The Pennsylvania State University

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Department of Energy and Mineral Engineering

GRAPHENE OXIDE SUPPORTED RUTHENIUM FOR CO METHANATION

A Thesis in

ENERGY AND MINERAL ENGINEERING

by

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ABSTRACT

The sustainable exploration of space requires minimization of re-supply from Earth through the implementation of In-Situ Resources Utilization (ISRU) strategies developed by NASA. One such strategy for lunar exploration is the production of oxygen from lunar regolith, a complex mix of minerals with large oxygen content. In the case of carbothermal-based oxygen production, reaction byproducts, i.e. carbon oxides, should be converted to methane for reintroduction into the carbothermal system. For this purpose, development of a methanation reactor to efficiently convert the mixed-carbon oxides into methane is essential to the integrity of the ISRU process.

Nickel has been the favored catalyst for the methanation reaction because of its activity, selectivity and catalyst life. Yet Ni and Ni-based catalysts are particularly sensitive to poisoning by sulfur and coking by carbon. For these reasons Group VIII metals, in general far less prone to such detriments, have been in focus as alternatives to Ni, particularly Ru. Presently recent literature on methanation catalysts is concerned with preparative techniques and catalyst support, factors markedly affecting catalyst properties.

The research reported here is focused on developing a new, more-efficient catalyst for the methanation component in NASA’s ISRU oxygen scheme. Efficiency generally translates into high catalyst exposure or high surface-area availability in heterogeneous catalysis. As a high surface area support graphene was chosen. Dispersion of Ru on graphene was achieved via a two-step decoration process using...
graphene oxide as a precursor. Notably GO production also facilitates graphene layer separation to create a high surface-area support. Yet agglomeration can occur during its reduction and deposition within a reactor bed, thereby lessening the effectiveness of the catalyst dispersion it supports. This is particularly problematic for nanoscale carbon materials as supports, given their high self-affinity between particles or platelets. Preventing this agglomeration will provide an increase in the accessibility to the surface metal sites on the support and ultimately could increase the performance activity of the catalysts. Towards this goal different Ru-based catalyst systems, using graphene, were prepared and compared.

The support of interest, graphene, was first prepared as graphene oxide (GO) by the modified Hummers process and later decorated with ruthenium using a poly-ol process. A traditional catalyst system of ruthenium supported on alumina (Al₂O₃) was also prepared using the same process so as to facilitate comparisons. Another catalyst was synthesized in which the alumina was also introduced in the synthesis process along with GO to produce a mixed catalyst with the alumina helping to separate the graphene sheets, thereby partially alleviating their agglomeration.

These catalysts were then impregnated within hierarchical alumina foams and loaded into a microchannel methanation reactor based upon a simple pipe construction and Swagelok fittings. The use of alumina foams provided excellent contact area for the methanation gases (H₂, CO) while maintaining a low pressure drop. The characterization techniques of FE-SEM and TEM identified the Ru catalyst particle size and dispersion on the graphene support. EDS identified the ruthenium elemental state with XPS measuring
the GO elemental content. By TGA analysis the ruthenium content in the catalyst was determined. With this well characterized and quantified catalyst, methanation tests were performed at a temperature of 409°C. For these the catalyst was first pre-reduced at 300°C in the presence of H₂. Reactant gas concentrations (i.e. the CO/H₂ ratio) and space velocities were varied to test catalyst activity and selectivity, using gas chromatography to analyze the product gas mixture after characterization of the different catalysts for activity and selectivity, hypothesis related to both measurement.

Amongst the catalyst systems of Ru/GO, Ru/Al₂O₃, Ru/ (GO+Al₂O₃), the mixed catalyst (Ru/ (GO+Al₂O₃)) performed the best with a CO conversion of 100 percent and selectivity of 100 percent towards methane. The comparisons made between the catalysts (Ru/GO)+bare Al₂O₃) and Ru/(GO+Al₂O₃) revealed that physical separation of the catalyst support layers, i.e. the graphene platelets, by the nanoalumina is the operative factor for highest activity. Graphene layer separation facilitates the Ru catalyst exposure, consequently the high Ru catalyst dispersion is effective. TEM images suggest this synergy of the mixed catalyst system with catalyst activity validating its impact.
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Chapter 1

INTRODUCTION

1.1 Motivation

The utilization of extraterrestrial resources will become a key element in the exploration of the Moon and Mars. Studies over the years have shown that the ability to process and refine materials that have been extracted and separated from space resources into useful products can have a substantial impact on individual missions and mission architecture concepts. In particular, the ability to locally make propellant, life-support consumables, and fuel-cell reagents can significantly reduce mission cost by reducing launch mass, providing affordable pre-positioning of consumables, enabling reusability, reducing risk by providing backup life-support consumables and reduced dependence on Earth. It enables extended surface operations by providing an energy rich environment and affordable access to multiple surface targets. Major life-supporting consumables include oxygen, hydrogen, water, and hydrocarbon fuels. The development and operation of in-situ manufacturing plants are required to enable the establishment of permanent lunar and Martian bases. Oxygen production for life support and propulsion will be the most important process for the manufacturing plants.

The Moon is comprised of metallic oxides, providing a nearly unlimited quantity of raw materials which can be processed as the source for oxygen. If an efficient process can be designed to extract the oxygen from the lunar soil, oxygen for life support and propulsion could be manufactured directly on the lunar surface. The metals reduced from their oxides during this extraction process (oxygen-extraction process) could also be important raw materials for a variety of products.
After detecting water as the source for hydrogen in shadowed lunar regions\(^1\), the potential impact of ISRU upon long-term lunar surface operations, Earth-lunar transportation, and even transportation to Mars and beyond changed enormously. The ability to produce oxygen and fuel from lunar resources would reduce if not eliminate the need to transport propellant to the Moon, and drastically curtail the scale of Earth launch requirements for lunar missions and sustained surface exploration.

One such process for the extraction of lunar oxygen is the carbothermal reduction process. The baseline carbothermal reduction process\(^1\) has three steps as shown in Figure 1.1.1:

1. Reduction of metallic oxides (e.g., FeO, Fe\(_2\)O\(_3\), SiO\(_2\), TiO\(_x\), Al\(_2\)O\(_3\), MgO, etc.) with a carbon source (e.g., methane) to form carbon monoxide and hydrogen,
2. Reduction of carbon monoxide with hydrogen to form methane and water, and
3. Electrolysis of water to form oxygen and hydrogen.

