \( k-1 \) and neuron \( i \) in layer \( k \), \( b_{i,k} \) is the bias in neuron \( i \) in layer \( k \), \( n_{i} \) is the number of neurons in layer \( k \), and \( \varphi_{i,k}(.) \) is the activation function applied at a neuron \( i \) in layer \( k \). In this work, we use a hyperbolic-tangent activation function.

The design of a proper FNN involves first the selection of a proper architecture, i.e. a suitable number of hidden layers with a suitable number of neurons in each layer. The
number of neurons in the input and output layers depends on the dimension of the given problem. The designed architecture is a parametric function in essence with the weights and biases to be determined. In supervised learning applied to regression problems, we are given a dataset of \( N \) instances \( \{ (x_1, y_1), (x_2, y_2), \ldots, (x_n, y_n) \} \subset \mathbb{R}^n \rightarrow \mathbb{R}^m \) where a certain mapping \( F: \mathbb{R}^n \rightarrow \mathbb{R}^m \), defined by \( F(x) = y \), is to be approximated. We construct a cost function \( c_f: \mathbb{R}^n \times \mathbb{R}^m \rightarrow \mathbb{R}^+ \) which evaluates the distance between actual dataset outputs (targets) \( y_i \) and network outputs \( \hat{y}_i \). If \( W_h \) is the set of weights and biases in the network, then its elements will be determined as follows:

\[
W_h = \arg \min_{w, b} c_f(y_i, \hat{y}_i) \quad (12)
\]

Minimization is usually done via backpropagation, a gradient-based method that is made suitable for neural network functions (Ojha et al., 2017). Several variants of backpropagation and other techniques have been conceived in the literature for the proper determination of a network’s parameters; however, the determination of the optimal architecture of the network lacks a formal method. In most of the applied science literature, including the work done on modeling dry reforming processes, this step often does not receive proper attention (Curteau and Cartwright, 2011). However, the architecture of the network has a significant effect on its generalization ability. A network with too many neurons and layers is at a risk of overfitting, the phenomena where training data is well approximated, while new data is poorly predicted. Too few neurons and layers lead to an underfitting network, performing poorly on both training and testing data (Goodfellow and Bengio, 2016). The architecture design activity is often done via a trial-and-error procedure, using several heuristics from experience. Other methods were proposed in literature, including pruning and constructive algorithms, hybrid methods, and evolutionary techniques (Curteau and Cartwright, 2011).

3.4.2: Genetic Algorithm (GA) for FNN Architecture Optimization

In evolutionary programming-based architecture optimization, a generation of networks with different architectures are evaluated according to their performance and evolved accordingly, until an optimal architecture is reached. Some evolutionary techniques such as the Neuro-Evolution of Augmented Topologies (NEAT) (Stanley and Miikkulainen, 2002) optimize both weights and structure at the same time, by either starting with a simple neuron and evolving it to a more complex network or starting with a complex network and then pruning its neuron until a satisfactory generalization ability is reached.

A different class of evolutionary techniques regard architecture optimization as a search on the space of possible topologies, where the objective function measuring the performance of the individuals in this space is a function of the number of hidden layers and neurons in every layer. By these techniques, every individual is trained using backpropagation learning and its performance evaluated before creating a new generation of networks with potentially improved performance based on the operators pertaining to the metaheuristic algorithm used (Ojha et al., 2017, Curteau and Cartwright, 2011). In this paper, we employ the second approach as it is more computationally efficient.
The genetic algorithm (GA) is a metaheuristic optimization algorithm inspired by Darwinian natural evolution. To minimize or maximize an objective function, an initial random population of possible solutions (individuals) is created. Every individual is encoded in a chromosome-like structure where every “gene” represents a certain property of the individual. The performance of each individual is then evaluated based on the objective function, and the population will then be evolved using different genetic operators, until termination criteria are satisfied and an optimal solution is reached. Details about the different genetic operators can be found in (Mitchell, 1999).

3.4.3: Chromosome Encoding of Neural Network Individuals
It has been shown that a FNN with three to four intermediate hidden layers is usually enough for regression problems (Demuth et al., 2014). The problem at hand thus boils down to the selection of appropriate number of neurons in each layer, where zero neurons indicate a nonexistent/unnecessary layer. An indirect encoding scheme is employed in this work, where a 16-bit binary chromosome is used to represent a certain network architecture, with every four bits representing the number of neurons in the corresponding layer of the network. The number of neurons in each layer is therefore found in the interval $[0; 15]$ (four bits: $2^3 + 2^2 + 2^1 + 2^0 = 15$).

3.4.4: Objective Function
Different objective functions have been used in the literature to evolve FNN’s, and have been applied to different practical problems, including identification and estimation of pollution sources (Carvalho et al., 2011), and modeling elastic deflection in a steel bar (Benardos and Vosniakos, 2007). Even though the objective functions varied in structure, they shared common parameters, including the training error, testing error, and terms penalizing network complexity. Network complexity is usually penalized by taking the exponential of the number of network parameters. In this paper, we partially train every network individual using backpropagation with Bayesian Regularization (BR), which explicitly yields an estimate of the effective number of parameters in the network, i.e. those parameters that did indeed contribute to the network output. A discrepancy between this number and the original number of parameters implies a network that is overcomplicated and prone to overfitting, and therefore we add their ratio as a parameter to maximize; thus, reducing the probability of overfitting. For every FNN individual created, the training was limited to 200 epochs to save computational time. The proposed GA tackles the following problem:

$$\{n_1, n_2, n_3, n_4\} = \arg \min_{n_i \in \{0,1,2...15\}} \left[ f_{obj}(n_1, n_2, n_3, n_4) = \alpha_i E_{\text{avg}} + \alpha_2 (1 - \gamma_e / \gamma) + \alpha_3 e^{0.01\gamma} \right]$$

(13)

Where $n_i$ is the number of neurons in layer $i$, $\gamma_e$ and $\gamma$ are respectively the effective and total number of parameters in the network, $\alpha_i$ is a penalty for term $i$ in the objective function, and $E_{\text{avg}}$ is an error criterion, taken as a weighted average of the testing and training errors:

$$E_{\text{avg}} = \rho_1 (SSE_{\text{train}}) + \rho_2 (SSE_{\text{test}})$$

(14)
where \( SSE \) is the sum of squared error, given by:

\[
SSE = \sum_{i=1}^{N} (y_i - \hat{y}_i)^2
\]

(15),

with \( y_i \) being target values and \( \hat{y}_i \) denoting network outputs. The subscripts \( \text{Train} \) and \( \text{Test} \) denote the training and testing parts of the dataset respectively. \( \rho_1 \) and \( \rho_2 \) are weighing factors found in \([0; 1]\) such that \( \rho_1 < \rho_2 \) to give more weight to the error originated from the testing set and ensure that the GA favors networks that perform better on new data.

### 3.4.5: Summary of the GA-NN Algorithm

Architecture optimization for this study will be performed according to the following algorithm:

<table>
<thead>
<tr>
<th>Algorithm: GA-NN</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Input:</strong> Thermodynamic model-generated dataset.</td>
</tr>
<tr>
<td><strong>Output:</strong> Fully trained network with optimal architecture.</td>
</tr>
<tr>
<td>1. Initialize a random population of networks.</td>
</tr>
<tr>
<td>2. Partially train every network using backpropagation with BR.</td>
</tr>
<tr>
<td>3. Evaluate the performance of each network using ( f_{obj} ) in equation (13).</td>
</tr>
<tr>
<td>4. Apply genetic operators to generate a new population of improved networks.</td>
</tr>
<tr>
<td>5. Repeat steps 2-4 until termination criteria are satisfied.</td>
</tr>
<tr>
<td>6. Extract neural network architecture with the best performance and train it properly.</td>
</tr>
</tbody>
</table>

### 3.4.6: Dataset Generation and Data Pre-processing

We fix the molar feed methane to \( \text{CO}_2 \) ratio to 60:40 and we use reactor temperature, pressure and catalyst diameter as variable inputs to the Gibbs free energy minimization algorithm discussed in [our previous paper] and Section 2 of this work. The outputs of the model are four matrices representing the equilibrium methane and \( \text{CO}_2 \) conversions respectively, \( \text{H}_2/\text{CO} \) ratio, and amount of carbon deposited on the catalyst expressed in molar percentage as function of temperature and pressure. Even though previous works in the literature use one network with multiple output neurons to catch all the outputs at the same time, in this work we use a separately trained network for each, thus avoiding the necessity of compromising between accuracies for each output during the GA run, and producing a more robust model. It is worth noting that any implicit dependency between the outputs will be captured by the networks during training. Furthermore, the thermodynamic model used to generate the training dataset does not capture the dependence of equilibrium parameters on time. The equilibrium results are obtained as a
function of catalyst particle diameter, and the diameter-time relation is studied in the sintering model.

Table 3-2 shows the range of each input used.

<table>
<thead>
<tr>
<th>Input</th>
<th>Unit</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>K</td>
<td>[973; 1273]</td>
</tr>
<tr>
<td>Pressure</td>
<td>bar</td>
<td>[1; 20]</td>
</tr>
<tr>
<td>Catalyst diameter</td>
<td>nm</td>
<td>[5; 50]</td>
</tr>
</tbody>
</table>

The training dataset was produced using the Gibbs energy minimization method, and around 2000 instances were used. The inputs were normalized to fall in the [-1; 1] range.

3.5: Optimization Procedure for the Time-Dependent Operating Conditions

The operating conditions should guarantee a high conversion for both methane and carbon dioxide, in addition to a H₂/CO ratio close to unity while minimizing carbon formation. Therefore, we chose an objective function that includes the conversions, H₂/CO ratio and the molar percentage of carbon with suitable penalization factors to achieve the desired objectives. The objective function computes the aforementioned parameters using the optimized ANN’s. The ANN’s provide an advantage over the Gibbs energy minimization model as they are smooth functions that can be handled efficiently by a gradient-based algorithm such as the interior-point algorithm employed in this study. The optimization results are validated against the thermodynamic model afterwards to guarantee physical significance of the results.

The catalyst batch lifetime is divided into \( n \) time steps. Initial conditions are defined to compute the first sintering rate, and the optimal pressure and temperature are determined. The new, sintered diameter is computed at the current optimal temperature using a differential form of the sintering equation, and is then employed in the next iteration to define new carbon limits and conversions. The problem is optimized again, and this iterative cycle continues until the last time step is reached. This algorithm adapts the sintering rate to the operating conditions to give a more accurate representation of catalyst under varying operating conditions as shown in Figure 3-2.
Define initial operation conditions \( T_0, P_0 \) and \( d_0 \)

Set the number of time steps to \( N \), initialize counter \( n \) to 1

\[
\min_{T,P} \left[ -X_{CH_4} - X_{CO_2} + 100C_s + 10(0.96 - \frac{H_2}{CO}) \right]
\text{s.t. } \begin{cases} T \in [973;1273] \\ P \in [1;20] \end{cases}
\]

Extract optimal temperature \( T_{opt} \) and pressure \( P_{opt} \)

Evaluate the new particle diameter using sintering kinetics

\( n \leftarrow n + 1 \)

\( n = N? \)

No

Yes

Extract profiles of \( T_{opt} = g(t) \) and \( P_{opt} = h(t) \)

Figure 3-2: Algorithm used to extract profiles of optimal temperature and pressure throughout a given simulation of a dry reformer’s lifespan.

3.6: Results

3.6.1: ANN Training

ANN’s having a multi-layer perceptron architecture with at least two hidden layers have been conceived by the GA to optimally model the methane conversion, \( CO_2 \) conversion, \( H_2/CO \) ratio and the molar percentage of carbon deposited on the catalyst. Robust performance has been observed for each of the networks, and Table 3-3 shows the architectures obtained along with the mean-squared-error (MSE), coefficient of determination (\( R^2 \)) and the standard deviation of the error exhibited by the networks on the testing set. Figure 3-3 through Figure 3-6 show regression plots where data points fall very close to the 45° line.
Table 3-3: Network architectures obtained by the GA and corresponding MSE exhibited on the testing set.

<table>
<thead>
<tr>
<th>Output</th>
<th>Network Architecture</th>
<th>Testing MSE</th>
<th>Coefficient of Determination</th>
<th>Standard Deviation of the error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane Conversion</td>
<td>12x5x6</td>
<td>7.01x10^-5</td>
<td>0.999</td>
<td>7.3x10^-3</td>
</tr>
<tr>
<td>CO2 Conversion</td>
<td>9x5x1</td>
<td>9.55x10^-4</td>
<td>0.999</td>
<td>2.28x10^-2</td>
</tr>
<tr>
<td>H2/CO Ratio</td>
<td>3x5</td>
<td>9.55x10^-6</td>
<td>0.996</td>
<td>7.1x10^-3</td>
</tr>
<tr>
<td>Molar Percentage of Carbon</td>
<td>5x4x3x3</td>
<td>1.26x10^-4</td>
<td>0.998</td>
<td>10^-2</td>
</tr>
</tbody>
</table>

Figure 3-3: Methane conversion: outputs from ANN vs. original dataset values.
Figure 3-4: CO₂ conversion: outputs from ANN vs. original dataset values.

Figure 3-5: H₂/CO ratio: outputs from ANN vs. original dataset values.
3.6.2: Sintering

Based on the Gibbs energy minimization study, typical fractions of steam and hydrogen at the dry reformer outlet are approximately 0.07 and 0.48. The initial catalyst diameter was chosen as 5 nm which is a typical diameter for a well-synthesized fresh nickel catalyst. Figure 3-7 shows the extent of sintering over an isothermal catalyst service life of two years for temperatures of 923 K, 973 K and 1023 K at 1 bar total pressure.
Temperature plays a very important role in the sintering rate, with an initial doubling time of 50 hours at 1023 K, 500 hours at 973 K and 4000 hours at 923 K. The rate of sintering decreases after the initial rapid period. The carbon limits are therefore expected to change rapidly over the first 1000-2000 hours before stabilizing later on in the reactor lifetime.

3.6.3: Dynamically Optimized Conditions
In this section, we display first the model outputs resulting from the optimization of the operation conditions. We use optimal temperature and pressure along with the corresponding particle diameter to predict the outputs from both the ANN’s and the Gibbs energy minimization method in order to validate the ANN results. In all of the following simulations, the ANN results agree well with the thermodynamic model. The time step was chosen as 200 hours, which is much larger than the time scale required for the reactor to reach a new equilibrium state, and smaller than the time scale of sintering, which guarantees a reliable time resolution which captures reactor behavior and sintering rate.

The optimal operating conditions determined by the optimization algorithms predict CH₄ conversions of approximately 66% and CO₂ conversions around 99% throughout the simulation time. Figure 3-8 shows the conversions of methane and CO₂. Both methane and CO₂ conversions decrease slightly throughout the catalyst but both remain satisfactory. The methane conversion appears to be much lower due to its non-stoichiometric amounts in the feed biogas. However, the conversion reached is fairly close to 100% of the maximum conversion allowed by stoichiometry for the dry reforming reaction.
A decrease in the H₂/CO ratio is also observed after an initial spike at 0-500 hours on stream where the ratio peaks at 0.995, after which it decreases to 0.99 at approximately 2 months. This shift is associated with the water-gas shift reaction being favored by the increasing pressure profile in the first 2000 hours. An increase in pressure has previously been shown to decrease the H₂/CO ratio as the extent of the dry reforming reaction is hindered and thus the reverse water-gas shift reaction progresses slightly further. The H₂/CO ratio eventually reaches an asymptotic value of 0.95, which is still acceptable (the ratio remains close to 0.95 even with simulation times of 100,000 hours). Figure 3-9 shows the evolution of the H₂/CO ratio with time.
Carbon formation remains negligible throughout the reaction time, with an upper limit of $10^{-5}$ %, so for practical purposes, the amounts formed can safely be neglected. The conditions at which carbon formation occurs correspond to the conditions of maximum conversion and highest H$_2$/CO ratio, and therefore there is a tradeoff between carbon formation and good performance. This observation is illustrated in our previous work (Abdel Karim Aramouni et al., 2017). Under current process conditions, carbon is formed essentially from the methane cracking reaction at high temperature and low pressure.

The catalyst diameter doubles quickly, reaching a diameter of 10 nm in 6000 hours, then increases in a monotonous fashion at a slower rate. The temperature dive in the first 2000 hours slows down the sintering rate and allows the catalyst to remain satisfactorily active and well dispersed for a longer time. Figure 3-10 shows the evolution of catalyst diameter with time under varying operating conditions.
Optimal temperatures and pressures each show two distinct patterns: both vary quickly below 500 hours, with the temperature jumping from 1200 to 1250 K quickly, and pressure increasing sharply. After 500 hours, pressure increases in a concave fashion while temperature remains constant at the upper bound. Figure 3-11 shows the optimal temperatures and pressures in function of time respectively.

During the first 5000 hours, the sintering rate is at its maximum and therefore the carbon limits are evolving very rapidly, which explains the rapid change in temperature and pressure. The fresh catalyst particles are still small, and as shown in our work (Abdel Karim Aramouni et al., 2017), a CH₄ conversion spike is observed when the carbon limits are crossed. The methane conversion is more sensitive to pressure change than temperature change around the carbon limits for smaller particle diameters, which is why optimization determines an abrupt increase in temperature and a slower increase in pressure.
Figure 3-11: Optimal temperature-time trajectory.

Figure 3-12 shows the temperature-pressure trajectory superimposed over the evolution of carbon limits with time. After the initial change in temperature during the first 500 hours, the temperature is kept constant at the upper bound and pressure increases slowly to avoid crossing the carbon limits, defined here as the zones of temperature and pressure where carbon is expected above 0.05% mol. Carbon limits initially define a region of low pressure and high temperature where carbon is expected at low catalyst diameters (low time on stream), then shift to cover a larger zone of temperature and pressure as sintering takes place. The increase in pressure allows for a low change in conversion while avoiding the dynamic limits of carbon formation. The carbon limits evolve very quickly in the first few months of operation (5000 years) and then become relatively stable and predictable.

As the catalyst diameter reaches 10-15 nm (after 10000 hours), another zone of high carbon presence becomes apparent at low temperatures and high pressures. This phenomenon has been linked to Boudouard carbon formation, but high conversion requires operating temperatures and pressures to be far away from the region in which this zone is crossed.

The first 5000 hours of operation are therefore the most critical in terms of catalyst deactivation, requiring a complex and accurate control of both temperature and pressure. After the 5000-hour threshold is crossed, only regular pressure increase is required to avoid the carbon limits. However, the requirement of a changing pressure in a dynamic optimization framework has a strong implication on plant economics: an increase in pressure can be achieved by increasing compression costs upstream, but will result in an
increased throughput and operating cost reduction due to a prolonged catalyst lifespan, and an economic study is required to balance product revenue and operating costs.

![Figure 3-12: Optimal reaction conditions and dynamic carbon limits.](image)

3.7: Conclusion
The effect of sintering in a dry reformer along with temperature and pressure were modeled using feedforward neural networks. The ANN design activity was automated using a GA search over the set of possible network topologies. The inclusion of the effective number of parameters in the GA’s objective function led to networks that performed well over testing data points.

In addition, the availability of the ANN’s has allowed a proper optimization of the operating conditions of a dry reformer, ensuring an industrially-viable catalyst lifespan by accommodating for sintering and the minimization of the deposition of solid carbon on the catalyst. The simulation over approximately four years has showed that acceptable operation can be maintained mainly by keeping the temperature at the highest bound (~1000 °C) and gradually increasing the pressure with time. The ANN model was suitable to be incorporated in an objective function for the optimization of the operation conditions since it was smooth and differentiable; whereas the thermodynamic model-based function was ill-behaved and constantly led the optimizer to fail. While optimization using the Gibbs energy minimization could have been done using a metaheuristic algorithm, faster gradient-based algorithms would be favored in the industry since fast results are required to modify operation conditions in real-time.

Regarding the optimal operating conditions over the lifespan of the dry reformer, it is worth noting that carbon limits change with time, and the optimal pressure increases to accommodate for these changes and remain as far as possible from the carbon limits. This
Dynamic optimization can thus alleviate some of the drawbacks presented by the dry reforming process, and make it a more viable option for large-scale industrial applications. However, an economic study is required to understand the tradeoff between savings from extended catalyst lifetime and increased operating costs from increasing pressure in the reformer.

3.8: Acknowledgments
The authors would like to thank the "Lebanese National Council for Scientific Research" (LCNRS) and the "Munib and Angela Masri Institute of Energy and Natural Resources" for funding this research.

3.9: Outlook
This chapter concludes the first section of this thesis which deals with equilibrium modeling and optimization of the reformer to minimize the likelihood of carbon formation. The upcoming chapters focus on experimental work in the development of carbon-resistant and active catalysts. Appendix 1 describes a rigorous approach for the kinetic modeling of a dry reformer to provide a complete theoretical understanding of the dry reformer.

3.10: References


Statement of contribution:

I, the undersigned Nicolas Abdel Karim Aramouni, hereby acknowledge my contribution to the publication titled “Dynamic optimization of dry reformer under catalyst sintering using neural networks”, published in Energy Conversion and Management (volume 157, p. 146-156, 2018), authored by Mr. Mazen Azzam, myself, Prof. Mohammad N. Ahmad, Dr. Mariette Awad, Dr. Witold Kwapinski and Dr. Joseph Zeaiter a follows:

1. I have performed the theoretical and computational work to generate the thermodynamic equilibrium dataset that Mr. Mazen Azzam used to train, validate and deploy the ANN structures.

2. I have developed the mathematical formulation of the sintering kinetic model and adapted it to the dry reforming problem.

3. I conceptualized the coupled thermodynamic-kinetic optimization algorithm that made use of the developed ANN models. Mr. Azzam handled the integration of the ANN structures into the algorithm.

4. I have contributed to the production of the manuscript by writing the sections related to the thermodynamic model, sintering kinetics, and interpretation of the optimization results.

This statement has been verified and signed by the collaborating co-authors.

Mr. Mazen Azzam
Dr. Mariette Awad

August 17, 2020
August 19, 2020
Chapter 4: Molybdenum and Nickel-Molybdenum Nitride Catalysts supported on MgO-Al₂O₃ for the Dry Reforming of Methane

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Keywords: Syngas, Nitrides, Whisker carbon, Interstitial alloys, CO₂

Declarations of interest: none

Abstract
8wt% and 16wt%Mo and 8wt%Ni 8wt%Mo nitride catalysts supported on MgO-Al₂O₃ were synthesized and tested for methane dry reforming at temperatures of 760-840°C. Two in-situ nitridation procedures involving heating the catalyst in NH₃/N₂ or H₂/N₂ gas at a space velocity of 44 s⁻¹ and 5°C/min heating rate, were assessed and compared with a conventional reduction procedure. The activity of the bimetallic nitride (89.5% CH₄ conversion) was much higher than that of molybdenum nitride (10.2% CH₄ conversion for 8%Mo), with a slightly better performance with H₂/N₂-treated catalysts. The bimetallic nitrides showed deactivation over 7 hours and poor stability at atmospheric pressure. The nitride phase was shown to transition into an oxide/carbide phase during reaction. Furthermore, hydrogen/nitrogen treatment caused partial reduction to occur, which explains the activity improvement in bimetallic Ni-Mo nitrides due to the presence of metallic Ni and Mo. Whisker carbon was significantly decreased although carbon formation was observed. The basic support improves coking resistance by enhancing CO₂ adsorption. Initial results indicate a unique activation site for both methane and CO₂ through a Mars-Van Krevelen mechanism, with a phase transformation followed by a carbide-oxide redox cycle mechanism taking place.

4.1: Introduction
The dry reforming of methane is a promising technology to produce syngas (a mixture of carbon monoxide and hydrogen used as an intermediate building block for chemical synthesis) from biogas issued from landfill and anaerobic digestion processes. The reaction pathway and typical operating conditions have been reported elsewhere (Azzam et al., 2018, Abdel Karim Aramouni et al., 2017, Nikoo and Amin, 2011). European biogas production is estimated to reach 50 billion cubic meters by 2030 (Lambert, 2017), highlighting the extensive availability of potential feedstock for such a technology. The potential impact of this process on greenhouse gas reduction is limited, yet it is a highly attractive option to enable the processing of CO₂ rich hydrocarbon streams or to utilize waste CO₂ streams (Mortensen and Dybkjær, 2015). Several technical limitations surface
when using biogas as a feedstock, especially the inability of traditional nickel-based catalysts to tolerate operating conditions and increased carbon formation (Selvarajah et al., 2016). Therefore, dry reforming technology has not reached a major large scale success yet. Many successful attempts at reforming CO₂-rich gas at an industrial scale have been documented (Teuner et al., 2001, Mortensen and Dybkjær, 2015), but all require a minimum amount of water as co-feed to avoid carbon formation.