The hydrogen formed in Steps 1 and 3 is recycled to Step 2. The methane formed in Step 2 is recycled to Step 1. This closed cyclic process does not depend upon the presence of water or water precursors in the lunar materials, an external hydrogen source is assumed. The carbothermal process will extract oxygen from lunar iron oxide and silicate minerals regardless of their precise composition and fine structure.
Figure 1.1.1 Diagram illustrating an entire ISRU cycle, of which the carbothermal reduction and methanation recycling are but individual steps in the overall process scheme.

The effluent gases in the carbothermal process need to be converted back to methane for the conservation of the carbon resource. For this methane formation, a catalytic system is needed that would effectively convert the effluent gases of CO and H\textsubscript{2} generated during process (1) back into methane, which could be utilized for continuous reduction of the lunar regolith, process (1). This methanation system should be compact, efficient, and easy to use. To develop such a system, traditional methanation reactors based on the Nickel (Ni) catalyst will not work as they are subjected to numerous limitations such as the required reactor size and catalyst amount, reflecting relatively low-efficiency conversion. Ni catalysts also suffer from poisoning and deactivation by carbide formation. Improvements are clearly needed.

Catalyst exposure and accessibility are key issues in heterogeneous catalysis. High surface area is not useful if mass transfer limitations exist. Support agglomeration, a particular problem with implementation of nanoscale support materials occludes or otherwise blocks catalysts. Circumventing this problem is paramount to realize implementation of high surface-area support structures.
Identification of such occurrence is problematic. Post-use extraction or directly synthesized catalysts naturally agglomerate due to the wet-processing involved. Therein simple visual examination by microscopy or physical testing such as by BET may not render much insight. Direct testing should in principle provide measurement of blocked or otherwise inaccessible catalysts as registered by lower activity. Yet preparation methods are varied and lower activity can simply reflect a different particle size, (dispersion) or as different shapes or number of exposed steps. Needed are comparisons of catalyst metrics upon the same support, by the same preparation method, and preferably synthesized within the same laboratory. This thesis reports such comparisons for Ru/Graphene Oxide and Ru/Alumina for methanation reaction.

1.2 Hypothesis

A general hypothesis for this type of study would be that catalysts upon mixed supports of different physical size/shapes, emphasizing geometric differences, will provide “apparent” catalyst enhancement as measured by activity and selectivity. Specific to this study, the Ruthenium (Ru) catalysts deposited upon nanocarbons such as CNTs or Graphene Oxide (GO) and alumina when mixed will provide higher activity than the summation of the individual contributions. Mixtures of particles with different sizes and shapes over varied length scales will facilitate dispersion, or more accurately, accessibility of catalysts particles. This is of particular interest for materials such as in Graphene, CNT’s or other similar nanocarbons as catalyst supports, as they can exhibit a high tendency towards self-agglomeration.
1.3 Research Objectives

The overall objectives of this work are the following:

1) To prepare four separately supported catalyst systems:
   a) Ruthenium (Ru) on Graphene Oxide (GO) - (Ru/GO),
   b) Ruthenium (Ru) on an alumina (A) support – (Ru/Al₂O₃),
   c) Ruthenium supported on the mixed-catalyst supports of (GO + alumina) – (Ru/(GO+ Al₂O₃)), and
   d) Ruthenium supported on GO+ bare alumina. ((Ru/GO) + Al₂O₃).

2) To test and compare the mixed catalysts and their components separately for activity and selectivity.

Two possible comparisons could be made between catalyst systems to test the hypothesis regarding the dispersion enhancement of Ru-GO with alumina. The first would compare Ru-GO to the physical mixture of Ru-GO with alumina. Here “physical mixture” is understood to mean solution dispersion. The alumina would not be decorated but merely added to the final dispersal solution of Ru-GO for impregnation into the alumina foams. The solvent stabilizing action is anticipated to be superior to simple mechanical mixing to achieve dispersion, even if performed “wet” as a paste, analogous to the incipient wetness approach. As the subsequent washings and after the poly-ol decoration step involve only physical mixing between the co-synthesized Ru decorated GO and alumina in the combined-catalyst process, this “physically mixed catalyst” via solution dispersion is considered analogous. It is also comparable to the case where no additional Ru is introduced, i.e. the alumina is not decorated.
The contrasting system would be two mixed-catalyst systems. The first system is again the co-synthesized Ru-GO + Ru-alumina system and the second is then being the physically mixed Ru-GO and Ru-alumina, but synthesized separately. However for the reasons just discussed, the physical mixture would be achieved by solution dispersion. As such, this separately synthesized catalyst will be nearly identical to the co-synthesized form, minus some rinsing steps. As these are expected to result in little additional co-mixing between the supports, the two systems prepared in this manner would be essentially identical, even though seemingly parallel, each containing two catalyst components. Therein comparison of the Ru-GO with and without alumina is deemed the superior comparison and the better to test the hypothesis. Finally this system can be viewed as “parallel” as the two compared systems do contain but one catalyst component each. Further details are outlined in the experimental section.

**Figure 1.3.1** Comparisons of the catalysts synthesized
1.4 Thesis Outline

In this thesis, I have studied the synthesis of the catalyst based on ruthenium and graphene oxide and made comparisons by selecting one of the most widely used traditional catalyst (catalyst based on Alumina and ruthenium) which underwent the same synthesis process as that of the catalyst support of interest. Chapter 2 provides a comprehensive literature review of previous studies on the methanation reaction and the catalysts used along with a brief overview of current research relevant to the catalysts of interest for this research. In Chapter 3, the detailed experimental method related to the synthesis of GO (i.e., support) and the catalyst based on this GO is presented along with the construction of the “Micro Channel Methanation Reactor,” the catalyst-specific reactor designed for this catalyst and reaction. The various characterization techniques such as FE-SEM, TEM, XPS, and TGA used to characterize the catalyst sample are also discussed. In Chapter 4 results from the synthesis, characterization and testing of the catalyst are discussed in detail. The conclusions generated from results and the recommendations for the future work on the catalysts are given in Chapter 5.
CHAPTER 2

LITERATURE REVIEW

This chapter presents the literature review on methanation and catalysts related to methanation. The first part gives the use of methanation and the general chemistry for methanation which includes an overview of the elementary reaction steps that occur in methanation. Some of the typical catalysts that were used in the previous studies and their causes for deactivation of the catalysts were also listed. Depending on these parameters, the typical support and some introduction to graphene oxide is also studied. The outline for this chapter is given below

2.1 Methanation-State of the Art
2.2 Methanation Chemistry
2.3 Catalyst Development
2.4 Factors Effecting the Activity of the Catalyst
2.5 Catalyst Metal Selection
2.6 Catalyst Support Properties
2.7 Carbon as Support
2.8 Graphene Oxide
2.1 Methanation – State of the Art

The methanation reaction was discovered more than a century ago, in 1902, by Paul Sabatier and Jean-Baptiste Senderens\(^2\). It is also referred to as the Sabatier and Senderens reaction. Methanation refers to the reaction between carbon monoxide and hydrogen to form methane and water as described by the equation

\[ 3H_2 + CO \rightarrow CH_4 + H_2O \]

It is an exothermic reaction with a standard formation enthalpy of \(-207\) kJ/mol and standard Gibbs energy of \(-142\) kJ/mol. Even though the reaction has been well known for more than 100 years and it is one of the classical, well-studied reactions in heterogeneous catalysis, new discoveries and improvements can still be made. While significant research focus has been on catalyst development, nickel continues to be the major catalyst for the reaction because of its activity plus selectivity for methane formation and most importantly, its low cost.

While methanation could be viewed as a process for CO removal from exhaust streams, or CO feedstock processing, an economical source of H\(_2\) is required. With the prevalence of natural gas, synthetic natural gas may only find niche applications at remote locations. Alternatively methanation catalysts have traditionally proven to be versatile as hydrogenation catalysts and may find use therein in either selective chemical synthesis or perhaps fuel reprocessing.

2.2 Methanation Chemistry

In the process of methanation, three independent reactions are very important, as follows:

\[ 3H_2 + CO \rightarrow CH_4 + H_2O \quad \Delta H^\circ_R = -206.28 \frac{kJ}{mol} \quad \ldots \ldots Methanation \ldots Reaction 1 \]
\[ CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H^\circ_R = -41.16 \frac{kJ}{mol} \quad \ldots \ldots water ~gas ~shift \ldots Reaction 2 \]
If the stoichiometric ratio of the reactants $\text{H}_2/\text{CO}$ is at least three or more, carbon monoxide reacts with hydrogen to yield methane and water after reaction 1, accompanied by a CO molar reduction of 50 percent. This reaction is called CO-methanation or CO hydrogenation. By means of the water gas shift reaction (WGS), the $\text{H}_2/\text{CO}$ ratio can be adjusted by converting CO with $\text{H}_2\text{O}$ to $\text{CO}_2$ and additional $\text{H}_2$ for recycling through reaction (1). The Boudouard reaction is also of great importance since carbon on the catalyst surface can be considered as a necessary intermediate during the methanation reaction, and it also can lead to catalyst deactivation.

The detailed methanation chemistry of CO and $\text{H}_2$ has been studied extensively and the kinetics for CO is well known\(^3\). Table 2.2.1 gives the possible elementary reactions that could happen. Divided into a series of 21 elementary steps, the mechanism proposes an oxygenated compound, e.g., a $\text{COH}_x$ complex, as an intermediate state. It is assumed that in the presence of hydrogen, carbon monoxide does not dissociate, but rather reacts in the first state with hydrogen to form a $\text{COH}_x$ complex, which has lower activation barrier energy for the C-O bond dissociation\(^4\). This $\text{COH}_x$ can either dissociate or react to form $\text{CH}_y$ that reacts further to form methane. The values of $x$ and $y$ depends on the conditions of the reaction.

The reaction steps are not thought to occur in the sequence as it is illustrated in Table 2.2.1, rather, the “mechanism” is a portfolio of the possible elementary steps listed in this Table. For example, some authors assumed a $\text{COH}$, $\text{COH}_2$, or $\text{COH}_3$ as an intermediate state with a variety of different RDS \(^4\)\(^-\)\(^9\).
Table 2.2.1 Reaction pathways possible with the RDS

<table>
<thead>
<tr>
<th>Reaction Pathway</th>
<th>Rate Determining Step (RDS)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2 + 2 * \rightarrow 2H *$</td>
<td></td>
<td>Dissociative adsorption of Hydrogen</td>
</tr>
<tr>
<td>$CO + * \rightarrow CO *$</td>
<td>RDS</td>
<td>CO-adsorption</td>
</tr>
<tr>
<td>$CO * + H * \rightarrow COH * + *$</td>
<td>RDS</td>
<td>COH- formation</td>
</tr>
<tr>
<td>$COH * + * \rightarrow CH * + O *$</td>
<td>RDS</td>
<td>Dissociation of COH complex</td>
</tr>
<tr>
<td>$COH * + * \rightarrow C * + OH *$</td>
<td>RDS</td>
<td>Dissociation of COH complex</td>
</tr>
<tr>
<td>$COH * + H * \rightarrow COH_2 * + *$</td>
<td>RDS</td>
<td>COH_2- formation</td>
</tr>
<tr>
<td>$COH * + H * \rightarrow CH * + OH *$</td>
<td>RDS</td>
<td>Dissociation of COH with H</td>
</tr>
<tr>
<td>$COH_2 * + H * \rightarrow CH * + H_2 O *$</td>
<td>RDS</td>
<td>Dissociation of COH_2 with H</td>
</tr>
<tr>
<td>$COH_2 * + H * \rightarrow COH_3 * + *$</td>
<td>RDS</td>
<td>COH_3- formation</td>
</tr>
<tr>
<td>$COH_3 * + H * \rightarrow CH_2 * + H_2 O *$</td>
<td>RDS</td>
<td>Dissociation of COH_3 with H</td>
</tr>
<tr>
<td>$CO * + OH * \rightarrow CO_2 * + H *$</td>
<td></td>
<td>$CO_2$- formation</td>
</tr>
<tr>
<td>$CO * + H_2 O * \rightarrow CO_2 * + 2H *$</td>
<td></td>
<td>$CO_2$- formation</td>
</tr>
<tr>
<td>$CO_2 * \rightarrow CO_2 + *$</td>
<td></td>
<td>$CO_2$- desorption</td>
</tr>
<tr>
<td>$O * + H * \rightarrow OH * + *$</td>
<td></td>
<td>OH- formation</td>
</tr>
<tr>
<td>$OH * + H * \rightarrow H_2 O * + *$</td>
<td></td>
<td>$H_2 O$–formation</td>
</tr>
<tr>
<td>$H_2 O * \rightarrow H_2 O + *$</td>
<td></td>
<td>$H_2 O$–desorption</td>
</tr>
</tbody>
</table>
\[
\begin{align*}
C^* + H^* & \rightarrow CH^* + * & \text{RDS} & \text{hydrogenation of C} \\
CH^* + H^* & \rightarrow CH_2^* + * & \text{RDS} & \text{hydrogenation of CH} \\
CH_2^* + H^* & \rightarrow CH_3^* + * & \text{RDS} & \text{hydrogenation of CH}_2 \\
CH_3^* + H^* & \rightarrow CH_4^* + * & \text{hydrogenation of CH}_3 \\
CH_4^* & \rightarrow CH_4 + * & \text{CH}_4^*- \text{desorption}
\end{align*}
\]