Generally, carbon deposits on catalysts can have multiple morphologies (Abdel Karim Aramouni et al., 2018, Grams et al., 2004), but the most significant and destructive form of carbon deposit is the carbon whisker. The growth of high-strength carbon whiskers on catalyst pellets is especially severe in aged catalysts that have suffered extensive sintering (Sehested, 2006, Helveg et al., 2011). The mechanism of whisker growth has been studied by many authors (Alstrup, 1988, Alstrup et al., 1998, Baker et al., 1972, Borowiecki, 1982) and can be roughly summarized as the formation of adsorbed carbon from the decomposition of gas molecules on the metal particle, followed by diffusion of carbon throughout the metal particle to the whisker formation site and whisker growth.

The proposed mechanisms by Baker (Baker et al., 1972), Rostrup-Nielsen and Trimm (Rostrup-Nielsen and Trimm, 1977) and Abild-Pedersen et al. (Abild-Pedersen et al., 2006) for whisker carbon growth all assume carbon transport from the adsorption site to the growth site to be the rate determining step, either through the bulk metal or through the surface atomic layers, with different conclusions about the driving force. As the carbon atom is significantly smaller than most transition metal atoms and noble metal atoms, the diffusion of carbon through catalyst metal crystals is interstitial. A potential strategy to inhibit carbon formation on the catalyst would be to create an interstitial alloy of the active metal and a blocking element. The interstitial alloy acts as a diffusion barrier and should reduce the amount of destructive whisker carbon formed. The most suitable candidates for alloying with nickel are nitrogen, arsenic, and phosphorous, through the use of ammonia, phosphine or arsine gas over nickel or nickel oxide particles at moderately high temperatures. Given that most pnictogen hydrides are very toxic and flammable, nitrogen offers the safest and simplest candidate atom through the use of ammonia as nitrogen source.

The catalytic activity of transition metal nitrides has been compared to that of noble metals in various processes (Gage et al., 2016a, Fu et al., 2017). Noble metals are known to be excellent catalysts for the dry reforming process (Abdel Karim Aramouni et al., 2018, Safarzamin et al., 2009, Wang and Ruckenstein, 2000, Dias, 2004), and are resistant to carbon formation since carbon does not diffuse easily in them (Helveg et al., 2011). Supported nickel nitride is therefore a potentially attractive cheap candidate catalyst for dry reforming. The problem however, is that nickel nitride is thermally metastable (Gage et al., 2016b), especially in the presence of hydrogen above 157°C and can oxidize in the presence of CO above 200°C.

Interstitial alloys with higher thermal stability are therefore needed to act as catalysts for the dry reforming process. The best known interstitial alloys for dry reforming catalysts are carbides, with molybdenum carbide being the best performing (Lavoie, 2014, Brungs et al., 1999, Claridge et al., 1998, Roohi et al., 2016). Claridge et al. (Claridge et al., 1998)
found the activity of molybdenum and tungsten carbides to be comparable to Iridium and Ruthenium due to the close electronic similarities. Yao et al. (Yao et al., 2016a) noted that pressures higher than atmospheric were necessary to prevent the oxidation of molybdenum carbide by CO₂. Furthermore, molybdenum nitride was demonstrated to be a good catalyst for a number of processes summarized by Spivey and Dooley (Spivey and Dooley, 2006). Molybdenum is therefore an attractive metal precursor as an interstitial alloy catalyst for dry reforming.

Two main techniques are used to prepare molybdenum nitrides, both involving a nitrogen precursor in a reducing atmosphere that reacts with the molybdenum precursor to give nitrides. The majority of research reports employed MoO₃ as a molybdenum precursor in the nitridation experiments. Many works in the field employed gaseous ammonia as a source of nitrogen in the ammonolysis synthesis process (Choi et al., 1992, Colling and Thompson, 1994, Li et al., 2011). Jauberteau et al (Jauberteau et al., 2015) reported three main reaction pathways for the synthesis of molybdenum nitride:

\[
2\text{Mo} + 1/2\text{N}_2 = \text{Mo}_2\text{N}
\]

\[
2\text{MoO}_3 + 6\text{H}_2 + 1/2\text{N}_2 = \text{Mo}_2\text{N} + 6\text{H}_2\text{O}
\]

\[
2\text{MoO}_3 + 4\text{NH}_3 = \text{Mo}_2\text{N} + 6\text{H}_2\text{O} + 3/2\text{N}_2
\]

It is therefore possible to synthesize molybdenum nitride from MoO₃ using either a hydrogen rich H₂/N₂ gas mixture or ammonia gas. Another possible pathway to synthesize molybdenum nitride from the oxide precursor is:

\[
4\text{MoO}_2 + \text{N}_2 = 2\text{Mo}_2\text{N} + 4\text{O}_2
\]

However, the reaction is severely prohibited by thermodynamics, and for all practical purpose, H₂ is necessary as co-feed with N₂ to produce nitrides [34].

Colling and Thompson (Colling and Thompson, 1994) prepared molybdenum nitride catalysts for hydrodenitrogenation supported on alumina and found that the surface area of the nitrides was dependent on the heating rate and the space velocity, with higher velocities yielding higher surface areas. This was attributed to the formation of water during the reduction/nitridation of molybdenum oxide, which enhances the rate of hydrothermal sintering of the product. Higher space velocities sweep water away from the surface of the nitride faster, thus reducing the sintering effects. Catalyst loadings below 8 wt. % were found to be more difficult to reduce, while higher loadings (16 wt. %) were found to behave in a similar fashion to bulk γ-Mo₂N, which is the most catalytically active phase. It was also found that lower loadings of molybdenum gave highly dispersed, amorphous molybdenum nitride phase while higher loadings gave crystalline particles. At molybdenum loadings less than that required to fill the monolayer, a two-dimensional molybdenum oxide structure forms on the surface of the support. Only at higher coverage do crystallites form. This is due to strong interaction between molybdenum and alumina, which explains the difficulty of reducing and nitriding low-loaded MoO₃/Al₂O₃.
The catalytic activity depended on the loading and heating rates and space velocities. Spivey et al. (Spivey and Dooley, 2006) reviewed the ammonolysis literature and concluded that endothermic effects would limit the use of ammonia as a nitridation agent on an industrial scale.

To the knowledge of the authors, the use of nitrides as catalysts for dry reforming has only been reported by Fu et al. (Fu et al., 2017), who compared the activity of bulk Mo$_2$N, NiMo$_3$N and CoMo$_3$N in the dry reforming of methane. The nitrides synthesized in their work showed low surface area, and a high activity in bimetallic nitrides. Mo$_2$N was shown to poorly adsorb CH$_4$ and CO$_2$ at the reaction temperature, which caused its low activity. Co-Mo and Ni-Mo nitrides performed much better, with a higher coking potential for NiMo$_3$N due to its higher CH$_4$ adsorption potential. As the bulk nitride phase has a low surface area, there is potential in improving its exposure to the reaction medium by dispersing it on a suitable support. The use of a basic support, which is known to enhance CO$_2$ adsorption, is expected to mitigate the observed coking tendency of NiMo$_3$N. In this study, we compare the performance of supported nickel, supported molybdenum nitride, and supported Ni-Mo nitride on a MgO-Al$_2$O$_3$ support for the dry reforming process. (Colling and Thompson, 1994).

4.2: Experimental

4.2.1: Materials
Aluminum tri-sec-butoxide (Al-TSB) (97%), Magnesium ethoxide (98%), sec-butanol, nickel nitrate hexahydrate (>97%) and ammonium molybdate tetrahydrate (>99%) were purchased from Sigma-Aldrich. Nitric acid (65%) was purchased from VWR. 25% ammonia solution was purchased from Lab-Scan. All aqueous solutions were prepared with deionized water.

4.2.2: Preparation of the 8wt. %Mo, 16t. %Mo and 8wt. %Ni/MgO-Al$_2$O$_3$ catalysts
The sol-gel technique was selected for the preparation of the supports for Mo/MgO-Al$_2$O$_3$ and Ni/MgO-Al$_2$O$_3$ catalysts due to its high resulting surface area and pore volume (Abdel Karim Aramouni et al., 2018). Active metal precursors can typically be incorporated prior to gelation, but this could not be achieved with ammonium molybdate as it is not soluble in alcohol. The introduction of a molybdenum precursor in an aqueous solution would cause the rate of hydrolysis to increase and the structural properties of the support to change. Hence, it was chosen to impregnate molybdenum on the synthesized support.

The magnesia-alumina support was prepared via a sol-gel method based on Rezgui et al. (Rezgui and Gates, 1997). Al-TSB and magnesium ethoxide were dissolved in sec-butanol at 80°C so that the molar ratio of Mg to Al was 1:4 and the concentration of Al-TSB was 1M. The sol was hydrolyzed with water and HNO$_3$ in sec-butanol so that the hydrolysis ratio is 2.5 and the pH was 2. Once the hydrolysis was complete, the formed gel was transferred to a Teflon-lined autoclave and was aged at 80°C for 24 hours. The sample was then filtered, washed with deionized water and ethanol, then dried first at 70°C for 24 hours, then at 100°C for 4 hours before being calcined in air at 750°C for 2 hours. Slow drying at long times below the boiling point of the solvent reduces stresses.
caused by sudden evaporation of encapsulated solvent bubbles in the gel and minimizes pore collapse.

The calcined support was loaded with molybdenum or nickel using an incipient wetness impregnation method. Calculated amounts of ammonium molybdate or nickel nitrate hexahydrate were dissolved in just enough deionized water to fill the pores of the support. The impregnated catalyst was subjected to the same drying and calcination conditions as the bare support.

4.2.3: Synthesis of the 8wt.% Ni 8wt.%Mo /MgO-Al₂O₃ catalyst
A slight modification in the experimental procedure was made for the synthesis of the Ni-Mo catalyst to take advantage of the solubility of nickel nitrate in sec-butanol. The incorporation of nickel nitrate during sol-gel synthesis of the support improves the dispersion of Ni [36] as compared to impregnation of the support with Ni, and it was therefore chosen to adopt this procedure here.

Al-TSB and magnesium ethoxide were dissolved in sec-butanol at 80°C for 30 minutes, and then nickel nitrate hexahydrate was introduced into the sol. The sol was hydrolyzed to form a green gel with water dissolved in sec-butanol and HNO₃ to reach a pH of 2. The gel was aged for 24 hours at 80°C in a Teflon-lined autoclave, and then was filtered, and subjected to the same washing, drying and calcination conditions as the other catalysts prepared. The obtained powder incorporating nickel was impregnated with molybdenum as described earlier, followed by drying and calcination.

4.2.4: Nitridation of the supported active metals
The supported nickel and molybdenum oxides were converted to nitrides in-situ prior to the catalytic tests following two procedures: The first nitridation method, based on Wise and Markel (Wise and Markel, 1994), consists of heating the catalyst in 15% N₂ in H₂ with a space velocity of 44 s⁻¹, at a heating rate of 5°C/min up to 700°C and maintaining the same temperature for one hour. The high hydrogen composition is necessary to remove the oxygen lost by molybdenum oxide during the nitridation mechanism. The second method consists of flowing N₂ gas saturated with ammonia by bubbling through 25 wt% NH₃ in water solution at 40°C the catalyst at 44 s⁻¹ under the same temperature program. Nitride samples prepared for further characterization were passivated by cooling down in 1% O₂ in N₂ to room temperature to avoid oxidation by ambient oxygen.

4.2.5: Reduction of the supported active metals as benchmark
The performance of the supported nitrides was compared to that of the reduced catalysts. A typical reduction procedure was used: the supported nickel and molybdenum oxides were heated in a mixture of 50% H₂ in N₂ from room temperature to 760°C at a heating rate of 15°C/min and a space velocity of 50 s⁻¹, and maintained at the same temperature for one hour. The substoichiometric hydrogen content (as compared to the nitridation reactions described by Jauberteau (Jauberteau et al., 2015)) and high heating rate are expected to promote reduction reactions instead of nitridation.
4.2.6: Catalytic tests

The catalytic tests were carried in a 4mm ID quartz tube inside a tubular furnace at atmospheric pressure. 10 mg of catalyst powder were mixed with quartz sand and placed inside the quartz tube. The packing was held in place with two quartz wool plugs. The packed reactor was first purged with N₂ gas for five residence times to remove all oxygen from the system, and then the nitridation step discussed in section 2.4. was started (Reduction, section 2.5., was adopted instead for the benchmark tests). Once the activation step was complete, the prepared catalysts were heated to reaction temperature in pure N₂ which was shown to be completely inert with respect to the nitrides (Wise and Markel, 1994). The flow was then switched to an equimolar mixture of methane and CO₂, delivered at the desired flow rate using mass flow controllers (Brooks). An internal standard (N₂) was added at 25% of the total flow in the catalytic tests on Ni-Mo samples due to the expansion in molar flow rate. Total flow rate was varied between 5 and 30 mL/min. Gases leaving the reactor were analyzed using an Agilent 7820 gas chromatograph equipped with a 6-port gas sampling valve, using a Porapak Q porous polymer column and a thermal conductivity detector. Argon (99.999%) was used as a carrier gas to maximize hydrogen sensitivity and the column was kept at a constant temperature of 50°C during the analysis. Two types of experiments were performed: first, catalyst stability tests were performed at 800°C and w/F=1.1x10⁻⁵ gcat.h/mL for each catalyst. Once the stabilization period was determined for each catalyst, the effect of w/F and temperature on conversion was investigated in a second round of tests.

4.2.7: Catalyst characterization

The BET surface areas, pore volumes and pore size distributions were measured by nitrogen adsorption-desorption at -196°C using a Micromeritics Gemini VII instrument. Prior to nitrogen adsorption analysis, the samples were degassed under nitrogen flow at 150°C overnight. SEM micrographs were acquired using a Tescan MIRA3 electron microscope. Thermogravimetric analysis of the spent catalyst samples was performed on a TA Q500 instrument. Samples were heated at 15°C/min until 950°C in air. X-ray photoelectron spectroscopy measurement of the catalysts was performed using a Kratos AXIS Ultra-DLD X-ray Photoelectron Spectrometer. Fresh catalyst samples for XPS analysis were subjected to the nitridation procedure and were then passivated by cooling down in 1% O₂/N₂ gas flow, and spent samples were measured as collected from the tubular reactor. The XPS peaks were identified by comparison with the NIST XPS database. X-ray diffraction spectra of the nitrided and passivated catalysts were acquired on a Bruker D8 Advance instrument.

4.3: Results

4.3.1: Physicochemical characteristics

Table 4-1 lists the N₂ adsorption results for the synthesized catalysts. There seems to be a decrease in the catalyst surface area and pore dimension as the molybdenum loading increases which is attributed to pore filling by Mo. The incorporation of the nickel precursor prior to gelation did not affect the final properties of the catalyst as the surface areas, pore sizes and pore volumes of the catalysts were comparable. The similar textural properties of 8wt.%Mo and 8wt.%Ni 8wt.%Mo samples indicates that the introduction of
Ni in the support does not modify the structure of the support, and it is likely that Ni is incorporated in a spinel structure with Al$_2$O$_3$ similarly to Mg.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area, m$^2$/g</th>
<th>BJH pore size, nm</th>
<th>BJH pore volume, cm$^3$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>8wt.%Mo/MgO-Al$_2$O$_3$</td>
<td>111.4</td>
<td>13.3</td>
<td>0.37</td>
</tr>
<tr>
<td>16 wt.%Mo/MgO-Al$_2$O$_3$</td>
<td>103.9</td>
<td>9.2</td>
<td>0.25</td>
</tr>
<tr>
<td>8wt.%Ni 8wt.%Mo/MgO-Al$_2$O$_3$</td>
<td>106.2</td>
<td>13.0</td>
<td>0.32</td>
</tr>
</tbody>
</table>

SEM micrographs of the 8wt.%Mo catalyst in Figure 4-1(top row) showed well-defined crystals of molybdenum oxide dispersed on the support, which contradicts the observations by Spivey (Spivey and Dooley, 2006) concerning the monolayer coverage. However, smaller rod-like structures are observed to blend in with the surface of the support. An eggshell distribution of the molybdenum phase on the metal oxide support is likely. The particle size distribution was non-homogeneous, and the occurrence of large crystals of active metal was attributed to the drawbacks of the impregnation method, in which uncontrolled crystallization takes place during the evaporation of the solvent, despite efforts taken to minimize this phenomenon by drying slightly below the boiling point for prolonged periods.
The MgO/alumina support has a texture typical of a sol-gel synthesis, and is composed of small primary particles that agglomerate to give a porous structure.

The bimetallic Ni-Mo catalyst shown in Figure 4-1 (middle row) exhibits a different morphology than that of 8 wt. %Mo sample. It shows flake/rod-like and spherical structures, attributed to the change in affinity between the molybdenum phase and the support that incorporates nickel. However, the support structure is the same despite the presence of nickel. The 16 wt. %Mo catalyst shown in Figure 4-1 (bottom row) exhibits a large network of interconnected flake-like structures that engulf the support completely.
These observations differ from observations in the literature concerning the effect of molybdenum loading on the shape and crystalline structure of the molybdenum phase (Spivey and Dooley, 2006). This is attributed to the effect of doping the alumina support with magnesia which increases the isoelectric point and hence modifies the affinity between the molybdenum phase and the alumina support (Kim et al., 1992).

Energy-dispersive X-ray mapping for Ni and Mo are shown in Figures A7-A10 in the supplementary files.

4.3.2: XRD measurements

Figure 4-2 shows the XRD spectra for the freshly nitrided and passivated catalysts. Strong peaks at 2θ=37°, 45° and 67° corresponding to the MgAl₂O₄ spinel support (PDF 00-001-1150) are observed in all samples. Identification of the active phases is challenging due to overlap between the spinel peaks and the molybdenum and nickel peaks. Low intensity peaks corresponding to molybdenum nitrides and oxides are not easily identified in the monometallic 8Mo and 16Mo samples. The main difference with the support peaks are the two broad, noisy peaks at 27° and 33°. Mo₂N peaks appear at 2θ angles of 37° (appearing as peak splits on the right of the main spinel peak), 44° and 63° (PDF 00-025-1366). The broad noisy peak observed at 2θ of 27° possibly corresponds to MoO₂ (PDF 01-074-4715) is. Several MoO₃ peaks expected in the 50-60° range (PDF 00-047-1320) are difficult to discern from the background noise and are thus not marked. No significant difference is observed between the four monometallic samples in terms of phase composition, with the support peaks being the main crystalline phases observed.

Bimetallic Ni-Mo samples reveal the presence of the same strong support peaks. NiAl₂O₄ spinel phase (PDF 00-010-0339) which could be due to the incorporation of nickel in the support network, overlaps with the support peaks and is hardly discernible. The bimetallic samples do not give very different patterns from the monometallic ones, and are largely dominated by the strong support peaks.

In this aspect, XRD analysis shows the strong support crystallinity, but does not offer much added information about the active phases present.
4.3.3: XPS measurements

XPS high resolution spectra for the Ni 2p, Mo 3d and N 1s regions performed on the nitrided catalysts are shown in the supplementary information (Figure A-1, Figure 0-2 and Figure A-3). All spectra show a high oxygen content due to the passivating surface oxide layer. Yet, the N 1s peak is identified at 398.5 eV. High resolution measurement and curve fitting is performed on the ~397 eV region to resolve the overlap between the Mo 3p peak and the N 1s signal. Inhomogeneous samples make it difficult to determine true atomic percentages. When the Mo 3p and the N 1s peaks are resolved, a peak at 397.95 eV attributed to the nitrogen in metal nitrides is clearly observed for all samples. The three remaining deconvoluted peaks at approximately 398 eV, 400 eV and 402 eV

Figure 4-2: XRD spectra of the nitrided samples
(that form the N 1s signal envelope) are attributed to Mo 3p interference, azide/ammonium adsorbed groups and C-N groups respectively.

Analysis of the Mo 3d region for monometallic samples reveals the presence of a peak at 229 eV indicative of a MoN phase present in all samples with the exception of the 8%Mo nitrided in H$_2$/N$_2$, and the 8%Ni 8%Mo sample nitrided in H$_2$/N$_2$. In the latter, a peak observed at 228.7 and its doublet separated by 3.3 eV is attributed to metallic Mo$^0$. Multiple oxide stoichiometries are observed in the passive layer on 8%Mo samples, where the molybdenum oxidation number varies from +4 to +6. This observation is expected for molybdenum, but it is interesting to note that the sample nitrided in NH$_3$/N$_2$ shows presence of (NH$_4$)$_2$MoO$_4$, which indicates a reaction between the oxide phase and the nitriding gas despite no observation of nitride. 16%Mo samples also show multiple oxide stoichiometries and a Mo$_2$N phase which has lower contribution, with a stronger presence of MoO$_3$. It is interesting that a weak nitride signal in the N 1s spectra is observed for 16%Mo nitrided in H$_2$/N$_2$ despite no observed nitridic Mo.

Bimetallic 8%Ni 8%Mo samples also show peaks attributed to nitridic N 1s, but only the sample nitrided in NH$_3$/N$_2$ shows a clear nitride phase on the Mo 3d spectra, as the sample nitrided in H$_2$/N$_2$ contains a signal corresponding to Mo$^0$ instead, which partially overlaps with any Mo$_2$N signal in this sample. In contrast, Ni 2p signals are only attributed to oxidized forms, namely Ni$_2$O$_3$, Ni(OH)$_2$ and NiAl$_2$O$_4$ spinel. The broad NiAl$_2$O$_4$ spinel peak at 857 eV overlaps with NiMoO$_4$ spinel generally observed at 856 eV and it is difficult to determine whether Ni bonds more with molybdenum or aluminum atoms in the support. The NiMoO$_4$ phase is observed in both bimetallic samples, and the coexistence of a monometallic Mo or Mo nitride phase with the bimetallic oxide shows that a limited amount of Ni and Mo alloy together, while segregated Mo-rich phases remain, which is attributed to the synthesis method and the presence of large crystals of the Mo phase. The exclusively oxidized nickel presence is explained by the higher affinity between nitrogen and molybdenum compared to that of nitrogen and nickel, in addition to the presence of nickel incorporated inside the support that has not reacted with Mo and N. the spinel presence confirms once again that the calcination temperature is too high.

Table 4-2 shows the metal content of the surface of the bimetallic samples. The low concentrations observed are attributed to the oxide layer blocking the surface of the samples, yet one can observe a high nitrogen content relative to the metals, slightly above three times higher than the Mo content. This includes adsorbed nitrogen species and nitridic nitrogen, which explains the excess N coverage. Interestingly, the nickel content is higher than the molybdenum content despite being synthesized as part of the support. This is evidence of Ni leaving the structure of the support towards the surface of the catalyst. The reduced sample has a lower Ni and Mo surface content, and consequently a lower N content as the amount of nitride formed is lower. After the nitridation in ammonia, a higher concentration of Al and a lower Mg content are observed on the surface.
Table 4-2: XPS quantitative data for the synthesized catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ni (at%)</th>
<th>Mo (at%)</th>
<th>N (at%)</th>
<th>Al (at%)</th>
<th>Mg (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8wt.%Ni 8wt.%Mo nitrided in NH₃/N₂</td>
<td>2.0</td>
<td>1.4</td>
<td>4.9</td>
<td>29.4</td>
<td>2.9</td>
</tr>
<tr>
<td>8wt.%Ni 8wt.%Mo nitrided in H₂/N₂</td>
<td>2.0</td>
<td>1.4</td>
<td>4.6</td>
<td>26.2</td>
<td>4.7</td>
</tr>
<tr>
<td>8wt.%Ni 8wt.%Mo reduced</td>
<td>1.8</td>
<td>1.2</td>
<td>3.4</td>
<td>26.5</td>
<td>4.6</td>
</tr>
</tbody>
</table>

4.3.4: Catalytic tests
The Mears and Weisz-Prater criteria for external and internal mass transfer resistance (Scott Fogler, 2016) were estimated and it was concluded that reaction rates were five orders of magnitude lower than transport rates on the surface and in the pores of the catalysts. It can then be safely assumed that mass transfer limitations were negligible in the current experiments. Figure 4-3 shows the steady state CH₄ and CO₂ conversions in function of w/F at various temperatures for all nitrided catalysts, and Figure 4-4 compares the performance of the Mo and Ni-Mo nitride catalysts prepared in H₂/N₂ and NH₃/N₂ to the performance of their reduced counterparts in function of w/F at 800°C. To test the stability of the synthesized catalysts, 24-hour deactivation tests were performed at 800°C and w/F=1.11x10⁻⁵ gcat·h/mL on the nitrided and reduced catalysts. Figure 4-5 shows the CH₄ and CO₂ conversions with respect to time for all nitrided and reduced catalysts. and Table 4-3 shows the H₂/CO ratios maintained by the catalysts during deactivation tests.
4.3.4.1: Molybdenum catalysts

Low conversion was obtained with the 8wt. % and 16wt. % Mo nitride catalysts over the range of space times studied, with maximum conversions of 15% and 20% for CH$_4$ and CO$_2$ respectively reached with a nitridation in H$_2$/N$_2$ and a temperature of 760°C for the 8wt. % Mo catalyst, and conversions of roughly 27% for both CH$_4$ and CO$_2$ reached with a nitridation in NH$_3$/N$_2$ and a temperature of 760°C for the 16wt. % Mo catalyst. For the monometallic Mo nitride catalysts, an increase in temperature seemed to decrease the catalyst activity, with the exception of the 16wt. % Mo sample nitrided in H$_2$/N$_2$ where the highest conversion is reached at 840°C. The CH$_4$ conversions achieved by the 8wt.%Mo catalysts (using both nitridation methods) are strongly reduced as the temperature increases from 760°C to 800°C, but recover partially at 840°C and at high w/F values.

The reduced molybdenum catalysts performed similarly to the nitrided ones except at the highest space time tested, with a maximum conversion of roughly 48% for CH$_4$ and 47.4% for CO$_2$ reached with the 16wt. %Mo catalyst at 800°C. The conversion reached is well below the expected equilibrium conversions of roughly 95% for CO$_2$ and 85% for CH$_4$. This indicates a strong kinetic limitation for all space times tested,
Despite giving very poor conversion at the space times studied, both 8wt.% and 16wt.% Mo catalysts initially gave a high conversion for a few minutes before quickly dropping below 20% and stabilizing. The low activity exhibited by the molybdenum nitride catalysts is caused by the low CH₄ and CO₂ adsorption on the Mo₂N phase at reaction temperature previously reported (Fu et al., 2017), in addition to the low thermal stability of molybdenum nitride at atmospheric pressure that creates nitrogen deficient structures (Wang et al., 2015). This can explain why the 8wt. %Mo catalyst exhibited a higher activity at lower temperature (Figure 4-3a-b). An increase in the molybdenum loading did not affect the conversion significantly. The samples nitrided in H₂/N₂ had the highest activity both for CH₄ and CO₂, while the samples nitrided in NH₃ and the reduced sample both showed very similar conversion and deactivation patterns with a stable terminal conversion of roughly 5% for CH₄ and 10% for CO₂.

8wt.% Mo samples give a consistent H₂/CO ratio around 0.6 regardless of the treatment method, indicating a low selectivity towards dry reforming and no noticeable effect of pretreatment method on the H₂/CO ratio. Meanwhile, the 16wt.% Mo samples give higher ratios (in the range of 0.8-0.9), and produce the highest ratio when reduced, and the lowest when nitrided in NH₃/N₂. The molybdenum loading therefore affects the reactivity of the precursor to the treatment method, in line with previous observations in the literature [31]. Estimation of the activation energy on monometallic Mo samples is difficult due to the masking of reaction kinetics with poor adsorption of reactants on the catalyst surface, and non-monotonous activity trends.

4.3.4.2: Ni-Mo Catalysts

A much better performance was exhibited by the Ni-Mo catalyst, with equilibrium being reached at temperatures above 800°C and space times higher than 1.1x10⁻⁵ gcat·h/mL. The Ni-Mo catalyst nitrided in H₂/N₂ (Figure 4-3c) showed an increase in activity as the temperature and space time are increased, with equilibrium reached at higher space times for all temperatures, especially when increasing the temperature from 760°C to 800°C. The comparable conversions at 800 and 840°C are attributed to the similar activity of active adsorption sites on the nitrided Ni-Mo sample at both temperatures (CH₄-TPD and CO₂-TPD tests by Fu et al [19] showed a peak activity for adsorption sites between 700 and 800°C on NiMo₃N). The catalyst nitrided in ammonia (Figure 4-3d) had a more monotonous behavior, with the catalytic activity slightly improved at 760°C compared to the sample nitrided in H₂/N₂, but a less drastic increase in activity was exhibited at 800°C. It can nevertheless be concluded from the catalytic tests that the nitrided Ni-Mo catalysts prepared in ammonia were more active in function of the varying w/F except at 800°C where the sample nitrided in H₂/N₂ shows a high increase in activity. The monotonous behavior of the catalyst nitrided in ammonia is attributed to the high activation energies observed. Comparing the effect of different activation methods for the Ni-Mo catalyst tested at 800°C (Figure 4-4b), it can be concluded that reduction gave the highest catalyst activity, as the catalyst manages to narrowly approach equilibrium at remarkably low space times. This is further highlighted by the activation energies in the order of 30-40 kJ/mol observed on the reduced sample (Table A.2). Nitridation of the catalyst in H₂/N₂ also gave very high catalytic activity, however a small drop in conversion was apparent.
at w/F< 1x10^{-5} gcat·h/mL. This indicates that reaction rates are slower on nitrided Ni-Mo crystallites. Nitridation in NH\textsubscript{3}/N\textsubscript{2} gave the slowest reaction rates as a strong drop in conversion was observed at w/F<1.1x10^{-5} gcat·h/mL. The reduced Ni-Mo sample also gave the highest H\textsubscript{2}/CO ratio, followed by the sample nitrided in H\textsubscript{2}/N\textsubscript{2} and the sample nitrided in NH\textsubscript{3}/N\textsubscript{2}.

Table A2 shows the activation energies calculated on the bimetallic Ni-Mo samples. Calculation of activation energies for the monometallic Mo samples was not attempted due to the non-monotonous conversion trends and the decreasing conversion with increasing temperatures observed. The reduced catalyst yielded a very low activation energy for both CH\textsubscript{4} and CO\textsubscript{2}, with a slightly lower value of 33.2 kJ/mol for CO\textsubscript{2} activation. In contrast, nitrided samples are less efficient catalysts for the activation of precursors as they show activation energies an order of magnitude higher. The sample nitrided in H\textsubscript{2}/N\textsubscript{2} is the worst catalyst in terms of activation energy, and the sample nitrided in NH\textsubscript{3}/N\textsubscript{2} gives intermediate results. CH\textsubscript{4} activation energy is slightly higher than CO\textsubscript{2} activation energy as previously observed in the dry reforming catalysis literature [41], but they have the same order of magnitude, which explains the similar conversion trends. Reaction rates for all tested samples at 800°C are shown in Table A3.
Figure 4-5: Comparison of deactivation rates between the nitrided catalysts and the reduced benchmark for the 8Mo catalyst (top row), 8wt.%Ni 8wt.%Mo catalyst (middle row), and 16Mo catalyst (bottom row) during reaction at 800°C at $w/F=1.11\times10^{-5}$ gcat·h/mL.

In terms of stability, an inversion in the performance trends occurred in the presence of nickel (Figure 4-4 c-d): nitridation in H$_2$/N$_2$ gave the best performance for the Ni-Mo catalyst, followed closely by reduction. Nitridation in NH$_3$/N$_2$ did not perform as well: The reduced Ni-Mo catalyst and the Ni-Mo catalyst reduced in H$_2$/N$_2$ performed comparably over 24 hours, reaching equilibrium with little to no activity loss. The NH$_3$/N$_2$ sample initially reached equilibrium, but quickly lost 20 to 40% in conversion over the first 5 hours on stream before stabilizing. The kinetic performance and stability for the Ni-Mo catalysts follow the same trend, with the reduced sample and the nitrided sample in H$_2$/N$_2$ giving the best results followed by nitridation in NH$_3$/N$_2$. This observation is in stark opposition to results obtained with monometallic Mo nitride catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Treatment method</th>
<th>H$_2$/N$_2$</th>
<th>NH$_3$/N$_2$</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>8wt.%Mo</td>
<td></td>
<td>0.58</td>
<td>0.61</td>
<td>0.63</td>
</tr>
<tr>
<td>8wt.%Ni 8wt.%Mo</td>
<td></td>
<td>0.88</td>
<td>0.82</td>
<td>0.94</td>
</tr>
<tr>
<td>16wt.%Mo</td>
<td></td>
<td>0.83</td>
<td>0.92</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Table 4-3: H$_2$/CO ratios at 800°C and $w/F=1.11\times10^{-5}$ gcat·h/mL.
Table A5 shows the selectivities of H₂ with respect to reacted CH₄ achieved in all samples at 800°C and w/F=1.11x10⁻⁵ gcat·h/mL. The bimetallic samples have selectivities close to 100%, while monometallic samples exhibit lower selectivities. In addition, reducing the catalyst precursor gives the highest selectivity, while nitriding in NH₃/N₂ consistently lowers the hydrogen output. It can be concluded that the nitrided catalysts promote the reverse water-gas shift reaction more than the reduced samples (the literature shows that water is the only other product containing hydrogen that is significantly produced in the dry reformer). However, H₂/CO ratios for the samples with hydrogen selectivities near unity are lower than 1. This observation, coupled with relatively elevated coking rates on monometallic catalysts compared to bimetallic samples suggesting a high surface coverage with carbon, and a CO₂ conversion slightly higher than that of CH₄, indicates that an excess of CO is produced potentially through the reverse Boudouard reaction (CO₂ + C = 2 CO). It is therefore likely that the initial decay in CO₂ activity over the first two hours on stream observed in Figure 4-5 for the 16wt%Mo samples, both nitrided in H₂/N₂ and reduced, is attributed to the formation and stabilization of a carbon-rich layer at the surface of the catalyst. The intermediate H₂ selectivities associated with nitridation in H₂/N₂ further advance the hypothesis that partial reduction occurs along with nitridation using this treatment method.

4.3.5: Spent catalyst characterization

4.3.5.1: Carbon formation

Thermogravimetric analysis of the spent catalysts after reaction at 800°C for 24 hours was performed and carbon formation rates were assessed. Due to the large difference in activity between different catalysts, comparison of carbon formation rates based on amount formed per time on stream is not applicable. The amounts of carbon formed are therefore normalized to the amount of CH₄ converted over the time on stream. Total carbon formation rates (expressed in mmolC/mol CH₄ converted) at 800°C and w/F=1.11x10⁻⁵ are shown in Table 4-4. TGA curves for the spent catalysts after reaction for 10 hours are shown in Figure A-4 in the supplementary files. SEM micrographs of the spent catalysts are shown in Figure 4-6.

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<th>Catalyst</th>
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The lowest amounts of carbon formation are exhibited by the bimetallic Ni-Mo catalyst nitrided in ammonia, in the order of 0.1-0.2 mmolC/mol CH₄. Nitridation of the bimetallic catalyst in H₂/N₂ and reduction results in higher but still very low carbon amounts. 8wt.%Mo catalysts give carbon amounts in the order of 1 mmolC/mol CH₄, and 16 wt.% Mo catalysts show rates in the order of 5 mmolC/mol CH₄. The high carbon content despite a very low conversion on 16wt.% Mo is attributed to the large flat surfaces observed on the sample, which create large ensembles that favor the formation of carbonaceous layers.

Mole balances on carbon are performed and shown in Table A4. After a very brief initialization period (20 minutes), carbon is conserved in the gas phase up to within 2-5%, with the differential being attributed to coke deposition on the catalyst or carburization of the active phase. Bimetallic Ni-Mo samples have the lowest carbon differential, which coincides with the very low carbon formation rates observed in TGA tests. The Ni-Mo sample nitrided in NH₃/N₂ has the lowest carbon differential out of all samples, which coincides with the lowest rate of carbon formation measured with TGA. The 16%wt Mo samples have the highest differentials, in the order of 3-5%, in line with the highest coking rates observed on these samples, especially the 16%wt Mo sample nitrided in NH₃/N₂. Similarly, intermediate coking rates observed with 8%wt Mo samples coincide with intermediate carbon differentials in the range of 2-3%.

Micrographs of the spent catalysts after reaction at 800°C in an equimolar mixture of methane and CO₂ flowing at 15 mL/min for 4 hours as illustrated in Figure 4-6 did not show any carbon whiskers forming on the catalyst particles except for the case of the 8wt.%Ni 8wt.%Mo catalyst nitrided in H₂/N₂. The whiskers seem to grow in clusters on certain areas of the catalyst surface and in moderate amounts when compared to a nickel
catalyst reduced in hydrogen. As the whisker formation is only observed in Ni-Mo samples, it is either associated with the presence

![SEM micrographs of the spent 8 wt.% Mo nitride catalyst prepared in H₂/N₂ (a) and NH₃/N₂ (b). Spent 16 wt.% Mo nitride catalyst prepared in H₂/N₂ (c) and NH₃/N₂ (d). Spent 8 wt.% Ni 8 wt.% Mo nitride catalyst prepared in H₂/N₂ (e) and NH₃/N₂ (f). Samples are taken after reaction at 800°C in an equimolar CH₄/CO₂ flow at 15 mL/min for 4 hours.](image)

of nickel or that of metallic Mo. However, no carbon whiskers were observed when ammonia was used as the nitridation gas, while the Mo₂N phase was observed. This supports the explanation that the H₂/N₂ gas partially reduced the active phase to its metallic form in addition to creating a nitride phase, as observed by the XPS results. This is further confirmed by the very similar catalytic performance of the Ni-Mo catalyst reduced and that nitrided in H₂/N₂. The metallic nickel or molybdenum crystallites
resulting from the reduction process would then yield carbon fibers as described previously in the literature (Alstrup, 1988, Alstrup et al., 1998, Baker et al., 1972, Borowiecki, 1982). As Ni leaves the spinel structure of the support to form particles on the surface of the catalyst, it retains a good dispersion, which explains the low amount of carbon formed. Amorphous and graphitic carbon layers on the surface of the catalysts were not visible under typical SEM magnifications, and it is thus difficult to notice and characterize any significant surface carbon features in samples not showing carbon whiskers.

4.3.5.2: XPS analysis

Figure 4-7: High resolution XPS scan of the Mo 3d region for the 8wt.% Mo catalyst nitrided in \( \text{H}_3\text{N}_2 \) (a) and ammonia (b), the 16wt.% Mo catalyst nitrided in \( \text{H}_3\text{N}_2 \) (c) and ammonia (d), and the 8wt.%Ni 8wt.%Mo catalyst nitrided in \( \text{H}_3\text{N}_2 \) (e) and ammonia (f) after reaction at 800 °C for 4 hours

Figure 4-7 shows the XPS analysis of the Mo 3d region for the different catalysts tested. All catalysts showed complete surface oxidation for molybdenum where no clear molybdenum nitride peak is observed at 228 eV. The catalysts exhibited different oxidation states of molybdenum which are also dependent on the loading: for the 8wt.%Mo nitride catalysts, \( \text{MoO}_3 \) doublet peaks were identified, and doublet peaks around 235 and 238.2 eV could not be identified based on the NIST database. This peak is probably the molybdenum oxide phase partially fusing with the support (Kim et al., 1992) to form a phase where molybdenum has a high oxidation number. This peak is not present in the 16wt. %Mo nitride catalysts, where only a mixture of molybdenum oxides
is observed. The occurrence of multiple stoichiometries of molybdenum oxide indicates either that MoO$_3$ was simultaneously undergoing partial reduction in parallel during nitridation, or that the nitride phase was oxidizing during the reaction. Catalysts with higher molybdenum loading, both nitrided in H$_2$/N$_2$ and ammonia (Figure 4-7c and Figure 4-7d), were more reactive towards either the nitridation gas or the reaction medium, as shown by the multiple stoichiometries of molybdenum oxides. A mixed oxide/carbide phase was observed on 16%Mo nitrided in H$_2$/N$_2$ and on 8%Ni 8%Mo nitrided in NH$_3$/N$_2$.

The influence of the molybdenum loading on the effectiveness of the nitridation procedure and surface oxidation states can be explained by the different phases of supported molybdenum oxide obtained below and above 8 wt.% loading (Colling and Thompson, 1994). This is clearly visible in the SEM micrographs of the 8wt. %Mo and 16wt. %Mo catalysts shown in Figure. Although the micrographs in Figure 4-1 do not agree with the observations of Colling and Thompson (Colling and Thompson, 1994), the different crystal structures of the 8wt. % and 16wt. %Mo catalysts are clearly visible, with bipyramid-like crystals in the 8wt. %Mo sample and flake-like structures in the 16wt. %Mo sample.

The combined Ni-Mo nitride samples show a NiMoO$_4$ phase present in addition to the molybdenum oxides (peak at 232.3 eV and doublet separation of 3.1 eV [42]). Furthermore, the Ni-Mo sample treated in ammonia contains a phase of molybdenum oxide/carbide. This observation coupled with the observation of N$_2$ loss from the catalyst during catalytic tests, shows that a transformation from Ni-Mo nitride to Ni-Mo carbide can take place in monometallic and bimetallic samples.

4.4: Discussion
CO$_2$ conversion is generally higher than CH$_4$ conversion, due to the reverse water-gas shift reaction taking place in monometallic samples nitrided with both methods. Bimetallic samples and reduced samples exhibit a higher CO$_2$ conversion due to their promotion of the reverse Boudouard reaction. Both methane and CO$_2$ conversions follow the same trend in Mo and Ni-Mo catalysts, with the exception of the 8wt.% Mo samples where a slight recovery in CH$_4$ conversion was observed at 840°C while a monotonous decrease in CO$_2$ conversion was maintained. The decreasing CO$_2$ conversion is attributed to the lower adsorption at high temperatures, while the recovery of CH$_4$ conversion may be due to methane cracking at high temperatures. In comparison, nickel catalysts have been shown to have two different activation sites for methane and carbon dioxide, namely the metal sites and the metal-support interface [41]. Dry reforming experiments using Ni based catalysts on MgO-Al$_2$O$_3$ have indeed shown different trends in CH$_4$ and CO$_2$ conversions, with the CO$_2$ conversion showing little variation while the methane conversion varies significantly with space time [43] as it is the kinetically relevant step in the reaction mechanism. This phenomenon results in an inversion in the conversion trends (CH$_4$ conversion becomes higher below a certain space time), which can be seen for example in Figure 4-3 c-d, where the CH$_4$ conversion is higher at lower w/F.
Unlike in the case of molybdenum nitride, the reaction mechanism on molybdenum carbide and phosphide has been studied in detail. Two main mechanisms were shown to occur on these interstitial alloys by Yao et al. (Yao et al., 2016b):

1. Redox type mechanism (Oxidation-Carburization cycle in the case of carbide):
   \[ \text{Mo}_2\text{C} + 5\text{CO}_2 \rightarrow \text{MoO}_2 + 6\text{CO} \]
   \[ \text{MoO}_2 + 5\text{CH}_4 \rightarrow \text{Mo}_2\text{C} + 4\text{CO} + 10\text{H}_2 \]

2. Noble metal type mechanism: dissociative adsorption of methane and CO\(_2\), recombination on the surface of the catalyst and desorption of CO and H\(_2\) (typical of traditional nickel reforming catalysts)

The prevalence of one mechanism over the other was found to be dependent on the nature of the alloy, with mechanism 1 being dominant in carbides and mechanism 2 in phosphides. It is likely that the reaction on molybdenum nitride follows similar pathways, as the redox cycle for nitrogen has already been observed in the Co-Mo nitride (McKay et al., 2007).

The similar conversion trends for CH\(_4\) and CO\(_2\) especially on the Ni-Mo catalyst would support the conjecture that mechanism 1 dominates over mechanism 2. However, this mechanism involves nitrogen transfer from the reactants to the lattice and simultaneously from the lattice to the products. Yet, nitrogen was detected in the product gas in trace amounts that eventually fade out for all catalysts and temperatures tested even though no nitrogen containing species were introduced during the reaction, except during the nitridation step. The nitrogen transfer cycle by itself is then unlikely to be sustained at steady state, as the catalyst loses nitrogen and no nitrogen-containing products are detected (except lost N\(_2\) initially). The redox mechanism is therefore not an appropriate explanation in the case of a nitride phase catalyzing the reaction. The initial loss of nitrogen accompanied by an initial drop in activity as shown in Figure 4-5 indicates that a phase transformation happens. Similar observations were made by Yao et al. (Yao et al., 2016b) with molybdenum phosphide: having first proven that molybdenum phosphide is stable in a CH\(_4\) atmosphere (MoP does not carburize), they observed that a mixture of CH\(_4\) and CO\(_2\) initiated a loss of phosphorous from the catalyst. It was then concluded that the molybdenum phosphide phase oxidized first to inactive MoO\(_2\) and/or Mo\(_x\)P\(_y\)O\(_z\). MoO\(_2\) was subsequently carburized by CH\(_4\) to yield terminal activity through the redox cycle mechanism, while the mixed phosphide/oxide phases were possibly reverted to MoP by reaction with CH\(_4\) and H\(_2\). Fu et al (Fu et al., 2017) also observed that overcarburization by CH\(_4\) dissociation and oxidation by H\(_2\)O caused the formation of mixed oxide and carbide phases from the nitrided catalyst.

The comparison of CH\(_4\) and CO\(_2\) activity trends in Mo and Ni-Mo nitrides, in parallel with the observation of oxide and carbide phases in XPS measurements after reaction (Figure 4-7) suggest that the nitride phase decomposes into mixed carbide and oxide phases and retains terminal activity through the carbide redox mechanism. The similarity in the CH\(_4\) and CO\(_2\) trends on the Mo catalysts does not suggest that the noble metal
mechanism carries on this catalyst system, which can also explain the low activity they display in addition to their poor CH$_4$ and CO$_2$ adsorption capacity at high temperature.

The presence of nickel in the catalyst drastically affects the activity of the catalyst, but the comparison of kinetic tests (Figure 4-4), stability tests (Figure 4-5) and activation energies (Table A2) are inconclusive in terms of which nitridation technique is the best. Nevertheless, it is apparent that the addition of nickel in the formulation renders the catalyst more sensitive to the composition of the nitriding gas and/or the heating rate: reduction and nitridation using H$_2$/N$_2$ are both performed using a mixture of hydrogen and nitrogen, but with different ratios, space velocities and heating rates. While the performance of the monometallic molybdenum catalysts is altered by modifying the H$_2$/N$_2$ ratio and flow rate, the difference is much less striking than that observed for the Ni-Mo samples. The similar activity of the 8wt. %Ni 8wt. %Mo catalyst reduced and nitrided in H$_2$/N$_2$ shown in Figure 4-5 (c-d) suggests that the active phase is undergoing partial reduction under the 85% H$_2$/N$_2$ nitriding gas, which is confirmed by XPS. The comparable carbon formation rates measured for these two samples also confirms this observation even though the bimetallic catalyst nitrided in H$_2$/N$_2$ however presents the highest activation energies. This is not the case for the Mo-only catalysts, as a notable difference in catalytic activity is observable between the reduced catalyst and the nitrided ones (Figure 4-4.a-c), while very little difference is achieved by modifying the nitridation procedure.

TPD studies by Fu et al (Fu et al., 2017) had concluded that bulk NiMo$_3$N had a strong coking potential despite its activity, as it has a higher CH$_4$ adsorption capacity compared to CO$_2$. In contrast to their conclusion, this work showed a much lower coking potential for the bimetallic nitride compared to molybdenum nitride when supported on a basic support with good oxygen mobility such as MgO-Al$_2$O$_3$. This improvement is attributed to the enhanced CO$_2$ adsorption by the basic support (Abdel Karim Aramouni et al., 2018), which promotes the formation of CO from surface carbon, as observed in this work.

Ultimately, the loss of N$_2$ during reaction at atmospheric pressure, the subsequent low activity of molybdenum nitrides and the initial deactivation of Ni-Mo nitrides makes them unsuitable for low-pressure operation, despite an improvement in their coking tendency when dispersed on a support with appropriate basicity. However, reformers are usually operated at higher pressures (Beurden, 2004), and hence nitrides could be potential candidates for dry reforming catalysts on an industrial scale. The presence of nickel in the catalyst is important to guarantee a high conversion, yet nitridation of the bimetallic catalyst decreases the amount of whisker carbon formed as compared with conventional nickel catalysts (Figure 4-8). As stated earlier, the use of monometallic nickel nitride is not feasible due to its poor activity. Creating a bimetallic nitride by alloying nickel with another metal whose nitride is more stable seems to yield better results, yet catalyst deactivation still occurs. Nevertheless, the presence of carbon whiskers is reduced significantly.
It has therefore been shown that the nitride catalysts can be used as efficient catalysts for the dry reforming of methane with decreased whisker carbon formation, although other non-destructive forms of carbon are still formed, as expected from the theoretical models. The nitrided bimetallic Ni-Mo catalyst showed a low rate of carbon formation even with the partial reduction and the presence of metallic phases which catalyzes whisker growth. This shows the efficiency of nitrogen in retarding the growth of carbon whiskers on the active metal particles.