* Empty site

C* adsorbed species

RDS rate determining step (proposed RDS from literature)

### 2.3 Catalyst Development

#### 2.3.1 Various Methanation Catalysts

Methanation catalysts are based on iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium or platinum. Some details of the widely used metals are described below

##### 2.3.1.1 Nickel

Nickel is pre-eminently the most used methanation catalyst as it is reactive and selective towards methane production. Nickel is primarily chosen as the catalyst by industry because of its comparatively low cost\(^1\). The nickel-based catalysts in use can be broadly classified as Raney nickel, supported nickel catalysts, nickel alloy and bimetallic catalysts having an operational temperature range of 250°C-450°C at a pressure range of 3000-6000 kPa \(^1\). Most commercial nickel catalysts contain 25-77 percent nickel dispersed on a refractory support of high surface-area particles such as alumina.
2.3.1.2 Cobalt

Cobalt is a very active catalyst for the hydrogenation of oxides of carbon. It is less selective than nickel towards the formation of methane under 300°C but it supersedes nickel in total hydrocarbon product yield above 300°C. In particular Raney cobalt has been reported as very active for CO methanation\textsuperscript{12} at such temperatures.

Interestingly cobalt catalysts were among the first developed for the production of liquid hydrocarbons from water gas by the Fischer-Tropsch process\textsuperscript{11,13}. In general, techniques for the preparation of nickel catalysts can also be applied to cobalt catalysts.

2.3.1.3 Iron

Methanation catalysts can be prepared from iron\textsuperscript{14} when the use of higher temperature arises. Reduced, promoted iron oxide is best used as a catalyst in the Fischer-Tropsch synthesis\textsuperscript{13}. In terms of unit surface area of active metal, iron is intrinsically as active as nickel. As a variation some nitride-iron catalysts are often compared with nickel and cobalt catalysts for their activity and selectivity\textsuperscript{14}.

At slightly elevated pressure (ca. 1000kPa) both cobalt and iron catalysts react with CO and H\textsubscript{2} to give olefins and alcohols as well as paraffins\textsuperscript{11,13}. Iron-containing catalysts of the type M [Fe (CN)\textsubscript{2}] have been used for the reduction of CO to produce hydrocarbons, especially CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8}. The cation M can be Ce, Cu, Co, Fe, Ni, Mn, Ag, Ca, Mg, or Zn or can be a composite of two or three cations\textsuperscript{15}. 
2.3.1.4 Group VIII Metals

The precious metals of Group VIII are catalytically active for methanation. Ruthenium, in particular, is highly active even at low temperature and under mild hydrogenation conditions (150-230°C, <300 kPa). However it is not often used due to its cost, and if used, only at low loadings (0.5 weight percent of the weight of catalyst) at which point yield is subpar relative to nickel\(^{11}\). It is of interest that at low temperature and high pressure ruthenium induces the production of high-molecular-weight paraffin wax as the reaction could be a combination of the water-gas reaction and the Fischer-Tropsch synthesis. Yet ruthenium and other group VIII metals are attractive not only for their activity but also for their operational resistance to sulfur poisoning.

2.3.1.5 Molybdenum and Tungsten

Molybdenum and tungsten are used for methanation only because of their resistance to sulfur poisoning. These catalysts are sulphided before use as methanation catalysts. They are moderately active, requiring relatively very high reaction temperature and hence are less selective to methane formation \(^{17}\). These metals are more used along with nickel supported on alumina or silica\(^{18}\). The addition of one of these metals will increase the sulfur resistance to almost all the methanation catalysts (even the Group VIII metals). Usually, finely divided molybdenum or tungsten are used as the catalysts.

2.4 Factors Affecting the Activity of the Catalysts

Methanation catalysts such as nickel can be supported on oxides such as alumina, zirconia, titania and silica. Methanation catalysts operate for long periods and in large catalyst beds. Catalyst life and strength are majorly important relative to the initial activity. The major problems that are faced are related to the factors causing or contributing to catalyst decay. These
problems can be generalized as sulphur poisoning, loss of activity due to too-low thermal stability, and carbon deposition.

Poisoning of the catalyst from any source results in the loss of activity mainly for the nickel based catalysts. Methanation catalysts are very sensitive to sulphur. Even a small amount of sulphur can cause an effect in the activity and can reduce the life of the catalyst. Thermal stability is another key issue for the catalysts. A favorable methanation catalyst should be stable at temperatures of 300-450°C. Within the limits of operation, the higher the temperature at which the heat of methanation is released the more effectively it can contribute to the overall thermal efficiency of the conversion process. Also, sulphur poisoning may be less of a problem at higher temperature because of decreased stability of a catalyst metal sulphided under the conditions of operation. Further detail about the catalyst poisoning is listed in appendix A.

From the methanation mechanism in table 2.2.1, carbon formation for methanation is evident and if the deposition of the carbon increases on the surface, it can act to reduce the activity of the metal by covering the active sites present on the catalyst surface. Choosing favorable conditions for temperature (>400°C) and metals especially tungsten, ruthenium, platinum, etc., which originally have the tendency to form very less carbon during the reaction, would aid in reducing this effect, which is observed frequently in nickel-based catalysts.