4.5: Conclusion
This work shows the potential for nitrided Ni and Ni-Mo samples to work as catalysts for the dry reforming of methane. Supported molybdenum nitride catalysts have a limited activity at atmospheric pressure, and show deactivation and poor thermal stability. Bimetallic Ni-Mo nitrides show much better activity despite their deactivation at low pressures. Ammonia as a nitriding agent gives good activity at higher space times for Ni-Mo precursors, but gives higher activation energies than a reduced catalyst and yields a catalyst that deactivates. The use of nitrides as catalysts significantly reduces the growth of carbon whiskers that has plagued nickel catalysts, and the observation of carbon whiskers on the surface of a Ni-Mo nitride catalyst was associated with metallic crystallites and a tendency for the bulk Ni-Mo nitride to adsorb CH$_4$ preferentially. Dispersion of the nitride phase on a basic metal oxide support improves the surface area of the catalyst and reduces coke formation by enhancing CO$_2$ adsorption. The nitridation procedure strongly affects the catalytic properties of the nitrides obtained. It has been shown that the use of H$_2$/N$_2$ as a nitrogen source causes partial reduction of the active phase in addition to the nitridation action, owing to the high strength of the N-N bond which makes ammonia a more potent nitridation agent. This is especially valid for Ni-Mo catalysts. Preliminary evidence indicates that CO$_2$ and CH$_4$ have the same active sites on the catalyst, and that a transition in the catalyst surface composition occurs. The nitride phase was shown to change to a mixed oxide and carbide phase with different catalytic properties. It is suspected that partial reduction of nickel crystallites contributes to the improvement of activity when compared to monometallic Mo nitride catalysts. Future work should explore the catalytic behavior of nitrides at pressures where they are more
stable, and optimize catalyst preparation to promote the alloying of Ni and Mo and prevent the formation of spinels.

4.6: Acknowledgements

The authors would like to acknowledge the Lebanese Council for Scientific Research [LCNRS, grant number 102909] and Science Foundation Ireland [grant number 16/RI/3734] for funding this research, in addition to Dr Fathima Laffir and Dr Karrina McNamara for their help in performing XPS measurements at the University of Limerick.

4.7: Outlook

This chapter has assessed the performance of transition metal nitrides as catalysts. It has been shown that the dispersion of the nitrides on an appropriate support enhanced their coking resistance, but their deactivation at low pressures makes them unsuitable for immediate selection as a candidate for industrial scale deployment. The upcoming chapters (Chapters 5 and 6) describe a family of catalysts based on the Ni-Co system which has a much better industrial track record.

4.8: References


Supplementary information

Figure A-1: High resolution XPS spectra of the Mo 3d region for the nitrided catalysts
Figure 0-2: High resolution XPS spectra of the N 1s region for the nitride catalysts
Figure A-3: High resolution XPS spectra of the Ni 2p region of the nitrided bimetallic Ni-Mo catalysts

Table A-1: XPS survey data for the spent catalysts

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Figure A-4: Thermogravimetric analysis of the spent catalysts after reaction at 800°C for 10 hours.

Figure A-5: Comparison of deactivation rates between a reduced 8wt.% Ni catalyst and the 8wt.% Ni 8wt.% Mo catalyst nitrided in H2/N2 and reduced at 800°C and w/F=1.11x10^-5 gcat.h/mL. Note: the Ni-Mo catalyst nitrided in ammonia is not shown since its activity is much lower.
Table A-2: Activation energies for CH₄ and CO₂ on the 8%Ni 8%Mo based catalysts

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<th>CO₂ activation energy (kJ/mol)</th>
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<td>141.1</td>
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Table 0-3: Reaction rates for CH₄ and CO₂ in ln(mol/gcat.s) at 800°C and w/F=1.11x10⁻⁵gcat.h/mL

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<td>-10.85</td>
<td>-9.94</td>
<td>-10.55</td>
<td>-10.36</td>
<td>-9.79</td>
</tr>
<tr>
<td>8Ni8Mo</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₃/N₂</td>
<td>-8.26</td>
<td>-7.60</td>
<td>-7.04</td>
<td>-8.03</td>
<td>-7.38</td>
<td>-7.08</td>
</tr>
<tr>
<td>H₂/N₂</td>
<td>-8.78</td>
<td>-7.18</td>
<td>-7.07</td>
<td>-8.28</td>
<td>-7.15</td>
<td>-7.11</td>
</tr>
<tr>
<td>reduced</td>
<td>-7.38</td>
<td>-7.12</td>
<td>-7.05</td>
<td>-7.34</td>
<td>-7.12</td>
<td>-7.06</td>
</tr>
<tr>
<td>16Mo</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂/N₂</td>
<td>-10.66</td>
<td>-10.27</td>
<td>-10.90</td>
<td>-10.90</td>
<td>-10.16</td>
<td>-9.86</td>
</tr>
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</table>

Table 0-4: Carbon balance for reactions at 800°C and w/F=1.11x10⁻⁵gcat.h/mL

<table>
<thead>
<tr>
<th>Treatment method</th>
<th>C in (mmol/s)</th>
<th>C out (mmol/s)</th>
<th>Differential (mmol/s)</th>
<th>% Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>8% wt Mo</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₃/N₂</td>
<td>1.06E-02</td>
<td>1.00E-02</td>
<td>2.62E-04</td>
<td>97.46</td>
</tr>
<tr>
<td>H₂/N₂</td>
<td>1.06E-02</td>
<td>1.00E-02</td>
<td>2.83E-04</td>
<td>97.25</td>
</tr>
<tr>
<td>reduced</td>
<td>1.06E-02</td>
<td>9.91E-03</td>
<td>3.86E-04</td>
<td>96.25</td>
</tr>
<tr>
<td>8% wt Ni 8% wt Mo</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>NH₃/N₂</td>
<td>1.06E-02</td>
<td>1.02E-02</td>
<td>2.29E-05</td>
<td>99.78</td>
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<td>H₂/N₂</td>
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<td>1.06E-02</td>
<td>4.21E-05</td>
<td>99.60</td>
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<tr>
<td>reduced</td>
<td>1.06E-02</td>
<td>1.05E-02</td>
<td>1.13E-04</td>
<td>98.93</td>
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<tr>
<td>16% wt Mo</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₃/N₂</td>
<td>1.06E-02</td>
<td>1.03E-02</td>
<td>5.77E-04</td>
<td>94.54</td>
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<tr>
<td>H₂/N₂</td>
<td>1.06E-02</td>
<td>9.88E-03</td>
<td>4.26E-04</td>
<td>95.89</td>
</tr>
<tr>
<td>reduced</td>
<td>1.06E-02</td>
<td>9.87E-03</td>
<td>3.56E-04</td>
<td>97.07</td>
</tr>
</tbody>
</table>

Table A-5: H₂ selectivity with respect to reacted CH₄

<table>
<thead>
<tr>
<th>Treatment method</th>
<th>H₂ selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃/N₂</td>
<td>0.45</td>
</tr>
</tbody>
</table>
Mass transfer parameters for the calculation of Mears and Weisz-Prater criteria to eliminate transport limitations in the experiments are shown in Table A-6 and Table A-7. The reaction rate observed on the best performing Ni-Mo catalyst is used for a conservative estimate.

**Table A-6: Mear's criterion parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed rate, mol/gcat.s</td>
<td>9.36E-04</td>
</tr>
<tr>
<td>Catalyst bulk density, g/mL</td>
<td>1000</td>
</tr>
<tr>
<td>Particle radius, m</td>
<td>3.00E-06</td>
</tr>
</tbody>
</table>

Figure A-6: SEM micrograph of the Ni-incorporated MgO-Al2O3 support
Mear’s ratio is much lower than 0.15, and therefore external transport limitations are negligible.

Table 0-7: Weisz-Prater criterion parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed rate, mol/gcat.s</td>
<td>9.36E-04</td>
</tr>
<tr>
<td>Catalyst bulk density, g/mL</td>
<td>1000</td>
</tr>
<tr>
<td>Particle radius, m</td>
<td>3.00E-06</td>
</tr>
<tr>
<td>Effective diffusivity, m/s</td>
<td>4.74E-05</td>
</tr>
<tr>
<td>Surface Concentration, mol/L</td>
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</tr>
<tr>
<td><strong>Weisz-Prater ratio</strong></td>
<td><strong>3.17E-08</strong></td>
</tr>
</tbody>
</table>

The Weisz-Prater ratio is well below unity, so no internal transport limitations are expected.
Chapter 5: Eclectic Trimetallic Ni-Co-Ru Catalyst for the Dry Reforming of Methane
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Keywords: nickel, cobalt, ruthenium, methane dry reforming, whisker carbon

Declaration of interest: none

Abstract: Ru-promoted Ni-Co catalysts supported on MgO-Al2O3 are tested for dry reforming activity in a fixed-bed reactor at atmospheric pressure. The effect of temperature (760-840°C) and contact time (5.56x10^6-3.33x10^5 gcat.h/mL) is investigated, and the catalysts maintain high stability for up to 47 hours on stream. The support synthesis method modifies the support surface area between 50 and 210 m²/g, which significantly affects dispersion. Whisker carbon is observed in spent samples with pore sizes higher than 15 nm. H2-TPR studies reveal the presence of spinels that are not completely reducible below 760°C, yet the catalysts give remarkable activity (>90% conversion). Four synthesis methods are tested for the support, with the sol-gel method in neutral conditions providing the best performance, with a small compromise on activity but a reduction in CH4 deactivation rate to -0.68%/day compared to -3.8% for the Ni/MgO-Al2O3 benchmark, and no whisker carbon formation. Further work will optimize the Ni/Co ratio in the active phase to decrease the carbon buildup on the catalysts.

5.1: Introduction
The renewed increase in global CO2 emissions by 1.2% in 2017 after two years of stagnation, reaching 37.1 Gigatonnes/yr (Olivier and Peters, 2018), highlights the urgent need to moderate greenhouse gas emissions in order to avoid further increase in global warming. A major portion of these emissions is due to energy production, which is largely based on fossil fuel combustion processes that are only slowly integrating renewable sources. As a prompt change in energy production practices is difficult, it is possible to mitigate greenhouse gas emissions by upgrading these gases and recycling them. In parallel, hydrogen is gaining traction as an attractive and clean source of energy (Alves et al., 2013), and is often produced through reforming of hydrocarbons.
In the dry reforming process (DRM), methane reacts with CO\(_2\) to produce syngas with a H\(_2\)/CO ratio close to 1, which is not ideal for hydrogen production but rather for the synthesis of alcohols via the Fischer-Tropsch process (Bereketidou and Goula, 2012). The chemistry of the process has been studied extensively (Abdel Karim Aramouni et al., 2018, Papadopoulou et al., 2012).

Catalyst performance is however a major bottleneck for the commercialization of this process. Supported nickel has been the most widely used catalyst for syngas production through methane reforming. It is also the most widely researched catalyst for dry reforming (Abdel Karim Aramouni et al., 2018, Fidalgo et al., 2011, Castro Luna and Iriarte, 2008, Hao et al., 2009, Therdthianwong et al., 2008). However, the use of nickel alone as an active metal has not been satisfactory enough to allow for the commercialization of the DRM process. The low water content and high operating temperatures in this process cause sintering and carbon formation on the catalyst, specifically in the form of carbon whiskers that often lead to pellet damage, catalyst deactivation and disturbances in the reactor flow and temperature profiles (Rostrup-Nielsen et al., 1993). Due to its relatively low Tamman temperature (the temperature at which bulk atoms experience significant mobility), nickel tends to sinter at the reaction temperatures, as nickel particles on the surface of the support migrate, coalesce and lose dispersion via two main mechanisms (Sehested, 2003, Azzam et al., 2018), namely particle migration at low temperatures and Ostwald ripening at higher temperatures. Table 5-1 shows the Tamman temperatures of selected catalytically active metals used for the dry reforming reaction.

Table 5-1: Tamman temperatures of most widely used metals for DRM catalysis (Argyle and Bartholomew, 2015)

<table>
<thead>
<tr>
<th>Element</th>
<th>Tamman temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>863</td>
</tr>
<tr>
<td>Co</td>
<td>877</td>
</tr>
<tr>
<td>Au</td>
<td>668</td>
</tr>
<tr>
<td>Ag</td>
<td>617</td>
</tr>
<tr>
<td>Pd</td>
<td>914</td>
</tr>
<tr>
<td>Pt</td>
<td>1014</td>
</tr>
<tr>
<td>Rh</td>
<td>1129</td>
</tr>
<tr>
<td>Ru</td>
<td>1362</td>
</tr>
</tbody>
</table>

Details of the carbon formation mechanism are discussed by several authors (Baker et al., 1972, Baker et al., 1973, Abild-Pedersen et al., 2006, Argyle and Bartholomew, 2015, Rostrup-Nielsen and Trimm, 1977, Alstrup, 1988). From a process engineering perspective, the temperature, pressure and reactant ratios should be optimized to guarantee good reactor performance and low carbon formation on the catalyst. From a catalyst design perspective, a high dispersion of the active phase is necessary to avoid carbon deposits (Abdel Karim Aramouni et al., 2017, Alstrup et al., 1998, Abild-Pedersen et al., 2006), with a particle size ideally below 5-6 nm. Avoiding carbon deposition is
therefore a complex task which is affected by the age of the catalyst and therefore its degree of sintering (Azzam et al., 2018).

The design of a suitable catalyst for dry reforming has been the subject of many reviews (Abdel Karim Aramouni et al., 2018, Lavoie, 2014, Pakhare and Spivey, 2014). Alumina doped with a small amount of basic metal oxide such as MgO is recognized as one of the best performing supports for a dry reforming catalyst (Zhang et al., 2015b, Shen et al., 2019), since basic metal oxides and the presence of surface oxygen with high mobility enhances the adsorption of CO\(_2\) and reduces carbon deposition (Phan et al., 2018, Rosset et al., 2020). The desired properties for a support in a dry reforming catalyst include good oxygen mobility and optimal metal-support interaction: too weak a metal-support bond strength increases the sintering rate of the active phase, while a very strong interaction can cause the formation of spinel structures that are very difficult to reduce. Spinels are however being studied as possible reforming catalysts in their unreduced form (Rouibah et al., 2017). Our group has reported the catalyst design tradeoffs in a previous work (Abdel Karim Aramouni et al., 2018). Many authors attempted to immobilize or confine the active phase to minimize its sintering on the support (El Hassan et al., 2016, Afzal et al., 2020, Cao et al., 2017). Catalyst preparation methods can also play a role in controlling catalyst morphology, dispersion and stability, and it is generally agreed that sol-gel methods give better properties than impregnation methods (Abdel Karim Aramouni et al., 2018, Horváth et al., 2011), but are more complex and costly.

Transition metals were found to be good catalysts for the DRM reaction, with important synergetic effects demonstrated in bimetallic transition metal catalysts with improvements observed in dispersion, activity and coking tendencies (Abdel Karim Aramouni et al., 2018, Zhang et al., 2007, Horváth et al., 2011). Mobile surface oxygen was also successfully exploited in some studies through the combination of nickel or other transition metals in the metal oxide lattice, driving the reforming reaction forward through cyclical redox mechanisms (Wong et al., 2017, Zhang et al., 2017). The Ni-Co bimetallic system has received considerable attention (Leban and Yıldırım, 2020, de Sousa et al., 2012) due to its good performance in terms of activity, stability and low carbon formation compared to other binary transition metal systems.

Cobalt is less active than nickel for the dry reforming reaction, but has a lower rate of carbon formation (El Hassan et al., 2016). Takanabe et al. (Takanabe et al., 2005) found similar conclusions, but noted that supported cobalt catalysts deactivated due to cobalt oxidation, while nickel deactivated due to carbon formation. The combination of nickel and cobalt dramatically improved overall stability, which was attributed to the acceleration of CH\(_4\) decomposition by nickel; the increased production and spillover of reductive hydrogen from Ni to Co combats the oxidation of metallic cobalt. Co seems to react more selectively with oxygen species from CO\(_2\) decomposition than carbon species arising from methane decomposition(Movasati et al., 2019). Both the works of Takanabe et al. (Takanabe et al., 2005) and Phan et al. (Phan et al., 2018) observed the formation of a Ni-Co alloy in the catalyst, at least after reduction, which supports the explanation of the strong synergetic effects in the bimetallic system. The alloy remained stable under reaction conditions. Whang et al. (Whang et al., 2017) noted that the presence of cobalt
in a Ni-Co bimetallic catalyst did not significantly improve the activity, but increased the carbon deposition on the catalyst, in contrast with other authors.

The solubility of carbon in nickel and other non-noble metals is also an important factor that determines their likelihood to catalyze whisker growth, as the formation of carbide is the precursor for carbon growth (Takanabe et al., 2005). Carbon is not soluble in noble metals, and they have therefore been investigated as catalysts for the dry reforming reaction with excellent activity and low to no carbon formation (Ferreira-Aparicio et al., 1999, Safariamin et al., 2009, Özkara-Aydınoğlu et al., 2009, Gangurde et al., 2018, Albarazi et al., 2013). The order of activity for noble and transition metals for dry reforming is Rh>Ru>Ir>Ni, Pt, Pd> Co> Fe, Cu (Gurav et al., 2012). Safariamin et al. (Safariamin et al., 2009) tested Ru based catalysts on alumina modified with ceria. They found Ru/Al2O3 to be a stable catalyst with no coke deposition, but with lower activity than ceria-doped Ru catalysts. This observation also highlights the role of the support in determining the performance of a catalyst, as changes in the support composition while keeping the same active phase composition give different activities (Albarazi et al., 2013).

Noble metals are however expensive and scarce, and their use in small amounts as promoters for transition metals is more commercially feasible. The use of noble metal promoters on supported non-noble metals has shown positive results. Doping of nickel catalysts with noble metals lowers the reduction temperature and increases the number of active sites (Bian et al., 2017). Wu et al. (Wu et al., 2014) tested the effect of Au and/or Pt as promoters for a nickel catalyst supported on alumina modified with Ce or Mg, and found that the presence of a noble metal increases the reducibility of NiO and its dispersion. The modification of alumina with Ce or Mg noticeably improved the performance of the monometallic Ni catalyst; Pt addition to Ni considerably increased the activity of the catalyst, while Au addition had much milder effects. The use of the two noble metals in a trimetallic Ni-Au-Pt catalyst showed little improvement over the Ni-Pt catalyst. There is however some potential in improving the performance of bimetallic non-noble metal catalysts by a small amount of a single noble metal promoter. El Hassan et al. (El Hassan et al., 2016) showed that the presence of rhodium in a bimetallic Co-Rh catalyst supported on either silica or SBA15 increases the sintering resistance of cobalt, promotes its reducibility, and minimizes the amount of gamma-type carbon deposits which are destructive. Furthermore, they noted that Co and Rh do not form bimetallic phases and thus act as two active phases with different reactivities in the process.

Ruthenium has the highest Tamman temperature of the most catalytically active metals (Table 5-1) and therefore should give the highest resistance to sintering. The present work evaluates the performance of a bimetallic Ni-Co catalyst doped with Ru supported on MgO-Al2O3. To the knowledge of the authors, the trimetallic Ni-Co-Ru system has not yet been reported in the literature. We investigate the effect of support properties on the performance of the catalyst as a first step in optimizing the catalyst design for the dry reforming process. The Ni/Co ratio will be optimized in a separate study. MgO-Al2O3 supports synthesized via four methods (sol-gel under acidic, neutral and basic conditions and co-precipitation), are impregnated with Ni, Co and Ru and tested in the dry reforming of methane.
5.2: Experimental

5.2.1: Materials
Magnesium nitrate hexahydrate (99%), aluminum nitrate nonahydrate (99.997%), nickel nitrate hexahydrate (>97%), cobalt nitrate hexahydrate (>98%), aluminum tri-sec-butoxide (Al-TSB) (97%), Magnesium ethoxide (98%), and sec-butanol were purchased from Sigma-Aldrich. Nitric acid (65%) was purchased from VWR. 25% ammonia solution was purchased from Lab-Scan. Sucrose was purchased from Sigma-Aldrich. n-Hexane was purchased from Surechem Products. Gamma-Alumina (99.5%) was purchased from Alfa-Aesar.

5.2.2: Synthesis of the co-precipitated support
MgO-Al₂O₃ support with Mg:Al ratio of 1:4 was synthesized using the method by Zhang et al (Zhang et al., 2015a) but using sucrose instead of glucose as a template with a ratio of Al/Sucrose of 1:0.15 (highest surface area).

Calculated amounts of aluminum nitrate hexahydrate and magnesium nitrate hexahydrate were mixed with 10 mL of deionized water to which sucrose was added in a sucrose:Al molar ratio of 0.15:1. The solution was stirred for 30 minutes. Ammonium hydroxide was then added drop wise to the mixture under vigorous stirring until a pH of approximately 9.5 was reached. A very rapid gelation followed by an increase in the pH was observed at pH=5 after an initially slow precipitate formation in the clear precursor solution. The white gel was aged for 2 hours then transferred to a Teflon lined autoclave and subjected to hydrothermal treatment at 80°C for 24 hours. The gel, now a light brown color, was washed with deionized water, dried at 120°C overnight, gently ground with a pestle and calcined at 750°C for 2 hours in air.

5.2.3: Synthesis of the sol-gel supports
The magnesia-alumina supports were prepared via a sol-gel method based on Rezgui et al. (Rezgui and Gates, 1997). Al-TSB and magnesium ethoxide were dissolved in sec-butanol at 80°C so that the molar ratio of Mg to Al was 1:4 and the concentration of Al-TSB was 1M. The sol was hydrolyzed with water in sec-butanol so that the hydrolysis ratio is 2.5. Three samples were prepared at different pH values. Nitric acid was added to the ‘acid’ sample so that the pH of the medium was 2. The ‘neutral’ sample was not modified with acid or base, and the pH of the ‘basic’ sample was raised to a value of 10 with ammonia. Once the hydrolysis was complete and a gel formed, the gels were transferred to Teflon-lined autoclaves and were aged at 80°C for 24 hours. The samples were then filtered, washed with ethanol, then dried first at 70°C for 24 hours, then at 100°C for 4 hours before being calcined in air at 750°C for 2 hours.

5.2.4: Impregnation of the supports
Determined amounts of Ni, Co and Ru precursors were dissolved in water (0.5 mL/g support) and stirred at 500 rpm for 30 minutes to form the impregnating salt solution. The volume of water was chosen to be of the same order of magnitude as the pore volume to minimize transport limitations in the impregnation process.
The supports are impregnated with nickel and cobalt nitrate along with ruthenium chloride following a two-solvent dry impregnation method described by Lopez et al (Lopez, 2006) to protect the support: the support pores are first wet using hexane (0.5 mL/g) to allow air to escape without large stresses, then the aqueous salt solution is added to the hexane/support mixture and manual stirring is maintained for 15 minutes. The use of a magnetic stirrer is challenging in this procedure due to the low liquid content and paste-like texture of the sample. Solvent replacement occurs and hexane is rejected from the solids. The supernatant hexane phase is separated before the wet powder is dried at 110°C for 6 hours before calcination at 750°C for 2 hours in air. The four supports are impregnated to form a 7.5wt%Ni 7.5wt%Co 0.25wt%Ru active phase. Two additional catalysts were synthesized as benchmarks: 7.5wt.%Ni/MgO-Al2O3 (support synthesized using the acidic sol-gel method) and a 7.5wt.%Ni/γ-Al2O3 catalyst. Nickel was loaded on the benchmark catalysts using the same two-solvent impregnation method.

The Ni-Co-Ru catalysts impregnated on the supports synthesized by the acidic, neutral and basic sol-gel process are referred to as acid SGM, neutral SGM and basic SGM respectively in the manuscript, while the catalyst impregnated on the co-precipitated support is referred to as the co-precipitated sample. All trimetallic catalysts in this work have the same active phase composition.

5.2.5: Catalytic tests
The catalytic tests were carried in a 4mm ID quartz tube inside a tubular furnace at atmospheric pressure. 10 mg of catalyst powder were mixed with quartz sand and placed inside the quartz tube. The packing was held in place with two quartz wool plugs. The packed reactor was first purged with N2 gas, then the active phase was reduced in 50% H2/N2 flowing at 40 mL/min. The catalyst was heated in the reducing gas flow to 760°C at 15°C/min and saturated for one hour before the hydrogen was cut off. The reduced catalyst was then heated to the desired reaction temperature in N2 and the flow switched to an equimolar mixture of methane and CO2, delivered at the desired flow rate using mass flow controllers (Brooks). Gases leaving the reactor were analyzed using an Agilent 7820 gas chromatograph equipped with a 6-port gas sampling valve, using a Porapak Q porous polymer column and a thermal conductivity detector. Argon (99.999%) was used as a carrier gas to maximize hydrogen sensitivity and the column was kept at a constant temperature of 50°C during the analysis.

Two types of catalytic tests were performed to evaluate the activity and stability of the catalyst: in contact time tests, the reduced catalyst was tested at various contact times ranging from 5.5x10^-6 gcat.h/mL to 3.3x10^-5 gcat.h/mL by changing the flow rate between 10 and 30 mL/min. Five measurements for each contact time were taken at intervals of 4 minutes, and the average conversion was calculated. Deactivation tests were carried out at a fixed space time (w/F) of 1.11x10^-5 gcat.h/mL at 800°C, and product samples were analyzed every 20 minutes. The contact time of 1.11x10^-5 gcat.h/mL was selected for the deactivation tests because it is the space time at which the conversions start to reach their equilibrium values.
5.2.6: Catalyst characterization

The BET surface areas, pore volumes and pore size distributions were measured by nitrogen adsorption-desorption at 77K using a Micromeritics Gemini VII instrument. Prior to nitrogen adsorption analysis, the samples were degassed under nitrogen flow at 150°C overnight. SEM micrographs were acquired using a Tescan MIRA3 electron microscope at 20kV using an in-beam secondary electron detector. Thermogravimetric analysis of the spent catalyst samples was performed on a TA Q500 instrument. Samples were heated at 15°C/min until 950°C in air. Carbon formation rates were calculated based on the sharp weight loss observed in the 400-700°C range. X-ray diffraction spectra were acquired using a Bruker D8 Advance instrument.

Temperature programmed reduction (H\textsubscript{2}-TPR) tests were performed on a Micromeritics AutoChem II instrument. Prior to the TPR runs, the samples were heated in-situ to 120°C under argon gas flow to remove physisorbed water then cooled down to ambient temperature. The flow was then switched to 4%H\textsubscript{2}/Ar and the sample was heated at 5°C/min until 900°C at 30 mL/min.

5.3: Results

5.3.1: Physicochemical properties

Table 5-2 shows the surface area, pore volume and average pore size of the synthesized catalysts. The co-precipitated support yielded the highest surface area. The surface areas achieved with the sol-gel procedure were highly sensitive to the pH, with a higher BET surface area reached with higher synthesis pH. The basic sol-gel sample (pH=10) gave the highest pore volume and average pore size of 0.80 cm\textsuperscript{3}/g and 15.5 nm respectively. While the co-precipitation method yielded a higher area, it had the smallest pore size of all the trimetallic samples.

<table>
<thead>
<tr>
<th>Ni-Co-Ru catalysts</th>
<th>Support</th>
<th>area, m\textsuperscript{2}/g</th>
<th>pore volume, cm\textsuperscript{3}/g</th>
<th>pore size, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid SGM</td>
<td>50.1</td>
<td>0.21</td>
<td>15.8</td>
<td></td>
</tr>
<tr>
<td>neutral SGM</td>
<td>129.6</td>
<td>0.45</td>
<td>13.9</td>
<td></td>
</tr>
<tr>
<td>Basic SGM</td>
<td>179.0</td>
<td>0.80</td>
<td>15.5</td>
<td></td>
</tr>
<tr>
<td>Co-Precipitated</td>
<td>210.1</td>
<td>0.45</td>
<td>8.7</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Benchmarks</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/MgO-Al\textsubscript{2}O\textsubscript{3}</td>
<td>115.1</td>
<td>0.26</td>
<td>7.1</td>
</tr>
<tr>
<td>Ni/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>52.3</td>
<td>0.11</td>
<td>6.0</td>
</tr>
</tbody>
</table>
Figure 5-1: XRD spectra of the calcined catalysts and the co-precipitated support. Peak labels: Ruthenium oxide (o), Nickel oxide (♦), Cobalt oxide (♣)

Figure shows the XRD spectra obtained for the four supported Ni-Co-Ru catalysts along with the XRD spectrum of the co-precipitated MgO-Al₂O₃ support. Interpretation of the XRD spectra is somewhat challenging due to the overlap in the peaks of the active phase components and the support phase. NiO, Co₃O₄, Al₂O₃ and NiAl₂O₄ all have a diffraction peak at 36.5° 2θ, and it is therefore difficult to tell whether a spinel structure is formed. However, a cobalt oxide peak is observed at approximately 59.5° which is not apparent in the support, indicating that a separate cobalt oxide phase exists. This observation hints to the existence of a nickel oxide phase as no Ni-Co alloying is explicitly observed. Ruthenium oxide peaks (labeled ‘o’ in Figure 5-1) are apparent with very weak intensities due to the low Ru content, which indicates that ruthenium is then present as a separate phase. The crystallite diameters are estimated for cobalt oxide from Scherrer’s equation and are displayed in Table 5-3. The NiO crystallite size could not be estimated from XRD data due to the overlap between cobalt and nickel oxide peaks in addition to overlapping with the support peaks, and the ruthenium oxide peaks are not analyzed since their amplitude is too low to accurately determine the width at half maximum for the Scherrer equation calculations.
The cobalt oxide crystallite size decreases with an increase in the surface area of the support. For the acid sol-gel sample, the crystallite size is roughly the same size as the average pore of the support, meaning that the particles are probably confined in the pores. The two-solvent impregnation method is therefore effective in maximizing the utilization of the support pore structure. As the surface area of the synthesized support increases, the cobalt particle size decreases due to the good metal-support interaction in this catalyst system. The high affinity between the active metals and the support causes the active phase to maximize its contact with the support surface rather than agglomerate in larger particles. One must note that the particle sizes reported in Table 5-3 are for cobalt oxide. Metallic cobalt particles obtained after reduction are expected to be smaller due to the significant volume change upon loss of oxygen.

SEM micrographs of the fresh catalysts are shown in Figure 5-2. The co-precipitated sample (Figure 5-2.a) does not show apparent mesopores, and presents a relatively flat support surface that is entirely covered with metal nanoparticles. Acid and basic sol-gel samples, on the other hand (Figure 5-2.b-c) have morphologies typical of a sol-gel synthesis, composed of an agglomeration of primary particles that form larger aggregates with significant porosity. The active phase nanoparticles cannot be easily distinguished from the primary particles of the support skeleton except for a few particles of ~100 nm in size, which shows the intimate contact and high dispersion achieved using the impregnation method. The neutral sol-gel sample (Figure 5-2.d) shows a different morphology, with flake-like primary particles that appear to have less porosity than the other sol-gel samples. Yet, the active phase is also well dispersed, as shown by the cobalt oxide crystallite sizes calculated in Table 5-3.

### Table 5-3: Cobalt oxide particle size from Scherrer's equation

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co$_3$O$_4$ particle size, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid SGM</td>
<td>15.2</td>
</tr>
<tr>
<td>Neutral SGM</td>
<td>9.4</td>
</tr>
<tr>
<td>Basic SGM</td>
<td>4.8</td>
</tr>
<tr>
<td>Co-precipitated support</td>
<td>4.7</td>
</tr>
</tbody>
</table>
Figure 5-2: SEM micrographs of the co-precipitated catalyst (a), the acid SGM catalyst (b), the basic SGM catalyst (c), and the neutral SGM catalyst (d)
### 5.3.2: H₂-TPR characterization

The H₂-TPR profiles for the synthesized catalysts are shown in Figure 5-3. Nickel supported on γ-Al₂O₃ shows a broad reduction profile at the 200-400°C range, and a small peak at 475 °C with a shoulder at 410-420 °C. Hydrogen consumption under 400 °C is attributed to the reduction of surface Ni³⁺ species, while the peak is attributed to the reduction of NiO. A second peak appears at 750 °C which highlights the strength of the metal-support interaction and the formation of NiAl₂O₄ spinel (Zhang et al., 2015b). The reduction of NiO occurs at lower temperatures on MgO-Al₂O₃, with a reduction shoulder at 250-350 °C and a peak at 450 °C, while the peak above 750 °C shifts to 850 °C despite the supposed weakening of Ni and Al₂O₃ interaction due to MgO addition. The presence of ruthenium and cobalt reduces the reduction temperature of the spinel phase to 830 °C in both the basic and neutral SGM samples, 815 °C in the basic SGM sample and 795 °C in the co-precipitated sample. It appears a high dispersion due to an increased surface area decreases the reduction temperature of the spinel phase, while the effect of Co and Ru weakens the interaction between Ni species and Al₂O₃. No visible peaks are attributed to the reduction of ruthenium species due to their low concentration, and supported ruthenium is known to reduce below 200 °C on alumina, with a lowered reduction temperature when the strong metal-support interaction is weakened by the introduction of a basic metal oxide such as MgO (Safarimarin et al., 2009).

When comparing the trimetallic catalyst with the benchmark Ni samples, a significant increase in hydrogen consumption appears in the 200-400°C range, meaning that the trimetallic catalyst reduces at lower temperatures. Two additional peaks are noticed, one sharp peak at around 300-400°C and a much broader shoulder in the 400-650 °C range that are attributed to the reduction of cobalt oxide in two forms, with the lower
temperature peak indicative of reduction of ‘free’ cobalt oxide species while the broader high temperature shoulder corresponds to the reduction of cobalt oxide species in stronger interaction with the support. Those two peaks are most noticeable in the neutral SGM and the co-precipitated sample. The first Co reduction peak is shifted to 270°C in the co-precipitated sample and to 250°C in the basic SGM sample due to the improved interaction between Ru and Co promoted by the high dispersions achieved in these samples (Table 5-3). Spinel structures identified in the high temperature peak (>790°C) do not reduce completely at the upper limit of temperature attainable in the TPR profile (900°C).

5.3.3: Catalytic tests

Figure 5-4 shows the methane and CO₂ conversions as a function of time achieved by the trimetallic Ni-Co-Ru catalysts in addition to the methane and CO₂ conversions for two benchmarks, namely 7.5Ni/MgO-Al₂O₃ and 7.5Ni/γ-Al₂O₃. The neutral SGM sample remains the most active over the course of 47 hours, with an average deactivation rate of 0.7 CH₄ % per 24 hours and 0.3 CO₂% per 24 hours. The support has a significant effect on the catalyst, as is shown by the different deactivation rates and activities for the four catalysts. Initial performance varies in the order: Basic SGM > Neutral SGM = Ni/MgO-Al₂O₃ > Co-precipitated > Acid SGM > Ni/γ-Al₂O₃.

After 47 hours on stream, the neutral SGM sample is the most active catalyst. All of the other catalysts show lower and decreasing activity, with the exception of Ni/γ-Al₂O₃ which shows very different behavior, and performs slightly better than the acid SGM sample in terms of CH₄ conversion above 40 hours on stream. All catalysts supported on MgO-Al₂O₃ show a monotonous, almost linear loss in activity over time in the range of 1-4 % per 24 hours, while the Ni/γ-Al₂O₃ catalyst exhibits a strong loss in conversion during the first 10 hours on stream (approximately 25% per 24 hours) then gradually recovers around 15% in methane and CO₂ conversion over 30 hours. The Ni/γ-Al₂O₃ benchmark nevertheless remains the least active catalyst tested in this work. The presence of MgO in the support affects both the activity of the catalyst and its deactivation rate, as is apparent from the very different performance of the nickel catalysts supported on
magnesia-alumina and alumina alone. The increase in conversion after approximately 8 hours on the Ni/γ-Al₂O₃ has been observed in the data published by Schwengber et al., (Schwengber et al., 2016) although a much milder deactivation-reactivation trend was observed on the 15% and 30% Ni/Al₂O₃ catalyst they tested. Yet, they did not discuss this observation. A similar minimum in CH₄ conversion was also observed on Ni/Al₂O₃ aerogel catalysts by Kim et al. (Kim et al., 2000), and was attributed to whisker carbon formation being driven by the methane cracking reaction. This phenomenon explains the subsequent increase in CH₄ conversion which we have shown in a previous study (Abdel Karim Aramouni et al., 2017), and is accordance with Alstrup’s model (Alstrup, 1988) of carbon formation. The model predicts the formation of a selvedge with high carbon concentration at the surface of the nickel crystals (commonly called the surface carbide layer) during an induction period prior to reaching supersaturation which restructures the crystallites and initiates filament growth. MgO is known to extend the induction period (Helveg et al., 2011), which should theoretically be of infinite duration to avoid coke formation.

The effect of space time (w/F) on conversion is shown in Figure 5-5 at temperatures of 760°C, 800°C and 840°C for all catalysts. At a temperature of 760°C, the basic SGM catalyst has the highest conversion for all w/F tried, closely followed by the neutral SGM sample, acid SGM and 7.5Ni/MgO-Al₂O₃. The co-precipitated catalyst produces 5-10% lower conversion than the Ni/MgO-Al₂O₃ sample but maintains a relatively flat profile both for CH₄ and CO₂. The worst performing catalyst remains the Ni/γ-Al₂O₃ benchmark which shows a clear transition between the kinetically limited regime at w/F below 0.8x10⁻⁵gcat.h/mL and equilibrium limited performance at w/F above 1.2x10⁻⁵gcat. All catalysts show a decrease in conversion at low w/F (apart from the co-precipitated sample), but the Ni-Co-Ru catalysts do not show a clear distinction between kinetic and equilibrium regions at 760°C in the range of space times studied, which indicates that the reaction rate on the trimetallic catalysts is much higher than on the nickel catalysts. The distinction is also not clear on the Ni/MgO-Al₂O₃ catalyst, which further highlights the beneficial effect of MgO addition to the support. CO₂ conversions are generally higher than CH₄ conversions due to the reverse water-gas shift reaction.
As the temperature reaches 800°C, the performance of the trimetallic catalysts and Ni/MgO-Al₂O₃ becomes comparable while the Ni/γ-Al₂O₃ remains lower, and the performance of all catalysts is virtually identical at 840°C with the exception of the Ni/γ-Al₂O₃ benchmark at low w/F. An increase in temperature increases the conversion for CH₄ and CO₂ due to both an increase in the equilibrium conversion and the reaction rates.

The equilibrium conversion is reached at 840°C for all samples at w/F above 0.8x10⁻⁵ gcat.h/mL. The order of activities in the trimetallic catalysts at 760°C seems to be related to the pore size, as they follow the same trend, with the catalysts having larger pore sizes performing better. This suggests the existence of pore transport limitations, but a rigorous treatment of the subject is beyond the scope of this paper and will be the subject of future work.

Figure 5-5: effect of w/F on CH₄ and CO₂ conversion at 760°C (a-b), 800°C (c-d) and 840°C (d-e) for all catalysts
5.3.4: Carbon formation

Figure 5-6: SEM micrographs of the spent (a) co-precipitated catalyst, (b) the acid SGM catalyst, (c) the basic SGM catalyst, and (d) the neutral SGM catalyst after reaction for 8 hours at 800°C and w/F=1.11x10⁻⁵ gcat.h/mL

Figure 5-6 shows SEM micrographs for the spent trimetallic catalysts after reaction. Despite the high activity and stability exhibited by these catalysts and the inhibition of carbon formation expected from the catalyst composition, whiskers are seen on the acid and basic SGM catalysts, but they differ in morphology. The acid sample shows a small amount of large whiskers, with diameters of a few hundred nanometers, while the basic sample is covered with a thick ‘blanket’ of thin whiskers with diameters thinner than 50 nm. This is explained by the significant difference in active metal particle size (and consequently in dispersion) on the acid and basic SGM catalysts as shown in Table 5-3. Higher particle sizes give thicker whiskers due to the nature of the mechanism of whisker growth. No whiskers are observed on the neutral SGM and co-precipitated catalyst samples. Yet, the deactivation of the catalysts does not seem to depend solely on the
presence of whiskers, as the basic SGM catalyst remains the most active with the exception of the neutral SGM sample over the 48-hour deactivation test.

Figure 5-7: SEM micrographs of the spent Ni/γ-Al₂O₃ (a) and the Ni/MgO-Al₂O₃ (b) after reaction for 8 hours at 800°C and w/F=1.11x10⁻⁵ gcat.h/mL.

The noticeable presence of carbon whiskers on the benchmark Ni catalysts is evident as shown in Figure 5-7, with the Ni/MgO-Al₂O₃ catalyst exhibiting a lower number of larger carbon nanotubes than the Ni/γ-Al₂O₃ catalyst. A highly developed network of carbon fibers is observed despite the low carbon formation rate on the Ni catalysts shown in Table 5-4.

Table 5-4: Carbon formation rates at 800°C and w/F=1.11x10⁻⁵ gcat.h/mL

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Carbon formation rate, mg/gcat.h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid SGM</td>
<td>50.5</td>
</tr>
<tr>
<td>Neutral SGM</td>
<td>8.1</td>
</tr>
<tr>
<td>Basic SGM</td>
<td>64.4</td>
</tr>
<tr>
<td>Co-precipitated</td>
<td>25.6</td>
</tr>
<tr>
<td>Ni/MgO-Al₂O₃</td>
<td>7.4</td>
</tr>
<tr>
<td>Ni/γ-Al₂O₃ (after 7h)</td>
<td>1.4</td>
</tr>
<tr>
<td>Ni/γ-Al₂O₃ (after 22h)</td>
<td>9.1*</td>
</tr>
</tbody>
</table>

* rate calculated after subtracting the mass of carbon formed below 10 hours on stream

Trimetallic Ni-Co-Ru catalysts give higher carbon formation rates than the Ni benchmarks despite their better activity. The acid SGM and basic SGM samples gave the highest carbon formation rates, at 50.5 and 64.4 mg/gcat.h respectively, much higher than the remaining trimetallic catalysts and the Ni benchmarks. These two samples are also the only two in which carbon whiskers were observed. There are different forms of carbon present on the catalyst, and not all carbon deposits contribute to their deactivation: there is no clear relation between activity/stability and carbon formation, in accordance with the observations of Horváth et al. (Horváth et al., 2011). The data suggests that the slightly higher activity exhibited by the basic SGM sample compared to the neutral SGM sample in Figure 5-5 is due to the methane cracking reaction driving whisker growth. The neutral SGM sample has carbon formation rates comparable to those of the Ni benchmark catalysts, but it does not form carbon whiskers. Interestingly, only Ni-Co-Ru catalysts
with pore sizes larger than 15 nm have developed whiskers. Despite the good metal-support interaction in this catalyst formulation, sintering is never completely avoided, and while small pores tend to confine the metal particles and limit their sintering (El Hassan et al., 2016), larger pores do not have this advantage. The metal particles located inside larger pores suffer from more severe sintering, and therefore can more easily increase in size, which facilitates whisker carbon growth (Abdel Karim Aramouni et al., 2017, Abdel Karim Aramouni et al., 2018). Whisker carbon is observed on Ni catalysts even with pores smaller than 15nm, which highlights the beneficial effect of the trimetallic system in mitigating carbon formation.

The unique behavior of the Ni/γ-Al_2O_3 catalyst in terms of stability was investigated by comparing the carbon formation rate after 7 hours and 22 hours on stream (to obtain data before and after the estimated induction period of approximately 10 hours). Very little carbon is deposited on the catalyst after 7 hours on stream, while the carbon formation rate increases by almost an order of magnitude once the 10-hour induction period is exceeded. The low initial carbon deposition rate is then attributed to the formation of the selvedge, and the higher subsequent carbon deposition rate corresponds to the steady-state growth of the whiskers from Ni particles. For the same nickel loading, the catalyst supported on alumina exhibits a higher steady state carbon deposition rate than the one doped with MgO, which is due to the enhanced gasification of surface carbon and increased oxygen mobility brought by the addition of MgO (Trimm, 1997, Abdel Karim Aramouni et al., 2018).

The data suggests that the neutral SGM support is the optimal support for the trimetallic system, as it gives remarkable stability and the optimal pore size to allow good exposure of the catalyst to the reaction medium without causing whisker growth. A very minor compromise on activity compared to the basic SGM is compensated by a significant stabilization of the catalyst and whisker carbon elimination.

Elevated coking rates observed on the acid and basic SGM catalysts are due to both reaction intermediates on the surface and whisker carbon presence, and are indirectly related to the metal loading. Good dispersions are obtained with the current metal loading even for the acid SGM sample, and it is therefore more likely that the Ni/Co ratio can be further optimized to affect the carbon formation rate.

5.4: Conclusion
The trimetallic Ni-Co-Ru catalysts have shown better stability and a much higher activity than the nickel-based catalysts, due to their ability to maintain a high conversion at space times where the nickel catalysts start to perform poorly. The addition of MgO to the support plays the dominant role in providing stability to the catalyst, and the presence of Co and Ru increases the catalyst activity but has a milder impact. Despite the excellent catalytic performance of these catalysts, carbon formation seems to remain substantial, with whisker carbon being present in samples having high pore sizes and large particles. In addition, a spinel structure that is difficult to reduce was observed. The pore size is shown to be an important parameter to consider in the synthesis of the catalyst, as too small a pore size increases internal mass transfer resistance, while larger pores increase the risk of carbon formation by facilitating particle sintering. Based on the results of this
work, the optimal pore size is slightly below 15 nm, as it appears that it is the limit above which whiskers develop. The neutral SGM catalyst has shown comparable coking tendencies to the benchmark Ni catalysts but with no filamentous carbon growth, and has almost zero activity loss over 47 hours. This catalyst is therefore selected as the optimal catalyst among the ones tested in this work, with this choice only incurring a minor tradeoff on activity as it is not the most active. This tradeoff has been highlighted in our previous work (Abdel Karim Aramouni et al., 2018). The presence of carbonaceous deposits on the catalysts suggests that the ratio of Ni and Co can be further adjusted to optimize the mutual stabilization between these two metals in the active phase.

5.5: Acknowledgements
The authors would like to acknowledge the Lebanese Council for Scientific Research [LCNRS, grant number 102909] and Science Foundation Ireland [grant number 16/RI/3734] for funding this research, in addition to Eng. Sary Fayyad and Eng. Layal Halawi for their help in the experimental work at the American University of Beirut.

5.6: Outlook
In the study of the Ni-Co-Ru catalytic system, the support properties and preparation methods were investigated in a first step while keeping the active phase unchanged. This chapter has shown that the sol-gel method in neutral pH gives the best support properties, but that there is still room for improvement. The effect of the Ni/Co ratio and the promoting role of Ru are still not explored in this study, and will be the focus of Chapter 6.

5.7: References


Chapter 6: Eclectic Trimetallic Ni-Co-Ru Catalyst for the Dry Reforming of methane. Phase 2: Variation of the Ni/Co ratio and the calcination temperature

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Keywords: nickel, cobalt, ruthenium, methane dry reforming, whisker carbon

Declaration of interest: none

Abstract

This work studies the effect of Ni/Co ratio and calcination temperature on the performance of trimetallic Ni-Co-Ru catalysts supported on MgO-Al2O3 synthesized by sol-gel method in neutral pH conditions. Higher activity was achieved with higher Ni/Co ratios, and the effect of calcination temperature on stability was small except for the bimetallic Co-Ru catalyst which deactivated by oxidation when calcined at 650°C and by coking when calcined at 750°C. A higher calcination temperature was generally associated with an increased coking rate due to the elevated sintering, while a lower calcination temperature slightly improved the reducibility of the catalysts. Promotion with 0.25wt% Ru improved the stability and reducibility of Ni-Co catalysts, with a small compromise on activity when calcined at high temperature. Coking rate was reduced by 51% with Ru addition. Excellent stability and the lowest coking rate (0.5 mgC/gcat.h) were achieved at the expense of a slightly lowered activity (3-5% lower conversion compared to 15Ni0.25Ru) with the 5Ni 10Co 0.25Ru catalyst calcined at 750°C.

6.1: Introduction

The dry reforming process is an emerging technology that allows the production of syngas with an H2/CO ratio of 1 from CO2-rich natural gas or biogas (Abdel Karim Aramouni et al., 2018). The chemistry of the process has been studied extensively (Abdel Karim Aramouni et al., 2018, Papadopoulou et al., 2012a). Typically, nickel-based catalysts have been used in syngas production from methane reforming and are widely researched (Albarazi et al., 2013, Abdel Karim Aramouni et al., 2017b, Al-Fatesh et al., 2011, Papadopoulou et al., 2012a). However, the difficult reactor conditions in dry reforming form an increased coking risk (Al-Fatesh, 2015, Abdel Karim Aramouni et al., 2017a), which limits the use of supported nickel alone as a catalyst for dry reforming of methane (DRM). Improvements in the performance and carbon resistance of nickel based catalysts have targeted three main aspects of catalyst design:
First, the use of basic metal oxide supports with good interaction with the active phase. The role of the support in DRM is to provide a high, stable surface area to effectively disperse the active phase and prevent its sintering, and to contribute to the reaction mechanism through activation of CO$_2$ (Papadopoulou et al., 2012b). The presence of Lewis base sites on the support enhances the adsorption of CO$_2$ (Alvarez et al., 2017), which accelerates the production of CO from surface carbon, hence minimizing the coking rate. MgO-Al$_2$O$_3$ was found to be one of the best supports for a reforming catalyst (Zhang et al., 2015, Abd Ghani et al., 2018).

Second, the use of a second active metal in a bimetallic catalyst exploits the synergy between the two active metals (often both transition metals) to improve active phase dispersion and coke resistance. The bimetallic Ni-based catalyst design has been reviewed by Bian et al (Bian et al., 2017). The Ni-Co bimetallic system has been of particular interest due to its superior performance compared to other bimetallic transition metal catalysts (Zhang et al., 2007). The synergetic mechanism between Ni and Co has been linked to their alloying (Phan et al., 2018) and to their mutual stabilization. The works of Takanabe et al (Takanabe et al., 2005) showed that Ni, which is more active for CH$_4$ dissociation, deactivated by coking, while Co, which is more active towards CO$_2$ activation, deactivated by reoxidation. In a bimetallic Ni-Co catalyst, hydrogen spillover from Ni to Co prevents its oxidation, while the high oxygen affinity of Co contributes to C* oxidation and reduces coking. Optimal Ni/Co ratio seems to be Ni-rich (Whang et al., 2017, Bian et al., 2017).