2.5 Catalyst - Metal Selection

With consideration of the deactivation mechanisms, a general comparison for the methanation catalysts is presented in table 2.4.1. Preparation strategies, conditions, advantages and disadvantages are selectively summarized. In choosing a catalyst for the methanation, these parameters require consideration.
**Table 2.4.1** Summary of various methanation catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Method to prepare catalyst</th>
<th>Methanation Conditions</th>
<th>Advantages</th>
<th>NOTE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel$^{19,24}$</td>
<td>Alternative synthesis routes for deposition upon substrates (Al$_2$O$_3$, SiO$_2$ etc.) include electrochemical reduction, flame spraying, poly-ol reduction, and standard approaches of co-precipitation, or impregnation.</td>
<td>Can be used in temperature range of 250-450°C, reduction is done at 270°C, Can be effective at H$_2$/CO 2.1-5.8, space velocities ranging from 500-56000 hr$^{-1}$.</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Preparation Method</td>
<td>Operating Conditions</td>
<td>dispersion (%)</td>
<td>selectivity</td>
</tr>
<tr>
<td>---------------</td>
<td>---------------------------------------------------------</td>
<td>---------------------------------------------------------------------------------------</td>
<td>----------------</td>
<td>------------</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Preparation by similar techniques as for nickel</td>
<td>Can operate at 250-600°C, but requires pre-reduction to at least 380°C, space velocities ranging from 500-6000 hr(^{-1}).</td>
<td>100</td>
<td>93</td>
</tr>
<tr>
<td>Iron</td>
<td>Iron in the form of iron oxide is used directly or preparation by electrolysis of a molten metal salt.</td>
<td>Nominal operative conditions of 300-450°C, space velocities of 100-4000 hr(^{-1}), can produce methane even at H(_2)/CO of 1-4. Low pressure is required to form methane (&lt; 1000 kPa)</td>
<td>95</td>
<td>94</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>Ethylene glycol route, electrolytic deposition</td>
<td>Can operate at 250-700°C, space</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
velocities of 100-34000 hr\(^{-1}\), effective even at a H\(_2\)/CO of 0.8-6, reduction temperature of 300\(^\circ\)C resistant to sulphur, limits carbon formation, does not sinter at reaction temperatures, can achieve dispersion of 60 weight percent.

Direct metal is not abundantly available.

Molybdenum and tungsten\(^{17,18,30,33,34,35}\) formed by direct reaction of the elements heated in vacuum or protective atmosphere

Operation at 500-600\(^\circ\)C, H\(_2\)/CO ratio of 3, space velocities 600-900 hr\(^{-1}\).

95 92 .0097 Resistant to sulphur, used as a promoter.
Low activity, selectivity for methanation. Cannot achieve good dispersion.
2.5.1 Finding a Proper Descriptor

Sabatier’s principle could be used in selecting a good catalyst; it states that the binding energy of the reactants to the catalyst surface must be strong enough that they produce reaction intermediates, but has to be weak enough to allow the products to leave the surface thus allowing more reactions to occur at that site. The optimal catalyst surface will be a trade-off between binding the reagents to the surface and not binding any of the reaction intermediates too strong relative to the product. Hence, the surface properties are very important for catalyst performance. Theoretical work investigating the methanation reaction has suggested that the activity of this reaction is dependent on two important parameters related to the catalyst surface, which are the CO dissociation barrier and the stability of the main intermediates that are formed.

2.5.2 Brønsted-Evans-Polanyi (BEP) Correlation

Density functional theory (DFT) calculations of the two parameters (the activation energy and the CO dissociation energy) for different metal surfaces have shown that there is a linear Brønsted-Evans-Polanyi (BEP) correlation between the activation energy for CO dissociation and the adsorbed CO dissociation energy as shown in Figure 2.5.2.1. This linear correlation can be explained by the C-O bond being so extended in the transition state under the dissociation that it is very close to the final state. That means that the bonding properties of the transition state vary like the adsorbed atomic C and O.
Figure 2.5.2.1 Plot showing a linear correlation is observed between the activation energy $E_a$ of CO dissociation and the adsorbed CO dissociation energy $E_{diss}$ for different metals, meaning that a BEP relation exist between the parameters\textsuperscript{38}.

2.5.3 Volcano Plot

It is often possible to correlate the catalytic activity with some kind of physical parameter to obtain a volcano plot\textsuperscript{36}. Volcano plots can be obtained for numerous reactions in many different forms dependent on parameters chosen for the investigation. The first time a volcano plot was made for the methanation reaction, the activity was plotted versus the heat of CO adsorption for a series of transition metals\textsuperscript{39}. However, when a BEP relation is observed it is normal that a volcano plot can be obtained for methanation by plotting the catalytic activity versus the CO dissociation energy. The volcano plot obtained this way is shown in Figure 2.5.3.1 where the measured activity is plotted for a series of elemental metal catalysts as a function of the dissociation energy on the most active sites of the metals\textsuperscript{37}.
Figure 2.5.3.1 Plot showing a volcano curve that is found when the activity in CO hydrogenation of different metals was plotted to the dissociative CO adsorption energy\textsuperscript{36}.

For the elements on the left leg of the volcano plot, e.g. Fe, the desorption of CO is the rate determining step. The adsorption is strong for these elements. For the elements on the right leg, such as Ni, the dissociation of CO is the rate determining step (weak adsorption). At the top of the volcano optimal conditions for both desorption and adsorptions are found. From the plot it is clear that cobalt and ruthenium are very active catalysts, since they are both located close to the optimum (top point) of the volcano. Furthermore it can be seen that the optimal value of the CO dissociation energy is close to 0.06 eV.

A simple intuitive approach would be to choose a metal which is closer to the top. Ruthenium being one of the ideal metals which is very less affected by sulphur poisoning, very stable at higher temperatures and is inert to carbon formation on the surface of the catalyst.
2.6 Catalyst Support Properties

Typical catalyst supports used in the methanation are oxides such as Al$_2$O$_3$, SiO$_2$, TiO$_2$, ZrO$_2$ etc. Catalyst supports can be inert during the reaction or can participate to yield a better catalyst, as generally judged by activity. Catalyst supports are dealt with comprehensively by Cusumano and others$^{19}$ who considered the subject in terms of the effect of the support on three parameters. They are surface area of the catalyst, thermal stability, and addition of stabilizing compounds.

I. Catalyst Surface Area

It is clearly evident that the higher the surface area, the more effective the catalyst. However, changes in surface area can alter crystallography and for small-enough particle sizes, also alter the electronic structure. Both can alter activity and selectivity.

II. Catalyst Thermal Stability

Loss of catalyst activity can occur through a decrease in active surface area due to sintering of the active metal, collapse of the support, and reaction between the active metal phase and support; all such effects are likely with highly exothermic, reducing reactions such as methanation.