Third, the use of a noble metal promoter in small amounts along with Ni or an active transition metal is seen as an advantageous way to benefit from the superior coking resistance and stability of noble metals while mitigating the issue of elevated cost and scarcity associated with them (Wu et al., 2014, El Hassan et al., 2016). Doping of nickel catalysts with noble metals reduces the reduction temperature and increases the number of active sites. The lowering of reduction temperature has also been explained by the hydrogen spillover mechanism: Hydrogen adsorbs and dissociates on noble metals, and the adsorbed hydrogen atoms diffuse on the support surface to reach non-noble metal species, enhancing their reduction. Ru and Rh are generally regarded as the most potent promoters for DRM catalysts (Abdel Karim Aramouni et al., 2017b).

Our laboratory previously reported a series of trimetallic Ni-Co-Ru catalysts supported on MgO-Al$_2$O$_3$ for the first time (Aramouni et al., 2020). In the first study, the effect of the support preparation method was investigated without changing the composition of the active phase. Two main conclusions were drawn from the work:

1. Support synthesis by the sol-gel method in neutral pH provides a high surface area and pore sizes under 15 nm, which prevented the formation of carbon whiskers by confining the active metal particles while still maintaining a satisfactory catalytic performance.
2. H$_2$-TPR studies revealed the existence of very strong metal-support interactions which caused a significant fraction of reduction to occur at temperatures above 750-800°C. This was attributed to the high calcination temperature employed after impregnation of the supports.
Based on our findings from the first phase of this project, we assess in this work the effect of the Ni/Co ratio on the performance of the catalysts supported on MgO-Al₂O₃ synthesized by sol-gel method in neutral pH. The final calcination step is performed either at 650°C or at 750°C to examine the effect of calcination temperature. A bimetallic Ni-Co catalyst supported on the same MgO-Al₂O₃ support is used as benchmark to study the effect of ruthenium as a promoter.

6.2: Experimental

6.2.1: Materials
Nickel nitrate hexahydrate (>97%), cobalt nitrate hexahydrate (>98%), aluminum tri-sec-butoxide (Al-TSB) (97%), magnesium ethoxide (98%), ruthenium (III) chloride hydrate and sec-butanol were purchased from Sigma-Aldrich. n-Hexane was purchased from Surechem Products.

6.2.2: Synthesis of the sol-gel support
The magnesia-alumina support was prepared via a sol-gel method based on Rezgui et al. (Rezgui and Gates, 1997). Al-TSB and magnesium ethoxide were dissolved in sec-butanol at 80°C so that the molar ratio of Mg to Al was 1:4 and the concentration of Al-TSB was 1M. The sol was hydrolyzed with water in sec-butanol so that the hydrolysis ratio is 2.5. Once the hydrolysis was complete and a gel formed, the gel was transferred to a Teflon-lined autoclave and aged at 80°C for 24 hours. The sample was then filtered, washed with ethanol, then dried first at 70°C for 24 hours, then at 100°C for 4 hours before being calcined in air at 750°C for 2 hours.

6.2.3: Impregnation of the support
Determined amounts of Ni, Co and Ru precursors were dissolved in deionized water (0.5 mL/g support) and stirred at 500 rpm for 30 minutes to form the impregnating salt solution. The volume of water was chosen to be of the same order of magnitude as the pore volume to minimize transport limitations in the impregnation process.

The support is impregnated with nickel and cobalt nitrate along with ruthenium chloride following a two-solvent dry impregnation method described by Lopez et al. (Lopez, 2006) to protect the support: the support pores are first wet using hexane (0.5 mL/g) to allow air to escape without large stresses, then the aqueous salt solution is added to the hexane/support mixture and manual stirring is maintained for 15 minutes. The use of a magnetic stirrer is challenging in this procedure due to the low liquid content and paste-like texture of the sample. Solvent replacement occurs and hexane is rejected from the solids. The supernatant hexane phase is separated before the wet powder is dried at 110°C for 6 hours before calcination at 650°C or 750°C for 2 hours.

The synthesized samples are denoted xNi yCo zRu, with x, y and z denoting the weight percentage of Ni, Co and Ru respectively in the sample.

6.2.4: Catalytic tests
The catalytic tests were carried in a 4mm ID quartz tube inside a tubular furnace at atmospheric pressure. 10 mg of catalyst powder were mixed with quartz sand and placed
inside the quartz tube. The packing was held in place with two quartz wool plugs. The packed reactor was first purged with N₂ gas, then the active phase was reduced in 50% H₂/N₂ flowing at 40 mL/min. The catalyst was heated in the reducing gas flow to 760°C at 15°C/min and saturated for one hour before the hydrogen was cut off. The reduced catalyst was then heated to the desired reaction temperature in N₂ and the flow was switched to an equimolar mixture of methane and CO₂, delivered at the desired flow rate using mass flow controllers (Brooks). Gases leaving the reactor were analyzed using an Agilent 7820 gas chromatograph equipped with a 6-port gas sampling valve, using a Porapak Q porous polymer column and a thermal conductivity detector. Argon (99.999%) was used as a carrier gas to maximize hydrogen sensitivity and the column was kept at a constant temperature of 50°C during the analysis.

Catalytic deactivation tests were carried out at a fixed space time (w/F) of 1.11x10⁻⁵ gcat.h/mL at 800°C, and product samples were analyzed every 20 minutes. The contact time of 1.11x10⁻⁵ gcat.h/mL was selected for the deactivation tests because it is the space time at which the conversions start to reach their equilibrium values.

6.2.5: Catalyst characterization

The BET surface areas, pore volumes and pore size distributions were measured by nitrogen adsorption-desorption at 77K using a Micromeritics Gemini VII instrument. Prior to nitrogen adsorption analysis, the samples were degassed under nitrogen flow at 150°C overnight. SEM micrographs were acquired using a Tescan MIRA3 electron microscope at 20kV using an in-beam secondary electron detector. Thermogravimetric analysis of the spent catalyst samples was performed on a TA Q500 instrument. Samples were heated at 15°C/min until 950°C in air. Carbon formation rates were calculated based on the sharp weight loss observed in the 400-700°C range. X-ray diffraction spectra were acquired using a Bruker D8 Advance instrument.

Temperature programmed reduction (H₂-TPR) tests were performed on a Micromeritics AutoChem II instrument. Prior to the TPR runs, the samples were heated in-situ to 120°C under argon gas flow to remove physisorbed water then cooled down to ambient temperature. The flow was then switched to 4%H₂/Ar and the sample was heated at 5°C/min until 900°C at 30 mL/min.

6.3: Results

6.3.1: Physicochemical characteristics

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area, m²/g</th>
<th>Pore volume, cm³/g</th>
<th>Pore size, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcined at 650°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15Ni 0.25Ru</td>
<td>250</td>
<td>0.57</td>
<td>6.5</td>
</tr>
<tr>
<td>10Ni 5Co 0.25Ru</td>
<td>199.9</td>
<td>0.46</td>
<td>6.7</td>
</tr>
</tbody>
</table>

Table 6-1: N₂ adsorption analysis results
Table 6-1 summarizes the N₂ adsorption analysis results for the catalysts calcined both at 650°C and 750°C and the MgO-Al₂O₃ support. At a calcination temperature of 650°C, an increase in the surface area is observed for the bimetallic Ni-Ru and Co-Ru catalysts when compared to the support. Catalyst samples containing all three metals exhibit a loss in surface area, with the lowest area achieved with the 5Ni 10Co 0.25Ru sample. Pore volumes follow the same trend. Interestingly, average pore sizes show an opposite behavior, with the largest pore size being for the 5Ni 10Co 0.25Ru sample. The Ni-Co benchmark shows the narrowest pore size and a moderately low pore volume, which is attributed to the presence of large particles of active phase crystals in the support pore structure due to a decreased dispersion without the presence of the Ru promoter.

Samples calcined at 750°C show a decrease in surface area compared to those calcined at 650°C, with the exception of the 10Ni 5Co 0.25Ru sample. This is due to an increase in sintering of the active phase at the higher calcination temperature. The 15Co 0.25Ru and 10Ni 5Co 0.25Ru samples calcined at 750°C exhibits a surface area higher than that of the support, and a comparable pore size. This indicates that the active metal phases did not fill the internal pores of the support, but rather concentrate on the surface where they form high surface area structures.
Figure 6-1 shows the SEM images of the fresh catalysts calcined at 650°C. One can observe a relatively uniform coverage of the 15Ni 0.25Ru catalyst surface with round particles 50-100 nm in size. It is hard to visually discern support from active phase on this catalyst due to the uniform coverage and the presence of charging. Trimetallic 10Ni 5Co 0.25Ru and 5Ni 10Co 0.25Ru samples show an agglomeration of active metal clusters on the surface of the support that is easily distinguishable. Active metal clusters of size about 1μm are visible, in addition to particles as small as 10-20 nm. 15Co 0.25Ru also shows large clusters of relatively large cobalt particles (70-150 nm) that agglomerate together rather than spread uniformly on the support. This shows that the affinity of nickel towards the MgO-Al₂O₃ support is higher than that of cobalt. Furthermore, the synergetic effect on dispersion is apparent in the two trimetallic samples that have better dispersed, smaller particles. Comparing the SEM images with N₂ adsorption analysis results (Table 6-1), the loss in surface area and pore volume compared to the support, coupled with only a small loss in pore size indicates that the active phase is mostly located on the surface, blocking certain pores but not filling them extensively. This observation is in contrast with previous conclusions in Phase I.
(Chapter 5) and may be attributed to the smaller pore sizes obtained with this support batch.

Figure 6-2: SEM micrographs of the fresh catalysts calcined at 750°C

Observation of the samples calcined at 750°C (Figure 6-2) gives similar conclusions concerning the different affinities of Ni and Co to the support and towards the improvement of dispersion from synergic effects. The surface of the 15Co 0.25Ru sample shows smaller agglomerates when calcined at higher temperatures, which shows a strengthening of the metal-support interaction, but still with little filling of the pores as shown by physisorption results. The 15Ni 0.25Ru sample shows a more elevated degree of sintering when calcined at higher temperature, which is shown by the presence of agglomerates of spherical Ni particles easily distinguished from the flaky support structure. This is expected since the Tamman temperature of Ni is lower than that of Co. The loss in surface area and porosity in the 15Ni 0.25Ru sample when calcined at 750°C is attributed to pore blockage by the Ni phase which binds more than the Co phase to the support, hence the different effect of temperature on the 15Co 0.25Ru and 15Ni 0.25Ru samples. Increased sintering is also observed with the two trimetallic samples 10Ni 5Co 0.25Ru and 5Ni 10Co 0.25Ru, as exhibited by the presence of some particles up to 150-200nm in size.
Unpromoted Ni-Co catalysts (Figure 6-3) show a lower dispersion than their counterparts promoted with Ru, with particles of sizes ranging from 50 nm and up to 400 nm are visible on the sample calcined at 650°C, and from 20 to 700 nm on the sample calcined at 750°C. It is clear that the presence of Ru increases the dispersion of Ni and Co phases on the support.
6.3.2: H₂-TPR analysis

Figure 6-4: H₂-TPR spectra for the catalysts reduced at 750°C

Figure 6-4 shows the H₂-TPR spectra for the bi- and trimetallic catalysts calcined at 750°C. A peak at 170°C is apparent on all samples which is attributed to Ru reduction, but it is much sharper on samples with lower to no Co content, which indicates a different interaction between Ni and Co with Ru. All samples containing nickel exhibit a linear ramp in the 200-350°C which is attributed to the reduction of surface Ni²⁺ in interaction with MgO.

The 15Ni0.25Ru sample has a broad shoulder in the 400-600°C range, a large peak at 700°C and a shoulder towards 800°C, which are attributed to the reduction of sublayer Ni²⁺, NiO and NiO in strong interaction with the support respectively. The 15Co 0.25Ru sample shows instead a sharp peak at 300-350°C and a broader one at 500-600°C which are attributed to the reduction of free cobalt oxide and cobalt oxide phase in strong interaction with the support respectively.

Trimetallic Ni-Co-Ru samples exhibit a combination of the reduction peaks identified for both the Ni-Ru and Co-Ru samples. The NiO reduction peak at 700°C is not noticeable in the 5Ni10Co0.25Ru, yet the strongly bound NiO is visible as a peak at around 800°C, although at a lower temperature compared to its position in the Ni-Ru sample. This is evidence for reduced NiO-support interaction and synergetic interaction with the cobalt oxide phase. The free cobalt oxide reduction peak increases in temperature as the nickel content increases, ranging from approximately 320°C for the 15Co0.25Ru sample to 350°C for the 10Ni5Co0.25Ru sample, while the broader cobalt peak at 500-600°C
remains relatively unchanged, despite the peak skewing towards higher temperatures in the 5Ni 10Co 0.25Ru sample. It can then be concluded that the free cobalt phase interacts with the nickel phase, while the cobalt phase in strong interaction with the support remains less affected.

All samples calcined at 750°C do not complete their reduction at the tested temperature of 760°C, but unlike the catalysts tested in Phase 1 of this work (Aramouni et al., 2020), the majority of the hydrogen uptake happens before this temperature. Only a small peak of highly bound NiO appears 800°C.

Figure 6-5: H2-TPR spectra for the catalysts reduced at 650°C

H2-TPR spectra for the samples calcined at 650°C are shown in Figure 6-5. Samples show TPR patterns skewed towards the higher temperatures, with the strongly bound NiO peak above 800°C appearing much sharper than in the samples calcined at 750°C. However, peak locations are shifted to lower temperatures, especially for bimetallic Ni-Ru and Co-Ru samples. The highest peak on the 15Ni 0.25Ru sample is shifted from 826°C when calcined at 750°C to 820°C when calcined at 650°C. On 15Co 0.25Ru, the broad peak at 570°C is lowered to 564°C when the calcination temperature is lowered, while the sharp peak at 322°C does not shift much, but is flattened and broadened at lower calcination temperature. Peak shifting is less significant in trimetallic catalysts. The effect of lower calcination temperature is therefore to shift the reduction peaks to lower temperature, which is attributed to decreased metal-support interaction. Despite the lower reduction activity under 400°C in Figure 6-5, calcination at 650°C is associated with an increase in
H₂ uptake in the 400-750°C range, with broader, less defined peaks that are attributed to a better dispersion which minimizes the segregation of phases of bulk metal oxide, spinel and free surface species.

Figure 6-6: H₂-TPR spectra for the bimetallic 7.5Ni 7.5Co samples calcined at 650°C and 750°C and the 7.5Ni 7.5Co 0.25Ru sample on the same support (from Phase 1 data (Aramouni et al., 2020)).

Figure 6-6 compares the TPR spectra of the bimetallic 7.5Ni 7.5Co catalysts calcined at 650°C and 750°C to the TPR spectrum of the 7.5Ni 7.5Co 0.25Ru catalyst calcined at 750°C tested in the previous work (Aramouni et al., 2020). The unpromoted sample calcined at 650°C clearly shows a higher H₂ uptake in the moderate-high temperature range (400-700°C) than its counterpart calcined at 750°C, although the free cobalt oxide reduction peak around 300-400°C (split into a shoulder at 300°C and a main peak at 390°C in the blue curve on Figure 6-6) shifts to a large shoulder at 290°C and a smaller peak at 440°C which overlaps with the broad 600-700°C peak. The strongly bound NiO peak is reduced from 850°C to 825°C when the calcination temperature is lowered.

The presence of Ru also contributes to improving the reducibility of the catalyst, which is seen in Figure 6-6 as a reduction in the temperature of the strongly bound NiO peak from 850°C to 834°C when comparing the two samples reduced at 750°C, in addition to an increased and sharpened sublayer Ni²⁺ reduction peak at 390°C. H₂-TPR analysis indicates that a lower reduction temperature and the presence of Ru promoter both improve the reducibility of the Ni-Co catalysts.
6.3.3: X-ray diffraction

Figure 6-7: XRD spectra of the trimetallic catalysts calcined at 750°C after reduction

Figure 6-7 shows the XRD spectra for the trimetallic catalysts calcined at 750°C, and the XRD spectra of the samples calcined at 650°C are shown in Figure 6-8. Samples calcined at 750°C show five major peaks at angles of 31.5, 37, 45, 59.5 and 65.5° that are attributed to the MgAl$_2$O$_4$ spinel in the support. It is difficult to discern the different oxide phases as NiAl$_2$O$_4$, NiO and MgCo$_2$O$_4$ give peaks the same angles as the MgAl$_2$O$_4$ support. Nickel-rich samples (15Ni 0.25Ru and 10Ni 5Co 0.25Ru) show a split peak at 43-45°C. The small sub-peak at 43° is attributed to MgNiO$_2$, which is evidence of strong metal-support interaction and partial fusing, which is beneficial in minimizing CO disproportionation (Hu and Ruckenstein, 2004). The cobalt-rich samples do not show this peak splitting. Instead, two close peaks are observed for the 5Ni 10Co 0.25Ru sample at 42.8° and 45°, which are attributed to Co$_3$O$_4$ and the support spinel signal respectively. The major peak at 45° cannot be assigned to one compound as most possible phases present give a peak at this angle. Weak signals corresponding to metallic Ni, Co and Ru are observed on the samples, in addition to NiO and Co$_3$O$_4$, which highlights an incomplete reduction or a reoxidation of the catalyst from exposure to ambient air.

The (220) peak for Ni at 76.5° and for Co at 76° shifts to a value of approximately 76.2° in both trimetallic samples, which corresponds to the formation of a Co-Ni alloy as expected. Other peaks attributed to the Ni-Co alloy overlap with the Ni peaks at 44.5 and 51.8° and are not distinguishable. Low-intensity peaks corresponding to Co$_2$RuO$_4$ are
observed on the trimetallic samples as well. The presence of a NiCoO$_3$ phase in the trimetallic samples is speculated, but due to the high number of low-intensity peaks exhibited by this compound, it is not possible to differentiate between background noise and NiCoO$_3$ signal. Nevertheless, the samples show evidence of alloying between active metals, and the partial fusing of the active phase with the support due to the elevated calcination temperature, in line with the observations of Fan et al. (Fan et al., 2015). No alloying between Ni and Ru is observed, as they are immiscible and have a high segregation energy (Zhou et al., 2018).

Figure 6-8: XRD spectra of the trimetallic catalysts calcined at 650°C after reduction

The most observable difference between a calcination temperature of 750°C (Figure 6-7) and 650°C (Figure 6-8) is the disappearance of the large sub-peak at 43°, which indicates a decrease in the formation of metal-support compounds such as MgNiO$_2$. Furthermore, peaks corresponding to NiAl$_2$O$_4$ and Co$_3$O$_4$ are less apparent when samples are calcined at lower temperature. Nevertheless, the formation of a mixed CoRuO$_4$ oxide and Ni-Co alloy is observed for all trimetallic samples. Due to the low signal intensity and the overlap between multiple signals, it is difficult to accurately quantify the metal particle size from Scherrer’s equation.

Figure 6-9 shows the XRD spectra for the 7.5Ni 7.5Co catalysts calcined at 650°C and 750°C. Metallic Ni and Co peaks are observed, and the peak splitting at 76° indicates the
presence of the Ni-Co alloy as well. Peaks corresponding the NiAl₂O₄ and MgCo₂O₄ have a lower intensity in the sample calcined at 650°C, which indicates the beneficial effect of lowering the calcination temperature in avoiding the formation of spinel compounds that are more difficult to reduce, in line with conclusions obtained from H₂-TPR tests.

6.3.4: Catalytic tests

Deactivation tests are performed over 24 hours at 800°C and w/F=1.11x10⁻⁵ gcat.h/mL for the catalysts calcined at 650°C (Figure 6-10) and 750°C (Figure 6-11). Most catalysts with the exception of 15Co 0.25Ru show a very stable performance (except for a brief stabilization period in the first hour on stream) with minimal loss in activity. The highest activity in the batch calcined at 650°C is exhibited by the 15Ni 0.25Ru sample. The order of activities follows the nickel loading, with the lowest activity attributed to the 15Co 0.25Ru sample, which deactivates within 7 hours on stream and has a minimal residual activity. This deactivation pattern is attributed to the poor oxidation stability of cobalt (Takanabe et al., 2005, Park et al., 2017). The benchmark Ni-Co catalyst is the worst performing catalyst out of those that contain Ni. Following the correlation between the Ni loading and the activity, the CH₄ conversion of the benchmark is expected to be around 92%, between the average conversion of 93% for 10Ni 5Co 0.25Ru and 90% for 5Ni 10Co 0.25Ru. Yet, the activity achieved by the benchmark is closely comparable to that of 5Ni 10Co 0.25Ru, averaging at 90% for the CH₄ conversion, but with a slightly higher deactiation rate in terms of CO₂ conversion. The promoting effect of Ru is therefore highlighted here.
CO₂ conversion is generally slightly higher than CH₄ conversion due to the reverse water-gas shift reaction consuming more CO₂, yet this is only observed for the 7.5Ni 7.5Co benchmark and the 15Co 0.25Ru sample from the batch calcined at 650°C. This means that the catalyst either does not activate the reverse water-gas shift reaction or that it catalyzes carbon formation through the methane cracking reaction, which is shown in Section 6.3.5.

Different results are obtained when the catalysts are calcined at 750°C. As shown in Figure 6-11, 15Co 0.25Ru apparently gives the highest activity in terms of CH₄ conversion and a satisfactory CO₂ conversion. However, two observations hint at a severe promotion of the methane cracking reaction on this catalyst which artificially increases the apparent activity: the CH₄ conversion is much higher than that of CO₂. In addition, a 10% loss in CH₄ conversion is exhibited during the first 2-3 hours on stream, which is gradually recovered over the next 3-5 hours on stream. This peculiar behavior has been observed with the 7.5Ni/γ-Al₂O₃ benchmark used during Phase I of the study (Aramouni et al., 2020), and was attributed to the initiation of the steady state carbon whisker growth mechanism through methane cracking. The initial drop in conversion is caused by the deactivation of the catalyst through coking, while the recovery in apparent conversion is due to the extra methane consumed by whisker growth. The 15Co 0.25Ru catalyst does not appear to deactivate quickly from oxidation when calcined at 750°C.

At both calcination temperatures, an increase in the Ni loading is associated with an increase in catalyst activity, with the order of activities being 15Ni 0.25Ru > 10Ni 5Co 0.25Ru > 5Ni 10Co 0.25Ru. However, the benchmark 7.5Ni 7.5Co calcined at 750°C gives higher CH₄ and CO₂ conversions than 15Ni 0.25Ru, but with CH₄ conversion being higher due to coking.

The calcination temperature of 750°C causes an increase in catalyst activity for all catalysts except 15Ni 0.25Ru and 5Ni 10Co 0.25Ru, and there does not appear to be a clear trend in the effect of calcination temperature and Ni/Co ratio on activity. However, the higher calcination temperature positively affects catalyst stability, with a significantly reduced deactivation rate in all samples, and especially 15Co 0.25Ru. This is attributed
to a strengthening in metal-support interaction at higher temperature which stabilizes the active phase against sintering.

Figure 6-11: CH₄ and CO₂ conversions for the catalysts calcined at 750°C

To understand the role of ruthenium as a promoter in this system, the catalytic performance of the benchmark 7.5Ni 7.5Co catalyst calcined at 750°C is compared to that of 7.5Ni 7.5Co 0.25Ru calcined at 750°C tested during Phase I and is shown in Figure 6-12. It appears that Ru addition decreases the activity slightly, but increases the stability. Average CH₄ conversion loss is around 1.2%/day without Ru, but is decreased to 0.7%/day with Ru. Similarly, average CO₂ conversion loss is 0.3%/day without Ru and 0.2%/day with Ru. The CO₂ conversions are not very different for both catalysts, but the unpromoted sample exhibits a much higher CH₄ conversion, which exceeds CO₂ conversion. In comparison, very little difference between CH₄ and CO₂ conversions are observed for the promoted sample, which suggests that the methane cracking phenomenon is less severe with Ru. Electron microscope imaging (Figures 13-14) and thermogravimetric analysis (Table 6-3) confirm this observation.
Table 6-2 shows the average H₂/CO ratios achieved with the different catalysts during the catalytic tests. With the exception of the 15Co 0.25Ru catalysts, a ratio slightly below unity is obtained due to the occurrence of the reverse water-gas shift reaction that consumes H₂. An increase in the nickel content increases the ratio for both calcination temperatures. All catalysts promoted with Ru exhibit a higher H₂/CO ratio when calcined at 650°C, while 7.5Ni 7.5Co has the highest ratio when calcined at 750°C. The active 15Co 0.25Ru sample calcined at 750°C showed a very low ratio, in agreement with Jabbour et al. (Jabbour et al., 2014), which indicates its poor selectivity towards dry reforming activity. The poorly stable 15Co 0.25Ru catalyst calcined at lower temperature showed a H₂/CO ratio of 1.34 which is higher than unity during the first 7 hours on stream (during which it was rapidly deactivating), before sharply decreasing to a terminal ratio of 0.67 after deactivation. This observation provides insight into the deactivation mechanism and is discussed in Section 6.4:

Table 6-2: H₂/CO ratios at 800°C and w/F=1.11×10⁻⁵ gcat.h/mL.

<table>
<thead>
<tr>
<th>*: from Phase 1 data ([Aramouni et al., 2020])</th>
<th>650°C</th>
<th>750°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>H₂/CO ratio</td>
<td></td>
</tr>
<tr>
<td>15Ni 0.25Ru</td>
<td>0.953</td>
<td>0.946</td>
</tr>
<tr>
<td>10Ni 5Co 0.25Ru</td>
<td>0.943</td>
<td>0.943</td>
</tr>
<tr>
<td>5Ni 10Co 0.25Ru</td>
<td>0.913</td>
<td>0.910</td>
</tr>
<tr>
<td>15Co 0.25Ru</td>
<td>1.34</td>
<td>0.67</td>
</tr>
</tbody>
</table>
6.3.5: Carbon formation

Table 6-3 summarizes the carbon formation rates calculated from TGA analysis of the spent catalysts after the deactivation tests. The highest rate of carbon formation is exhibited by the 15Co 0.25Ru sample calcined at 750°C, which confirms the methane cracking phenomenon observed in Figure 6-11. Yet, this catalyst does not deactivate like the 15Co 0.25Ru catalyst calcined at 650°C. This is attributed to the stabilization of the Co phase by the formation of solid solutions with the support at higher calcination temperature, in accordance with Bian et al (Bian et al., 2017) who attributed the good performance of Co when supported on MgO and Al₂O₃ to the probable formation of solid solutions. Furthermore, Zhang et al (Zhang et al., 2014) noticed a significant effect of the calcination temperature on the performance of Co catalysts supported on activated carbon, with a decrease in activity as the calcination temperature increases. This was attributed to more severe sintering and loss of surface area at higher temperatures. The opposite trend observed in this work, which highlights the important role of a basic support with good oxygen mobility.

For all catalysts with the exception of 5Ni 10Co 0.25Ru, higher carbon formation rates are obtained with a higher calcination temperature. However, for the 5Ni 10Co 0.25Ru sample, carbon formation is almost eliminated at 750°C. It is probable that the strong metal-support interaction which is shown by the high temperature reduction peak in Figure 6-4 for this catalyst stabilizes the metallic particles and prevents their agglomeration, thus avoiding coking.

Table 6-3: carbon formation rates after reaction at 800°C and w/F=1.11×10⁻⁵gcat.h/mL for 24 hours

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Carbon formation rate, mg/gcat.h</th>
</tr>
</thead>
<tbody>
<tr>
<td>15Ni 0.25Ru</td>
<td>1.0</td>
</tr>
<tr>
<td>10Ni 5Co 0.25Ru</td>
<td>18.3</td>
</tr>
<tr>
<td>5Ni 10Co 0.25Ru</td>
<td>25.1</td>
</tr>
<tr>
<td>15Co 0.25Ru</td>
<td>0.86*</td>
</tr>
<tr>
<td>7.5Ni 7.5Co</td>
<td>22.9</td>
</tr>
<tr>
<td>7.5Ni 7.5Co 0.25Ru**</td>
<td>-</td>
</tr>
</tbody>
</table>

Coking rates obtained with catalysts that contain Ni and Co are higher than those for bimetallic Ni-Ru catalysts. When calcined at 750°C, the Co-Ru sample has the highest coking rate. The coking trend Co>Ni-Co>Ni is in agreement with the findings of Fan et al. (Fan et al., 2010), despite the addition of ruthenium. The beneficial effect of Ru is however manifested by a reduction of the carbon formation rate by more than 50% in the 7.5Ni 7.5Co benchmark, in addition to an improved stability. This signifies that the
presence of the Ru promoter does not seem to stabilize Ni or Co preferentially against coking, but rather promotes both metals.

Figure 6-13, Figure 6-14 and Figure 6-15 show the SEM micrographs of the spent catalysts calcined at 650°C, 750°C and the spent benchmark Ni-Co catalysts respectively, after reaction at 800°C for 24 hours at w/F=1.11x10⁻⁵ gcat.h/mL.

When calcined at 650°C, 15Co 0.25Ru shows severe sintering which is visible as large clusters on its surface with sizes of 500 nm to 1 μm. The increase in particle size is also affected by the large uptake of oxygen due to reoxidation. The 5Ni 10Co 0.25Ru sample shows the most severe coking with complete coverage of the surface with long carbon filaments that appear to have detached metal particles from the support (visible as bright white dots on the whisker coat). A much better performance is exhibited by the samples with high Ni content, with the 10Ni 5Co 0.25Ru sample showing a very small amount of
short, thin filaments sparsely located on the catalyst surface. Furthermore, many particles with sizes smaller than 50 nm are visible on the surface, evidence of good dispersion and moderate sintering compared to 15Co 0.25Ru. Similar observations are made on 15Ni 0.25Ru, with somewhat larger metal particles observed. Consequently, short carbon whiskers are also visible, but with larger diameters and less uniformity.

Figure 6-14: SEM micrographs of the spent catalysts calcined at 750°C after reaction at 800°C for 24 hours

SEM imaging of the spent catalysts with calcination temperatures of 750°C shows a higher number of longer whiskers on the 15Ni 0.25Ru and 10Ni 5Co 0.25Ru samples. The observation of a number of particles around 50-100 nm in size suggests that sintering is slightly higher in this sample. No whiskers are present on 5Ni 10Co 0.25Ru, and surface particles of sizes around 50 nm are also observed, which reveals again a good resistance to sintering, as very few particles larger than this size are seen. 15Co 0.25Ru is completely coated with a blanket of whiskers, which confirms the activity trend observed in Figure 6-11. The intensity of whisker growth observed in microscope imaging is in accordance with carbon formation rates calculated in Table 6-3.
The effect of Ru promotion in minimizing whisker growth is apparent in Figure 6-15, where the 7.5Ni 7.5Co 0.25Ru catalyst tested in Phase I did not show any whiskers on its surface, while unpromoted 7.5Ni 7.5Co samples did so. The sample calcined at 650°C shows a denser web of filaments enveloping the catalyst microparticle, as compared with the sample calcined at 750°C where a looser network containing a smaller amount of longer filaments is observed.

6.4: Discussion

6.4.1: Effect of calcination temperature

The results obtained in this study show that an increase in calcination temperature is accompanied with an increase in carbon formation rate except for 5Ni 10Co 0.25Ru. This can be attributed to the lower dispersion and higher particle size achieved at higher calcination temperatures due to an increase in sintering. When using the impregnation method, the formation of metal crystallites during calcination is uncontrolled, and it mostly occurs during the initial phase of heating. This generally limits the achievable dispersion, despite the attractive practicality of this method. Subsequent soaking at the calcination temperature serves to strengthen the interaction between the newly formed crystallites from decomposed precursors and the support (2009). The calcination process is therefore a balance between catalyst sintering and stabilization by strengthening the metal support interaction. This is most clearly observed with the 15Co 0.25Ru catalyst, whose stability drastically increases at a higher calcination temperature. The theoretical works of Chen at al. (Chen et al., 2020) provide a strong foundation to interpret this trend: their work concluded that smaller Co particles deactivate by oxidation, while larger Co particles—with larger, dominant (111) facets that promote C*-C* coupling—deactivate by carbon formation. In comparison, this work only observed carbon formation on the Co-Ru sample that is calcined at high temperature. The increased sintering is therefore responsible for the switch in the dominant Co deactivation mechanism when increasing the calcination temperature. The high H2/CO observed for the deactivating catalyst calcined at 650°C is attributed to the low CO production due to O* consumption from oxidation. The remaining surface C* explain the carbon formation on this catalyst.
Increasing the treatment temperature has a conflicting effect on activity, which is in mild disagreement with Al-Fatesh et al. (Al-Fatesh et al., 2019) who observed that an increase in calcination temperature on Ni-Co catalysts increased activity. The disagreement is explained by the different affinities of Ni and Co to the support: Nickel was shown to have a higher affinity than cobalt towards MgO-Al2O3, while Co was observed to have a better affinity towards the Al2O3-ZrO2 support in their work.

Temperature programmed reduction tests have shown a decrease in reducibility as the calcination increases, in agreement with Chang et al. (Chang et al., 2004), but this effect was most prominent in bimetallic Ni-Ru and Co-Ru samples. Trimetallic Ni-Co-Ru catalysts did not show noticeable TPR peak shifts, which is attributed to the synergetic effect of Ni-Co through the hydrogen spillover mechanism that helps enhance Co reduction despite the strengthened metal-support interaction at high calcination temperature.

6.4.2: The role of Ru

Good activity observed on Ru-containing catalysts despite their carbon content and sintering agrees with Horvath et al. (Horváth et al., 2011), which suggests that carbon deposits may have a role in CO production. The lower H2/CO obtained in 7.5Ni 7.5Co 0.25Ru compared to its unpromoted counterpart, in parallel with a lower carbon content in the promoted sample, suggests that Ru acts to promote coke gasification into CO. This observation is in perfect agreement with the literature which attributed this to the elevated oxygen affinity and high O* coverage of Ru (Zhou et al., 2018, Jones et al., 2008).

The poor miscibility between Ni and Ru (less than 3 mol%) and high segregation energy is attributed to the improvement of active phase dispersion. The presence of Ru also seems to weaken the interaction between NiO and the support, which improves the reducibility of strongly bound NiO. Trimetallic Ni-Co-Ru samples synthesized in this work have a Ru/Ni molar ratio that is higher than 3% which dictates the presence of separate Ni-rich and Ru-rich phases. 15Ni 0.25Ru has Ru/Ni molar ratio of 2.9%, which signifies that Ni and Ru may exist as a homogeneous phase on the support. SEM imaging within the achievable resolution does not provide a clear change in morphology that would suggest a different segregation pattern occurs in 15Ni 0.25Ru.

San Jose-Alonso et al. (San José-Alonso et al., 2013) noted that Co catalysts with low loading (1% wt) deactivated spontaneously by oxidation while those with higher loading (9% wt) deactivated by coking, and the Co particle size determines the deactivation mechanism. The 15Co 0.25Ru catalyst tested in this work would therefore be expected to deactivate by coking due to its high loading, but the apparent oxidation of the sample calcined at 650°C proves that the presence of Ru increases the dispersion of the Co phase despite the high loading. Ru therefore plays a catalytic role and a structural role in the Ni-Co-Ru system, and is therefore best described as a bifunctional promoter (van Santen, 1991).

6.4.3: Ni/Co ratio

A higher Ni/Co ratio in the catalyst gives a higher activity and a higher H2/CO ratio, which indicates that the reverse water-gas shift reaction is less activated on Ni-rich
catalysts. The hypothesis that enhanced H₂ production from methane cracking on Ni-rich samples is causing the increased H₂/CO is not probable, as shown by the low rates of carbon formation obtained with 15Ni 0.25Ru. The lower H₂/CO ratio observed when the Co content is increased can also be attributed to the consumption of H* by the hydrogen spillover mechanism from Ni to Co sites that stabilizes Co against oxidation.

At a calcination temperature of 650°C, the increased presence of cobalt increases the carbon formation rate, which shows that Co plays the role of providing supplementary metal surface for CH₄ dissociation to form coke.

The presence of Co and Ru, both having high oxygen affinity, with Ni on the support surface suggests that the kinetically relevant CH₄ activation step proceeds differently than on Ni catalysts. The typical CH₄ activation step on a Ni surface is: CH₄ + * + * → CH₃* + H*, while that on Co and Ni-Co catalysts is changed to CH₄ + * + O* → CH₃* +OH* due to the high O* coverage (Tu et al., 2017). While the distribution of Ni, Co and Ru on the surface is not clear, the high oxygen affinity of Ru is expected to provide further O* to drive the CH₄ activation step through the O*-mediated mechanism, in addition to promoting C* gasification.

The optimal Ni/Co loading is found to be 10Ni 5Co, as the 10Ni 5Co 0.25Ru sample calcined at 750°C provides a good activity and very high stability in addition to minimal coking. Several works in the literature have also reported optimal Ni-Co ratios with high Ni content (Whang et al., 2017, Bian et al., 2017). Nevertheless, this choice of optimum constitutes a small activity tradeoff against a good stability and coke resistance, which has been highlighted in our previous works (Abdel Karim Aramouni et al., 2018, Aramouni et al., 2020).

6.5: Conclusion
This work has shed some light on the influence of the Ni/Co ratio and that of Ru on the performance of the trimetallic catalysts. Optimal performance was obtained at higher Ni/Co ratio, as the activity of the catalyst was associated with the increased presence of Ni. The presence of a small amount of Co contributed to the elimination of coke and whisker growth due to the high oxygen affinity of Co. Promotion with Ru improved the stability and coking resistance of Ni-Co catalysts, with a small compromise on activity when calcined at high temperature. While the speciation of Ni, Co and Ru and the reaction mechanism on the surface are not well understood yet, it is safe to say that the presence of Co and Ru increases O* coverage, and therefore the kinetically important CH₄ activation step likely proceeds through an O*-mediated mechanism. Ru plays the role of a structural promoter as its high segregation energy with Ni increases dispersion, but also plays a role in the elementary CH₄ activation step and carbon gasification by enhancing O* adsorption. High calcination temperature was shown to increase sintering and strengthen the metal-support interaction, but its effect was only significant in the Co-Ru catalyst that deactivated by different mechanisms depending on the calcination temperature. Further work should investigate the phase distribution of Ni, Co and Ru to better understand the role of hydrogen spillover and O* coverage on the reaction mechanism. The low Ni-Ru miscibility can be exploited and tuned further to maximize
dispersion. Furthermore, the effect of total metal loading, which impacts the performance of Co in the catalyst, can be further explored.

6.6: Acknowledgements
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6.7: References
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CHEN, S., ZAFFRAN, J. & YANG, B. 2020. Dry reforming of methane over the cobalt catalyst: Theoretical insights into the reaction kinetics and mechanism for catalyst deactivation. *Applied Catalysis B: Environmental*, 270.


Chapter 7: Conclusion and recommendations

This work has approached the problem of carbon formation in the catalytic dry reformer from both a theoretical and experimental perspective, in order to provide a better understanding of how whisker carbon forms on the catalyst and how to avoid it, and in parallel, develop catalysts that can better tolerate the harsh operating conditions without catalyzing whisker growth extensively.

The development of corrected thermodynamic studies has shown that coking is a function of temperature, pressure and catalyst dispersion, and Chapter 2 provides a theoretical tool that can accurately predict coking tendencies with a given catalyst state. Combination of this improved understanding of the thermodynamics of carbon formation with sintering kinetics allows for the time-dependent optimization of the operation of a dry reformer to correct for the dynamic carbon limits that vary as the catalyst ages. The use of artificial neural network (ANN) models provides a smooth and differentiable representation of the effect of temperature, pressure and dispersion on the thermodynamic equilibrium data. Such a model is advantageous for reactor optimization studies because it is computationally cheap and suitable for use in a gradient-based optimization algorithm. The work clearly shows that temperature must be kept constant at its upper bound while pressure must be increased gradually during time on stream to avoid coking.

Experimentally, two major campaigns were conducted:

The investigation of supported Mo and Ni-Mo nitrides as catalysts for dry reforming show that these catalysts tend to deactivate at atmospheric pressure, and transition into an oxide/carbide phase that retains a terminal activity. Dispersion of the nitride phase on a basic metal oxide support improves the surface area of the active phase and reduces coke formation by enhancing CO$_2$ adsorption. Coking tendencies are greatly reduced with Ni-Mo nitride compared to conventional Ni catalysts, and therefore this family of catalysts may find industrial success in conventional reformers where the operating pressure is generally above atmospheric pressure.

Trimetallic Ni-Co-Ru catalysts supported on MgO-Al$_2$O$_3$ gave remarkable activity and stability over long times on stream. The presence of basic MgO in the support was shown to improve carbon gasification and reduce coking rates, and the narrow pores of the support plays a role in confining the well-dispersed active metal particles to reduce sintering, thus minimizing whisker growth. A high activity was observed with high Ni/Co ratios, and the Ni-Ru and Ni-Co-Ru catalysts had a much higher stability than the Co-Ru sample. The calcination temperature affected the deactivation mechanism of the Co-Ru sample, with oxidation deactivating the catalyst at lower calcination temperature, and coking causing the deactivation at higher calcination temperatures. The promoting effect of Ru was clearly demonstrated, with the coking rate approximately halved with the
addition of Ru, along with an improvement in stability at the expense of slightly reduced catalytic activity.

Experimental results strongly confirm the observed tradeoff highlighted in Chapter 1 between activity, stability and reducibility (ease of activation) in both experimental campaigns.

Future work should assess the performance of supported bimetallic Ni-Mo nitride catalysts at higher operating pressures where they are more stable and optimize the Ni/Mo ratio. A thorough temperature programmed adsorption/desorption study of CH$_4$ and CO$_2$ on the supported bimetallic nitrides is not available in the literature so far, and would yield valuable information that may improve the potential of this family of compounds to function as dry reforming catalysts. Based on the successful Ni-Co-Ru campaign of experiments (Chapters 5 and 6), it is recommended to study the speciation of the Ni-Co-Ru system on the surface of the basic MgO-Al$_2$O$_3$ support by theoretical tools such as density functional theory (DFT). The high segregation energy between Ni and Ru, combined with the alloying tendency and synergy between Ni and Co, offers a potential to tune the Ru/Ni ratio so that the segregation tendency favors an increased dispersion of the active phase.

The methane cracking process is closely related to the dry reforming process, and it produces high-purity hydrogen and high-quality coke. Obviously, nickel catalysts are an attractive choice for this process, especially if they are sintered and are prone to coking. The opportunity to recycle spent dry reforming catalysts (that are sintered and promote coking) into the methane cracking process should also be investigated.

From an industrial perspective, the efficient integration of the dry reformer into larger process trains is still under research. Optimal heat integration and supply chain integration, economic and environmental feasibility are still under development, and there is a strong need of process design studies that provide an understanding of economies of scale, optimal process layout and optimal supply-chain scenarios for the commercialization of dry reforming as a competitive syngas production technique.
Appendix 1: Heterogeneous non-isothermal, multi-reaction and multi-scale fixed-bed dry reformer model

This MATLAB model for the dry reforming fixed bed reactor couples a catalyst pore diffusion-reaction model and an axial convection model to account for reaction inside catalyst pellets and transport in the packed bed. This model represents the phenomena at the pore, pellet and reactor scale and constitutes a high-fidelity multiscale model. The use of this model in a scale-up and reactor design study was not possible in the thesis timeframe due to severe work disruptions brought by the COVID-19 pandemic and other dramatic events happening in Lebanon during 2020. Nevertheless, the code is included in this thesis as supplementary information. The algorithm behind the code is summarized in Figure 0-1.

![Algorithm for the diffusion-limited fixed-bed dry reformer model](image)

Subscript s denotes a physical parameter in the solid (pellet) scale. Physical parameters without a subscript denote fluid phase parameters.

The catalytic reactor model is described in the works of Rawlings and Ekerdt (Rawlings and Ekerdt, 2002). In brief, an internal pellet diffusion-reaction model is coupled with a fluid phase balance model where the fluid exchanges heat and mass with the catalyst pore.
system through the pellet surface. Heat balances are solved simultaneously in the pellet and fluid phase models. The model assumes plug-flow behavior in the fluid phase, catalyst particle much smaller than the diameter of the reactor, and that axial dispersion is negligible. The boundary value problem is solved using the bvp5c solver on MATLAB.

Subscript \( i \) denotes species in the system, and subscript \( j \) denotes reactions. The superscript \( \sim \) denotes a property in the catalyst domain.

Nomenclature:

- \( R_i \): rate of formation/consumption of species \( i \) per reactor volume
- \( \tilde{r}_{ij} \): rate of formation of species \( i \) in reaction \( j \) per volume of catalyst
- \( D_i \): effective diffusivity of species \( i \).
- \( C_i \): concentration of species \( i \).
- \( K \): thermal conductivity
- \( T \): temperature
- \( \Delta H_{rj} \): heat of reaction \( j \)
- \( K_m, K_T \): Mass and thermal convection coefficients.
- \( V \): reactor volume
- \( N_i \): molar flow of species \( i \) in fluid phase.
- \( Q \): volumetric flow rate of fluid.
- \( \rho \): density
- \( U^0 \): Overall heat transfer coefficient
- \( q_{\text{ext}} \): external heat flux
- \( P \): Pressure
- \( \varepsilon_b \): catalyst bed void fraction
- \( A_c \): reactor cross-sectional area
- \( S_p/V_p \): catalyst pellet surface to volume ratio

Intraparticle balances:

\[
D_i \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\tilde{C}_i}{dr} \right) = -\sum_j \tilde{r}_{ij} = -\tilde{R}_i
\]
\[ k \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d \tilde{T}}{dr} \right) = \sum_j \Delta H_{Rj} \tilde{r}_j \]

Boundary conditions:

\[ \frac{d \tilde{c}_i}{dr} = \frac{d \tilde{T}}{dr} = 0 \text{ at } r = 0 \]

\[ D_i \frac{d \tilde{c}_i}{dr} = k_{mi} (c_i - d \tilde{c}_i) \text{ at } r = R \]

\[ k \frac{d \tilde{T}}{dr} = k_T (T - \tilde{T}) \text{ at } r = R \]

Fluid phase balances:

\[ \frac{d N_i}{d V} = R_j \]

\[ Q \rho c_p \frac{dT}{dV} = -\sum_i \Delta H_{Rj} \tilde{r}_j + \frac{2}{R} u^0 (T_{\text{cat}} - T) + 2\pi R q^*_{\text{ext}} \]

\[ \frac{dP}{dV} = - (1 - \epsilon_b) \frac{Q}{D_p \epsilon_b} \left[ 150 \left( 1 - \epsilon_b \right) \mu_f \frac{D_p}{D_p} + \frac{7 \rho Q}{4 A_c} \right] \]

Coupling catalyst balances and fluid balances:

\[ R_i = -(1 - \epsilon_b) \frac{S_p}{V_p} D_i \frac{d \tilde{c}_i}{dr} \bigg|_{r=R} \]

\[ \sum_j \Delta H_{Rj} \tilde{r}_j = (1 - \epsilon_b) \frac{S_p}{V_p} k \frac{d \tilde{T}}{dr} \bigg|_{r=R} \]

MATLAB code:

```matlab
function [Z,result] = mainPBR(F0,T0,P0,bed_L,bed_D,bed_eps,pellet_eps,d_cat,d_pore,rho_cat,qext)
```
% F0: initial molar flows for CH4, CO2, CO, H2, H2O, mol/s;
% Code uses SI units unless specified otherwise

% All mol fractions should be nonzero in F0 so that rates are finite

% defining global variables for the reactor model
global dpore; % in nm
global epsbed;
global epscat;
global rhocat;
global D;
global dcat;

dpore=d_pore;
epsbed=bed_eps;
rhocat=rho_cat;
epscat=pellet_eps;
D=bed_D;
dcat=d_cat;
% first attempt: We will solve the Z dimension balances 'manually'
% before potentially switching to an ode solver.
% The 'result' output is a structure array, with each element
containing
% two objects: 'solid' and 'fluid', representing conditions at
every
% subdivision of the reactor volume. 'Solid' is a structure that
contains the
% pellet profile solved by bvp5c, and fluid is a vector containing
the 5
% flows, T and P.