III. Stabilizing Compounds For Catalysts

The addition of the stabilizing compounds to the catalyst system, either to the catalyst or to the support, improves catalyst performance by making it less susceptible to poisoning and by maintaining dispersion. Metals such as barium, tungsten, etc., were added to improve the resistance to sulphur, reduce the formation of carbon on the catalyst surface and improve their stability towards high temperature.
2.6.1 Carbon as Support

Carbon is ubiquitous and one allotrope, graphite, is known to be an active catalyst in reducing reactions. Graphitic carbon may also be used as a support material on which other catalytic components may be dispersed, to optimize their exposure to the chemical reactants. Carbon (graphite) is stable and not prone to defect formation as most oxides are. It is resistant to corrosion and elevated temperatures. By preparative chemistry it can facilitate high catalyst dispersion. Beyond physical properties, from a chemical perspective, carbon is a semi-metal and can readily donate electrons to supported metals. More accurately the electron density within the metal (particle) d-bands is increased. Known in CO dissociation by noble metals is the back-donation of electron charge into the CO $\sigma^*$ anti-bonding orbital. While forward charge transfer occurs from the CO $\pi$ bond, this back transfer is what facilitates CO dissociation upon chemisorption and/or by insertion reactions. A catalyst with “enhanced” electron density can also stabilize H-atoms, thereby promoting H$_2$ dissociation and H-atom mobility.

Graphitic material applications in the vast field of catalysis are very few. The major catalytical use of carbon materials is in the form of charcoals and carbon blacks to support metals. In addition, charcoals are sometimes used to support compounds such as sulfides and halides. Graphite is used to support metals, but the most important feature of graphite is its ability to form intercalates, which are the catalysts for specialized reactions for hydrogenation, dehydrogenation, isomerization, alkylation, hydrodealkylation, polymerization and ammonia formation.
2.6.2 Intercalation

The forces between the layers of carbon atoms in graphite are weak and because of this, certain molecules can penetrate the interlayer spaces and interact strongly with the layers. This phenomenon is termed as “intercalation”. This strong interaction changes the properties of the graphite and can enhance its adsorptivity, and for this reason, some graphite intercalates are catalytically active. Particular interest lies in this phenomenon because conceivably it might provide a means of preparing catalysts for the direct gasification of coal or carbon in steam or hydrogen\textsuperscript{18}.

More directly, it has been claimed that methanation catalysts incorporating graphite intercalated nickel, platinum or palladium are better than conventional catalysts by the metrics of activity, resistance to sulphur poisoning and longevity, the latter attributed to inhibition of particle sintering by the graphite lattice.

2.6.3 Ru/ Carbon Systems

Ruthenium supported on carbon materials, especially nanotubes has been used effectively especially for applications in superconductor materials. Ruthenium oxide supported on various carbon nano-composites was synthesized by different methods which include the colloidal approach\textsuperscript{41}, the sol-gel process\textsuperscript{42}, the impregnation method\textsuperscript{43}, electrochemical oxidation\textsuperscript{43}, the chemical CVD method\textsuperscript{44} and the magnetic sputtering\textsuperscript{45} in an Ar/O\textsubscript{2} atmosphere were used for this application. The carbon composites were first functionalized using strong reagents like nitric acid and sulphuric acid to create the carboxylic functional groups which helped in supporting the ruthenium particles on the surface. The particle size that was obtained using these techniques ranged from 2-10 nm\textsuperscript{44} and up to 80 percent metal loading by weight\textsuperscript{41} was obtained using the
colloidal method. Most of these methods used high surface area carbon materials (activated carbon-1200 m$^2$/g, CNTs- 600-1400 m$^2$/g) as support materials. When using the CNTs, the ruthenium particles were well dispersed on the surface and the particle size that was obtained was about 2 nm$^4$. As the percentage metal loading by weight increased on the support, the particle size of the ruthenium also increased resulting in a decrease of the specific surface area. The use of high surface area materials provided the advantage of increasing the electronic conductivity by at least 46 percent, power density and energy density by at least 8 times when compared to the bare oxide systems used as the composite electrodes.

Another application of using ruthenium on carbon is in the preparation of fuel cells especially direct methanol fuel cells. Mixed-metal catalysts containing Pt, Ru were used as electrodes. Alloys with ruthenium such as PtRuW or Pt$_{44}$Ru$_{41}$Os$_{10}$Ir$_5$ were used$^4$ for support on the graphitic carbon nanotubes for the preparation of the electrodes. Methods such as Ion beam sputtering$^4$, solvent dissolution process$^4$, modified poly-ol process$^9$ etc. Most of these processes produced nano size particles on the carbon nanotube surface with the particle size ranging from 2-6 nm$^8$. The surface of the CNTs were modified using strong acid (90 percent HNO$_3$ or >60 percent H$_2$SO$_4$). Up to 50 weight percent of the metal was deposited on the CNT’s which provided a uniform metal density on the surface. The high conductivity of CNTs, good catalyst morphology and suitable catalyst composition were the key factors for the preparation of the electro catalysts$^{51}$. These catalyst-enhanced electrodes increased the cell performance by increasing the power density by 68 percent when compared to the traditional Pt/carbon electrodes$^{50}$.

Ruthenium on carbon was also used in the catalysis in the oxidation of alcohols, synthesis of ammonia, and conversion of synthesis gas to diesel fuel (as a Fischer-Tropsch catalyst). The
experimental conditions and some of the results obtained for these reactions are listed in table 2.6.2.1.

**Table 2.6.2.1 Summary of catalytic systems with Ru/C.**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Catalyst</th>
<th>Pretreatment</th>
<th>Experimental Conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis gas to diesel fuel(^{52})</td>
<td>Ru/CNT* prepared by impregnation, Ru particle size 6.2nm, 30 weight percent Ru/CNT.</td>
<td>Reduction in H(_2) gas at 573 K for 2 h.</td>
<td>H(_2)/CO :: 1:1 Flow rate=20 ml/min P= 2 MPa, T=533 K, t=10 h.</td>
<td>34 (Ru/CNT) 100 (overall) .2</td>
</tr>
<tr>
<td>Oxidation of alcohols(^{53})</td>
<td>Ru/ Activated carbon*, 10 weight percent Ru/C.</td>
<td>-</td>
<td>To oxidize alcohols in toluene at 50°C in oxygen</td>
<td>93 99 (after 5h) -</td>
</tr>
<tr>
<td>Ammonia synthesis(^{54,58})</td>
<td>Ru/ activated Carbon* prepared by impregnation in rotary evaporator. Ru content was 8</td>
<td>Reduction in H(_2) at 450°C for 2 h.</td>
<td>H(_2)/N(_2)= 3, P=3 MPa, T=450°C, t= 6h.</td>
<td>100 95 .034-.036</td>
</tr>
<tr>
<td>Hydrogenation of n-butane&lt;sup&gt;55&lt;/sup&gt;</td>
<td>weight percent, 10 nm.</td>
<td>Reduction in 10 percent H₂/He gas mixture at 400°C for 2 h.</td>
<td>H₂/n-butane :: 10/1, T=500°C, t=2 h</td>
<td>93</td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>------------------------</td>
<td>-------------------------------------------------</td>
<td>---------------------------------</td>
<td>-----</td>
</tr>
<tr>
<td>Ru/carbon prepared by incipient wetness method, with 2 weight percent Ru, particle size of Ru was 3.4 nm.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The carbon support was first pretreated with a strong acid (mostly HNO₃) to oxidize the surface of the carbon and create the surface oxygenated functional groups.