Z=linspace(0,bed_L,100*bed_L); % generate 100 points per meter (at
every cm)

deltaZ=Z(2);
% second entry is equal to step size ^^

dummyresult(length(Z))=struct('solid',[],'fluid',[]);
% preallocating memory space to reduce exec time
% Create an empty structure with the last element defined (defines all
% before it too!)
dummyresult(1).fluid=[F0;T0;P0]; % Set 1st fluid data= initial
conditions

for i=1:length(Z)

if (i>1)
    T=dummyresult(i-1).fluid(6);
    P=dummyresult(i-1).fluid(7);
    F=dummyresult(i-1).fluid(1:5);
else
    T=T0;
    P=P0;
    F=F0;
end

[Deff,cp,viac_gas,rho,Dgas,k_thermal,h_thermal,Kc] =
pcprops(T,P,F); % invoke pcprops

opts=bvpset('RelTol',1e-2,'AbsTol',1e-4,'Jacobian',@ode_jac); % Solver tolerances, Jacobian
cat_profile = bvp5c(@pellet_ode, @pellet_bcond, initsol(), opts);
%solve pellet profiles
dummyresult(i).solid = cat_profile; %append pellet results to structure array

if (i > 1)
  % compute derivatives for fluid balance (Euler's method for now)
  df = -dummyresult(i-1).solid(6:10, end) .* Dgas * (6/dcat) * (1-epsbed); % df/dv
  p = dummyresult(i-1).fluid(7); % Getting F, P, T at previous iteration
  t = dummyresult(i-1).fluid(6);
  f = dummyresult(i-1).fluid(1:5);
  Q = sum(f) * 8.314 * t / p; % total volumetric flow, m3/s
  dt = (qext * pi * D + (1-epsbed) * (6/dcat) * k_thermal * dummyresult(i-1).solid(12, end) + (4/D) * h_thermal(dummyresult(i-1).solid(11, end) - t)) / (Q * rho * cp); % dt/dv
  dp = -((1-eps)/(dcat*epsbed^2)) * (Q/(0.25*pi*D^2) * ((150*(1-epsbed) * (visc_gas/dcat) + 7*rho*Q/(4*0.25*pi*D^2)))); % Ergun deriv = [df; dt; dp]; % d('fluid' vector)/dV
  Fnew = [f; t; p] + 0.25*pi*D^2*deltaZ.*deriv; % Euler's method to solve the fluid balance
  dummyresult(i).fluid = Fnew;
end
end

result = dummyresult; % return function output

%---------------------------------------------------------------------
% function dcdr = pellet_ode(r, C)
% C: vector containing the 5 concentrations of each component, the 5 dc/dr for each component (CH4 CO2 CO H2 H2O), % then T, dT/dr and dCarbon/dr % C is a 13x1 vector
% rates = kinetic_model(r, C(1:5) * 8.314 * T, T); % 6x1: first 5 are rxn rates, 6th element is the heat generation rate
vect = zeros(12, 1); % removed last element
vect(1:5) = C(6:10); % setting dc/dr in dcdr variable = dc/dr in C vector;
vect(6:10) = ((rates(1:5))./Deff') - 2.*C(6:10)/r; % diffusion-rxn model, d2C/dr2
vect(11) = C(12); % setting dT/dr in dcdr variable = dT/dr in C vector
vect(12) = (rates(7)/k_thermal) - 2*C(12)/r; % Pore heat equation
% vect(13) = rates(6); % carbon formation rate. We are not tracking the total amount.
dcdr = vect;
% Boundaries conditions for pellet_ode
%----------------------------------------

function res = pellet_bcond (ya,yb)

% ya and yb are two 13x1 vectors that have the values of vector C in
% pellet_ode()
% at the left and right side boundaries (r=0 and r=R)
% res is the residual function that should be zero when boundary
% conditions are met
A=[]; % Boundary cond at r=0
B=[]; % Boundary cond at r=R

f=dummyresult(i).fluid(1:5);
t=dummyresult(i).fluid(6);
p=dummyresult(i).fluid(7);

A(1:5)=ya(6:10);
% dC/dr=0 at r=0
A(6)=ya(12);
% dT/dr=0 at r=0 (symmetry in pellet)
Cbulk=(f./sum(f))*p/(8.314*t);

B(1:5)=(Deff'.*yb(6:10)-Kc'.*(Cbulk-yb(1:5))))';
B(6)= k_thermal*yb(12)-h_thermal*(dummyresult(i).fluid(6)-yb(11));

res=[A'; B']; % res should have the same dimension as C, so I added a
% length equal to 13;
end

% Initial guess for pellet model
%-----------------------------

function g= guess (r)

temp=[];
temp(1:2)=0.0004*exp(2444.66*r); % Choose a function that has zero
derivative at zero and similar shape/values as expected solution

temp(3:5)=(-9.527e-10)*exp(5000*r)+67.7;
temp(6:7)=0.0004*2444.66*exp(2446.66*r);
temp(8:10)=5000*(-9.527e-10)*exp(5000*r);
temp(11)=5.913e-7*exp(3957*r)+501.4;
temp(12)=3957*5.913e-7*exp(3957*r);
%temp(13)=(1.359e-11)*exp(5004*r);
g=temp;
end

% Calculation of Pellet_ODE Jacobian matrix
%------------------------------------------

function dcdy = ode_jac(r,C)

rho_pellet=rhocat/epsbed;

% Jacobian is sparse , so I start by a 13x13 zeros matrix and
%it
yaacoubian= zeros (12); %switched 13 to 12

for j=6:10
    yaacoubian(j-5,j)=1;
    yaacoubian(j,j)=-2/r;
end
mat=rate_deriv(C);

yaacoubian(6:10,1:5)=mat(1:5,1:5)*((4*3.14*(r^2)*rho_pellet))./D_eff;
%yaacoubian(13,1:5)=mat(end,:)*((4*3.14*(r^2)*rho_pellet));

yaacoubian(11,12)=1;
daacoubian(12,12)=-2/r;
%yaacoubian(13,13)=1;

dcdy=real(yaacoubian);

function mat=rate_deriv(C)

pbar=C(1:5)*8.314*T/1.01325e5 ;
R=8.314;

pch4=pbar(1);/%pbar;
pco2=pbar(2);
pco=pbar(3);
ph2=pbar(4);
ph2o=pbar(5);

k1=1.29e6*(exp(-(102065/(R*T))));
k3=6.95e3*(exp(-(58893/(R*T))));
k4=5.55e9*(exp(-(166397/(R*T))));
k5=1.34e15*(exp(-(243835/(R*T))));

kp1=6.78e14*(exp(-(259660/(R*T))));
kp2=56.4975*(exp(-(36580/(R*T))));
kp3=2.98e5*(exp(-(84400/(R*T))));
kp4=1.3827e7*(exp(-(125916/(R*T))));
k2=0.35e6*(exp(-(81030/(R*T))));
kp5=1.9393e9*(exp(-(168527/(R*T))));

kco21=2.61e-2*(exp(37641/(R*T)));
kco22=0.5771*(exp(9262/(R*T)));
kco25=2.81e7*(exp(-(104085/(R*T))));
kh41=2.6e-2*(exp(40684/(R*T)));
kh43=0.21*(exp(-(567/(R*T))));
kh44=3.49;
kh22=1.494e-2*(exp(36864/(R*T)));
kh23=5.18e7e-2*(exp(-(133210/(R*T))));
kh24=1.83e13*(exp(-(216145/(R*T))));
kco5=7.34e-6*(exp(100395/(R*T)));
kh204=4.73e-6*(exp(97770/(R*T)));

J =
(2*k3*kch43^2*(- ph2^2/kp3 + pch4))/((kch43*pch4 + conj(pch2^2*(3/2)))/kh23 + 1)^3 - (k1*kch41)/((kch41*pco2)/(((pco^2*ph2^2)/(kp1*pch4*pco2) - 1)*((kh41*pch4 + kco21*pco2 + 1)^2) -
(2*k1*kch41^2*kco21*pch4*pco2)/((pco^2*ph2^2)/(kp1*pch4*pco2) - 1)*((kh41*pch4 + kco21*pco2 + 1)^3 +
(k1*kch41)/((pco^2*ph2^2)/(kp1*pch4*pco2) - 1)*((kh41*pch4 + kco21*pco2 + 1)^2))) -
(k1*kch41)/((pco^2*ph2^2)/(kp1*pch4*pco2) - 1)*((kh41*pch4 + kco21*pco2 + 1)^3)} -
(2*k1*kch41^2*kco21*pch4*pco2)/((pco^2*ph2^2)/(kp1*pch4*pco2) - 1)*((kh41*pch4 + kco21*pco2 + 1)^2)
1)^2*(kch44*pch4 + kco21*pco2 + 1)^2) -
(k2*kco22*kh22*ph2*(kch44*pch4 + conj(ph2^(3/2))/kh24 + ph2o/(kh2o4*ph2) + 1)^2) + (2*k4*(pco/kp4 - ph2o/ph2))/((kh2o4*2*ph2*(kch44*pch4 +
conj(ph2^(3/2))/kh24 + ph2o/(kh2o4*ph2) + 1)^3) +
(k2*kco22*kh22*ph2)/((kp2*(kco22*pco2 + kh22*ph2 + 1)^2);

-(2*k4*kch44*(pco/kp4 - ph2o/ph2))/((kh2o4*2*ph2*(kch44*pch4 +
conj(ph2^(3/2))/kh24 + ph2o/(kh2o4*ph2) + 1)^3) +
(k2*kco22*kh22*ph2)/((kp2*(kco22*pco2 + kh22*ph2 + 1)^2);

% Jacobian of the reaction rates
mat=J;
end
end

%---------------------------------------------------------------------
% Initialization of guess structure for pellet model
function modelinit = initsol()
radial = linspace(0,dcat*0.5,100);
modelinit= bvpinit(radial,@guess);
end
end
%end to mainPBR which nests the pellet model functions

%------------------ Initialization of guess structure for pellet model
function modelinit = initsol()
radial = linspace(0,dcat*0.5,100);
modelinit= bvpinit(radial,8guess);
end

% end to initial solution guess function
end
% end to mainPBR which nests the pellet model functions

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function [Deff,cp,visc_gas,rho,Dgas,k_thermal,h_thermal,Kc] = pcprops(T,P,F)
    %Calculates physicochemical properties needed for the PBR model.
    % Takes T
    % in kelvin, P in Pa, F: molar flow rate (mol/s) vector (Uses SI units)
    % F= [ch4,co2,co,h2,h2o];

    %initializing global variables
    global dpore; % in nm
    global epsbed;
    global epscat;
    global D;
    global dcat;
    % for testing, uncomment
    % dpore =4;
    % epsbed=0.38;
    % epscat=0.65;
    % D=0.2;
    % dcat=0.01;

    R=8.314;

    M=[16,44,28,2,18]; %molar masses of F;
    tau=2.7; % bed tortuosity, correct
    sigma= 0.6; %constriction factor, correct

    %effective diffusivity assuming knudsen diff., m^2/s
    Deff=epscat.*sigma.*((1/3)*dpore*(10^-9).*sqrt(8*8.314.*T./(3.14.*0.001*M)))./tau;

    y=F/sum(F); %mole fractions

    %Calculating specific heat of the gas mix: J/mol.K
    % Assuming ideal gas, cp is independent of pressure
    % cp= R*(a1 + a2T + a3T^2 + a4 T^3 + a5T^4), matrix rows are a1-a5
    for


    cpi=zeros(5,1);
    for
    i=1:length(F)
    cpi(i)=R*(a(i,1)+T*a(i,2)+a(i,3)*T^2+a(i,4)*T^3+a(i,5)*T^4);
    end

    cp=dot(cpi,y);
%calculation of viscosities from interpolated data for each component then finding mu mix:
Tc=T-273;
uch4=0.000025*Tc+0.012048; %interpolant in centipoise
uco2=0.0008*Tc^-0.5985;
uco=0.0019*Tc^0.4664;
uh2=0.008*Tc^0.4866;
uh2o=0.000038*Tc+0.008243;
ucomp=[uch4, uco2, uco, uh2, uh2o];

visc_gas=0.001*dot(y, ucomp); %converted to Pa.s

density calculation:
%assuming ideal gas for now, can modify later
MWavg=dot(y, M);
rho=0.001*MWavg*8.314*T/P; %in kg/m3

%Gas phase diffusivity calculation, extrapolated from reference diffusivities at Tref and 1 atm:
Dgasref=[0.726, 0.185, 0.185, 0.726, 0.292]; %cm2/s
Tref=[298, 315.4, 315.4, 298, 307.7]; %couples: CH4/H2, CO2/CO, CO/CO2, H2/CH4, H2O/CH4, EMCD

Dgas=Dgasref.*(T./Tref).^1.75.*(1e5/P)*1e-4; %in m2/s

%Calculation of thermal conductivity;
% W/m2.K
ki=[];
ki(1)=0.03143*((T/279)^1.351)*(P/1e5)^0.01604; %CH4
ki(2)=0.0688*((T/973)^0.9236)*(P/0.5e5)^0.0008345; %CO2
ki(3)=0.003062*((P/0.5e5)*(T/973)^0.784); %CO
ki(4)=0.1786*((T/279.9)^0.7821)*(P/1e5)^0.003123; %H2
ki(5)=0.09332*((T/973)^1.412)*(P/0.5e5)^0.00241; %H2O
k_thermal=dot(ki, y); %W/m2/K

%Calculation of dimensionless numbers
v=sum((F)*R*T/P)/(0.25*3.14*D^2);
Re=rho*v*D/visc_gas; %Reynolds nb
Pr=visc_gas*cp/k_thermal; %Prandtl number
Sc=visc_gas./(rho*Dgas); %Schmidt number
Jh=(2.06*Re^-0.575)/epsbed; %Colburn factor
Nu=Jh*Re*(1/3); %Nusselt number from Chilton-Colburn analogy
Sh=(sqrt(Re/(1-epsbed)).*Sc.^(1/3))*((1-epsbed)/epsbed); %Sheerwood nb from Thoenes-Kramer model

%Heat and mass transfer coefficients:

h_thermal=Nu*k_thermal/dcat; %Convective heat transfer coefficient, W/m.K
Kc=Sh.*Dgas/dcat; %Vector with external mass transfer coef for each species

end

function [Deff, cp, visc_gas, rho, Dgas, k_thermal, h_thermal, Kc] = pcprops(T, P, F)
%Calculates physicochemical properties needed for the PBR model.
Takes T %in kelvin, P in Pa, F: molar flow rate (mol/s) vector (Uses SI units)

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%F= [ch4,co2,co,h2,h2o];

%initializing global variables
global dpore; %in nm
    global epsbed;
    global rhocat;
    global cpcat;
    global epscat;
    global D;
    global dcat;
% for testing, uncomment
   % dpore =4;
    % epsbed=0.38;
    % epscat=0.65;
    % D=0.2;
    % dcat=0.01;

R=8.314;

M=[16,44,28,2,18]; %molar masses of F
tau=2.5; %bed tortuosity, correct
sigma= 0.6; %constriction factor, correct

%effective diffusivity assuming knudsen diff.
Deff=epscat.*sigma.*((1/3)*dpore*(10^-9).*sqrt(8*8.314.*T./(3.14.*0.001*M)))./tau;

y=F/sum(F); %mole fractions

%Calculating specific heat of the gas mix:
%Assuming ideal gas, cp is independent of pressure
%cp= R*(a1 + a2T + a3T^2 + a4 T^3 + a5T^4), matrix rows are a1-a5
for each component in F
    a=[-1.63552643,1.00842795e-2,-3.36916254e-6,5.34958667e-10,-3.1551833e-14;
       4.63659493,2.74131991e-3,-9.95828531e-7,1.6037011e-10,9.1610348e-15;
       3.0484853,1.351728e-3,-4.85794075e-7,7.88536486e-11,-4.6980432e-16;
       2.770378,2.97318329e-3,-7.7376969e-7,9.44336689e-11,-4.2690959e-15];

    cpi=[];
    for i=1:length(F)
        cpi(i)=R*(a(i,1)+T*a(i,2)+a(i,3)*T^2+a(i,4)*T^3+a(i,5)*T^4);
    end
    cp=dot(cpi,y);

%calculation of viscosities from interpolated data for each component then finding mu mix:
Tc=T-273;
uch4=0.000025*Tc+0.012048; %centipoise
uco2=0.0008*Tc^0.5985;
uco=0.0019*Tc^0.4664;
uh2=0.008*Tc^0.4866;
uh2o=0.000038*Tc+0.008243;
% density calculation:
% assuming ideal gas for now, can modify later
MWavg=dot(y,M);
rho=0.001*MWavg*8.314*T/P; % in kg/m3

% Gas phase diffusivity calculation, extrapolated from reference diffusivities at Tref and 1 atm:
Dgasref=[0.726,0.185,0.185,0.726,0.292];%cm2/s
Tref=[298,315.4,315.4,298,307.4]; % couples: CH4/H2, CO2/CO, CO/CO2, H2/CH4, H2O/CH4, EMCD
Dgas=Dgasref.*(T./Tref).^1.75.*(1e5/P);

% Calculation of thermal conductivity;
% W/m2.K
ki=[0.03143*(T/279)^1.351*(P/1e5)^0.01604; %CH4
0.0688*(T/973)^0.9236*(P/0.5e5)^0.0008345; %CO2
0.003062*(P/0.5e5)*(T/973)^0.784; %CO
0.1786*(T/279.9)^0.7821*(P/1e5)^0.003123; %H2
0.09332*(T/973)^1.412*(P/0.5e5)^0.00241; %H2O

k_thermal=dot(ki,y);

% Calculation of dimensionless numbers
nu=dot(P*R*T/P)/(0.25*3.14*D^2);
Re=rho*v*D/visc_gas; % Reynolds nb
Pr=visc_gas*cp/k_thermal; % Prandtl number
Sc=visc_gas./(rho*Dgas);
Jh=(2.06*Re^-0.575)/epsbed; % Colburn factor
Nu=Jh*Re*Pr^((1/3)); % Nusselt number from Chilton-Colburn analogy
Sh=(sqrt(Re/(1-epsbed))).*Sc.^((1/3))*)((1-epsbed)/epsbed); % Sheerwood nb from Thoenes-Kramer model

% Heat and mass transfer coefficients:
h_thermal=Nu*k_thermal/dcat; % Convective heat transfer coefficient
Kc=Sh.*Dgas/dcat; % Vector with external mass transfer coef for each species

% function dFdr = kinetic_model(r,Pi,T)
% returns a 7x1 vector containing dF/dr for CH4 CO2 CO H2 H2O C and DeltaH
% total
% global rhocat;
% global epsbed;
rho_pellet=rhocat/epsbed;
R=8.314; % J/mol.K
pbar=Pi/1e5;

pch4=pbar(1);/%pbar;
pc02=pbar(2);
ppo=pbar(3);
ph2=pbar(4);
\[ \text{ph2o} = p\text{bar}(5); \]

\[ k_1 = 1.29 e 6 \times \exp\left(-\frac{102065}{(R \times T)}\right); \]
\[ k_2 = 0.35 e 6 \times \exp\left(-\frac{81030}{(R \times T)}\right); \]
\[ k_3 = 6.95 e 3 \times \exp\left(-\frac{58893}{(R \times T)}\right); \]
\[ k_4 = 5.55 e 9 \times \exp\left(-\frac{166397}{(R \times T)}\right); \]
\[ k_5 = 1.34 e 15 \times \exp\left(-\frac{243835}{(R \times T)}\right); \]
\[ k_{p1} = 6.78 e 14 \times \exp\left(-\frac{259660}{(R \times T)}\right); \]
\[ k_{p2} = 56.4971 \times \exp\left(-\frac{36580}{(R \times T)}\right); \]
\[ k_{p3} = 2.98 e 5 \times \exp\left(-\frac{84400}{(R \times T)}\right); \]
\[ k_{p4} = 1.3827 e 7 \times \exp\left(-\frac{125916}{(R \times T)}\right); \]
\[ k_{p5} = 1.9393 e 9 \times \exp\left(-\frac{168527}{(R \times T)}\right); \]
\[ k_{c021} = 2.61 e -2 \times \exp\left(37641/(R \times T)\right); \]
\[ k_{c022} = 0.5771 \times \exp\left(9262/(R \times T)\right); \]
\[ k_{c025} = 2.81 e 7 \times \exp\left(-104085/(R \times T)\right); \]
\[ k_{c41} = 2.6 e -2 \times \exp\left(40684/(R \times T)\right); \]
\[ k_{c43} = 0.21 \times \exp\left(-567/(R \times T)\right); \]
\[ k_{c44} = 3.49; \]
\[ k_{h22} = 5.18 e 7 \times \exp\left(-133210/(R \times T)\right); \]
\[ k_{h24} = 1.83 e 13 \times \exp\left(-216145/(R \times T)\right); \]
\[ k_{c05} = 7.34 e -6 \times \exp\left(100395/(R \times T)\right); \]
\[ k_{h2o4} = 4.73 e -6 \times \exp\left(97770/(R \times T)\right); \]

\[ r_1 = (k_1 \times k_{c021} \times k_{c41} \times p_{c4} \times p_{c02}) / (((1+(k_{c021}\times p_{c02})+(k_{c41}\times p_{c4})))^2) \times (1- ((p_{c02}/p_{c4})^2)/(k_{p1}\times p_{c4}\times p_{c02}))); \]
\[ r_2 = (k_2 \times k_{c022} \times k_{h22} \times p_{c02} \times p_{h2}) / (((1+(k_{c022}\times p_{c02})+(k_{h22}\times p_{h2}))^2) \times (1- ((p_{c02}/p_{h2})^2)/(k_{p2}\times p_{c02}\times p_{h2}))); \]
\[ r_3 = ((k_3 \times k_{c43}) \times (p_{c4}- ((p_{c4}^2)/k_{p3})) / ((1+(k_{c43}\times p_{c4})+(p_{c4}^2)^1.5)/k_{h23})); \]
\[ r_4 = ((k_4 \times k_{h2o4}) \times (p_{h2o}/p_{c0}) - (p_{c0}/k_{p4}) / ((1+(k_{h2o4}\times p_{c0})+(p_{c0}\times k_{h2o4}^2)+(p_{c0}^2)^1.5)/k_{h24})); \]
\[ r_5 = ((k_5 \times k_{c05} \times k_{c025}) \times (p_{c02}/p_{c0}) - (p_{c0}/k_{p5}) / ((1+(k_{c05}\times p_{c0})+(p_{c0}^2/(k_{c05}\times k_{c025}))^2); \]

\[ d_{c4} = -(r_1) - (r_3); \]
\[ d_{c02} = -(r_1) - (r_2) - (r_5); \]
\[ d_{c0} = (2 \times (r_1)) + (r_2) + (r_4) + (2 \times (r_3)); \]
\[ d_{H2} = (2 \times (r_1)) - (r_2) + (2 \times (r_3)) + (r_4); \]
\[ d_{h2o} = (r_2) - (r_4); \]
\[ d_{c} = -(r_4) - (r_5); \]

\[ \text{rxns} = [r_1, r_2, r_3, r_4, r_5]; \]

%heats of reaction:
\[ dh_1 = 247; \text{kJ/mol} \]
\[ dh_2 = 41.7; \text{kJ/mol} \]
\[ dh_3 = 74.87; \text{kJ/mol} \]
\[ dh_4 = 131.325; \text{kJ/mol} \]
\[ dh_5 = 172; \text{kJ/mol} \]

\[ \text{heats} = [dh_1, dh_2, dh_3, dh_4, dh_5]; \]

\[ \text{dhtot} = \text{dot} (\text{rxns}, \text{heats}) \times 1000; \text{%kJ/mol} \]
\[ \text{dFdw} = [d_{c4}; d_{c02}; d_{c0}; d_{H2}; d_{h2o}; d_{c}; d_{h2o}] \]

\[ \text{dFdr} = \text{dFdw} * ((4 \times 3.14 \times (r^2) \times \rho \_pellet)); \]

end
Appendix 2: Gas chromatography quantification method

The experimental setup necessitates the use of on-line gas sampling for real time analysis of reactor gases. An Agilent 7820 gas chromatograph equipped with a 6-port gas sampling valve, using a Porapak Q porous polymer column and a thermal conductivity detector was used for this purpose.

![Diagram of 6-way valve in its two configurations]

Figure 0-1: 6-way valve in its two configurations

**Carrier gas selection:**

As hydrogen is a product of the reforming process, it is impossible to use hydrogen as the carrier gas. Three gases are left to choose from: argon, nitrogen and helium. The use of nitrogen is not generally recommended as the best practice by GC manufacturers, and due to the possibility of it being used in the reactor during reduction of catalysts, its use will be avoided.

As for the sensitivity of the TCD in detecting biogas and syngas components, it is useful to investigate the relative thermal conductivities between different species and the carrier gas.
Two conclusions can be drawn from these numbers:

- When using helium, the detector is not very sensitive to hydrogen, but relative conductivities of other species are in the range of 1/3 to 1/6, ensuring excellent sensitivity. However, H$_2$ is the only species that is more conductive than helium, and therefore peak inversion will be present, necessitating polarity inversion at known retention times.

- When using Argon, the relative conductivity of species other than hydrogen are in the range of 1.25 to 2.5, meaning that the sensitivity is less than when using helium but all the peaks will be of the same sign and therefore peak integration will be simpler. However, negative peaks are obtained and the TCD polarity needs to be inverted.

It was then chosen to use argon as the reference gas for the TCD.

The optimal analysis conditions were:

- Argon flow: 20 mL/min
- Column temperature kept at 50°C with no temperature ramp
- Inverted TCD polarity in low sensitivity mode

**Quantification of analytes:**

First, pure samples of each gas were analyzed to identify the retention times for each compound. After that, multiple samples of varying concentrations were analyzed in order to relate peak area to concentration.
Table 0-1: Retention times for analyte gases

<table>
<thead>
<tr>
<th>Gas</th>
<th>Retention time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>0.57</td>
</tr>
<tr>
<td>N₂</td>
<td>0.65</td>
</tr>
<tr>
<td>CO</td>
<td>0.70</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.94</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.65</td>
</tr>
</tbody>
</table>

Figure 0-3: Calibration curve for CH₄

\[ y = 117.38x + 27.332 \]
\[ R^2 = 0.9998 \]

Figure 0-4: Calibration curve for CO₂

\[ y = 36.152x + 33.618 \]
\[ R^2 = 0.9994 \]
Figure 0-5: Calibration curve for H$_2$

Figure 0-6: Calibration curve for CO