The use of the carbon materials as support in heterogeneous catalysis is because of their specific characteristics<sup>56, 57</sup> such as high resistance to acid/basic media, ability to control certain limits of the porosity and surface chemistry, and easy recovery of precious metals supported on the carbon by burning the support. New support materials in carbon have always been explored for their high specific surface area. One such material of interest is Graphene Oxide.

### 2.7 Choice of Support: Graphene Oxide

During the last half decade, chemically modified graphene (CMG) has been studied in the context of many applications, such as polymer composites, energy-related materials, sensors, paper like materials, field-effect transistors (FET), and biomedical applications, due to its excellent electrical, mechanical, and thermal properties<sup>58, 59</sup>. These chemical modifications begin with graphite oxide (GO). Fig. 2.7.3.1 illustrates its structure(s) and production methods.
Graphene oxide contains a range of reactive oxygen functional groups, which renders it a good candidate for use in the aforementioned applications (among others) through chemical functionalization.

2.7.1 Synthesis History of Graphene Oxide (GO)

GO has a history that extends back many decades to some of the earliest studies involving the chemistry of graphite\textsuperscript{61-63}. There are three main approaches done to synthesize GO in the history. The first was in 1859 by a British chemist B. C. Brodie who was exploring the structure of graphite by investigating the reactivity of flake graphite. In his reactions with “potash of chlorate” (KClO\textsubscript{3}) and slurry of graphite in fuming nitric acid (HNO\textsubscript{3}), he determined the final material was composed of carbon, hydrogen and oxygen and resulted in an overall increase in mass. He also found that this material was easily dispersible in pure or basic water but not in acidic media and hence he named it as “Graphic acid”.

After 40 years, the second attempt to synthesize GO was made by L. Staudenmaier. He improved the process by adding the chlorate in multiple stages during the course of the reaction rather than in one single addition. This slight change in the procedure resulted in an overall extent of oxidation similar to Brodie’s multiple oxidation approach\textsuperscript{65}.

Nearly 60 years after Staudenmaier, Hummers and Offeman developed an alternate oxidation method by reacting graphite with a mixture of potassium permanganate (KMnO\textsubscript{4}) and concentrated sulfuric acid (H\textsubscript{2}SO\textsubscript{4}), again achieving similar levels of oxidation\textsuperscript{66}. Though others have developed slightly modified versions, these three methods comprise the primary routes for forming GO, with few modifications thereafter.
The products of these reactions show strong variability, depending not only on the particular oxidants used, but also on the graphite source and reaction conditions. Because of the lack of understanding of the direct mechanisms involved in these processes, parallels of processes are drawn from other systems. For example, Brodie and Staudenmaier used KClO₃ and nitric acid (most commonly fuming at greater than 90 percent purity) treated together. Nitric acid is a common oxidizing agent (e.g., aqua regia) and is known to react strongly with aromatic carbon surfaces. The reaction results in the formation of various oxide-containing species including carboxyls, lactones, and ketones. KClO₃ is a strong oxidizing agent and typically used as an in-situ source of di-oxygen, here, serving as the reactive species.

2.7.2 Structural Models Of GO

Understanding the structural model of GO is important as it gives information about the functional groups on the surface of GO which are of real value in the decoration of any metal on the surface of GO. The chemical structure of GO has been the subject of considerable debate over the years and even till today, no unambiguous model exists. The primary reason for this is the complexity of the material due to its amorphous nature, non-stoichiometric atomic composition and the lack of precise analytical techniques for characterizing such materials. Early structural models were based on elemental composition, reactivity and X-Ray diffraction studies. The first proposed structure by Hofmann and Holst’s consisted of epoxy groups spread across the basal planes of graphite which were arranged in a sp² hybridized system. Later, Ruess proposed a variation of this model by accounting the hydrogen content of GO, altering the basal plane structure to an sp³ hybridized system, with the epoxides in the 1,3 positions and a hydroxyl group in the 4 position forming a regular lattice in the carbon ring structure. In 1969, Scholtz and Boehm suggested a model which removed the epoxide and the ether groups, substituting regular
quinoidal species in a corrugated backbone \cite{72}. Another model by Nakajima and Matsuo relied on the assumption of a lattice framework which formed 2-stage graphite intercalation structures \cite{73,74}. Figure 2.7.3.1 shows all the proposed structures.

![Graph of structural models of GO](image)

**Figure 2.7.3.1** Picture showing the summary of the structural models of GO\cite{71-74}

Recent models on GO have rejected the lattice-based model and have focused on a nonstoichiometric, amorphous alternative. The most well-known model is one by Lerf and Klinowski. Figure 2.7.3.2 shows the structure of GO proposed. They used solid state Nuclear
Magnetic Resonance (NMR) spectroscopy to characterize the material and to understand the chemical structure\textsuperscript{75}.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Picture showing the variations of Lerf-Klinowski model showing the presence of the carboxylic group at the corners\textsuperscript{75}}
\end{figure}

In their experiments\textsuperscript{75,76}, they found that there was significant interplatelet hydrogen bonding through the alcohols and epoxide functional groups, contributing significantly to the stacked structure of GO. The behavior of water in GO has also been characterized by a neutron scattering experiment confirming that water is strongly bound to the basal plane of GO through the hydrogen bonding interactions with the oxygen in the epoxide of the GO which can be seen in figure 2.7.3.3. These functional groups that are present in GO can be reduced or oxidized depending on the application.
Figure 2.7.3.3 Picture showing hydrogen bonding in the GO layers

2.8 Summary of Literature

The purpose of this study was development and testing of a new Ru-based catalyst system for this reaction with higher activity. Details of the rate laws, e.g., reaction orders or activation energies of elementary steps, were not the focus and so are not reviewed here. Rather for the ISRU application, activity and selectivity are the two key metrics of consideration while developing the catalyst, as described in the following chapters.
CHAPTER 3

EXPERIMENTAL DESCRIPTOR

This chapter presents the catalyst preparation methods, characterization techniques and reactor development. Catalyst preparation includes the synthesis of the support Graphene Oxide (GO), catalyst decoration i.e., decorating ruthenium on GO, alumina, and on the mixed catalyst system (GO and alumina). Catalysts have been characterized with Field Emission Scanning Electron Microscopy (FE-SEM) and Transmission Electron Microscopy (TEM) to characterize dispersion and for measurement of particle size. X-ray Photoelectron Spectroscopy (XPS) identified the Ru elemental state and GO elemental content. A new micro-channel methanation reactor with hierarchical structure was fabricated for the hybrid Ru-GO catalysts. Reactant conversion of carbon monoxide and hydrogen into methane and water was measured by gas chromatography (GC). The outline for this chapter is given below:

3.1 Catalyst Synthesis

3.2 Catalyst Characterization

3.3 Micro Channel Methanation Reactor

3.4 Catalyst Packing in the Reactor

3.5 Gas Analysis by Gas Chromatography (GC)
3.1 Catalyst Synthesis

The catalyst preparation was performed in a two-stage process. In the first stage, the support material, Graphene Oxide (GO), was synthesized using the modified Hummers process. In the second stage, this prepared support material was decorated with Ruthenium using a Polyol process. With the commercially purchased alumina support material, only the second stage decoration process was applied. The various materials used for the synthesis of the Graphene Oxide (GO) and the catalysts based on Ruthenium are listed in the table 3.1.1.

Table 3.1.1. The list of materials used and their suppliers for the synthesis.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>Phase</th>
<th>Purity</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Graphite Powder</td>
<td>G.P.</td>
<td>Solid</td>
<td>99.99%</td>
<td>Reade Inc.</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>C₂H₆O₂</td>
<td>Liquid</td>
<td>98%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Nickel Chloride Hexa Hydrate</td>
<td>NiCl₂.6H₂O</td>
<td>Solid</td>
<td>99.999%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Alumina nano powder (&lt;50 nm)</td>
<td>Al₂O₃</td>
<td>Solid</td>
<td>99.98%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Sulphuric Acid</td>
<td>H₂SO₄</td>
<td>Liquid</td>
<td>98%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Hydrochloric Acid</td>
<td>HCl</td>
<td>Liquid</td>
<td>70%</td>
<td>VWR Inc.</td>
</tr>
<tr>
<td>Potassium Permanganate</td>
<td>KMnO₄</td>
<td>Solid</td>
<td>&gt;99%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Potassium peroxydisulphate</td>
<td>K₂S₂O₈</td>
<td>Solid</td>
<td>&gt;99%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>H₂O₂</td>
<td>Liquid</td>
<td>30%</td>
<td>VWR Inc.</td>
</tr>
<tr>
<td>Phosphorous Pentoxide</td>
<td>P₂O₅</td>
<td>Solid</td>
<td>99.99%</td>
<td>Sigma Aldrich</td>
</tr>
</tbody>
</table>
3.1.1 Synthesis of Graphene Oxide (GO)

GO, used as a support material, was synthesized by the modified Hummers process\(^6\). Few changes were made to the initial oxidation process of the natural graphite. Different reagents were used to enhance the number of the (oxygen) surface functional groups relative to the original method. The synthesis procedure follows.

**Synthesis of GO by the Modified Hummers Process**

1. Natural graphite powder of 1 g was added to 1.5 ml of concentrated H\(_2\)SO\(_4\) and kept aside. Later, 0.5 g of K\(_2\)S\(_2\)O\(_8\) and 0.5 g of P\(_2\)O\(_5\) were added to this mixture and stirred with a glass rod. The mixture then changed color from black to dark blue, indicating the start of the reaction.

2. This mixture was thermally isolated for 6 hours so that the temperature of the solution could be brought down to room temperature.

3. When the solution temperature is near ambient (room) temperature, it is then diluted with about 40 ml of D.I. water.

4. This solution was then vacuum filtered and washed simultaneously with D.I. water until the pH of the filtrate was neutral.

5. The collected filtrate was dried overnight at ambient temperature on a hot plate to eliminate any presence of water. This drying process takes about 12-14 hours to get a moisture-free sample. The temperature for drying should not be raised more than 50\(^\circ\)C. This dried material is the oxidized graphite powder which can be used for the synthesis of GO.
6. About 1 g of the oxidized graphite powder was added to a beaker containing 23 ml of sulphuric acid (H₂SO₄), which was maintained at 0°C by an ice bath as a safety measure.

7. Using a magnetic stirrer, 3 g of KMnO₄ was added to the solution while slowly stirring and cooling. The rate of addition was controlled carefully to prevent the temperature of the suspension from exceeding 20°C.

8. After the addition of KMnO₄, the ice bath was removed and the temperature of the suspension was allowed to reach 35°C. It was then stirred continuously for 2 hours while maintaining the temperature at 35°C.

9. As the reaction progressed, the mixture gradually thickened with a diminishing effervescence. Before reaction completion, the mixture became pasty with the evolution of a small amount of gas. This paste was brownish grey in color, an indicator of reaction completion.

10. Next 46 ml of D.I. water was added to this paste slowly (over ~ minute) which caused a violent effervescence and the temperature rose to ~ 98°C. This diluted solution turned brown in color and was maintained at this temperature for about 30 minutes.

11. The reaction was terminated completely by dilution with 140 ml of D.I. water and 2.5 ml of 30% hydrogen peroxide (H₂O₂) solution. The H₂O₂ was added to reduce the residual permanganate and manganese dioxide to colorless, soluble manganese sulfate. After the addition of the H₂O₂, the color of the diluted solution changed to bright yellow.

12. The suspension containing the manganese sulfates was filtered out resulting in a yellow-brown filter cake. This filtering was conducted while the suspension was still warm to avoid the precipitation of the slightly soluble salt of metallic acid that had formed as a side reaction.
13. This yellowish-brown cake is mainly GO yet it contains a substantial content of metal-ion impurities, accounting for the observed color. This cake was subjected to a three stage washing process.

14. A series of multiple rinsing stages was done with D.I. water, a 1:10 HCl solution, ethanol followed by filtration and centrifugation. The HCl solution was used to remove the metal ions introduced during the preparation process. The final solution pH was measured closer to 6, suggesting washing was complete. This procedure typically takes about 2-3 weeks.

15. Upon conclusion of the washing process, the sample was vacuum filtered. Most of the water was removed leaving the GO with little bound moisture.

16. This GO with little bound moisture was then dried under vacuum keeping the temperature below 40°C until obtaining a clean and dry GO powder.

17. The GO was then characterized using TEM to determine sheet separation and XPS to identify oxygen functional groups.

3.1.2 Synthesis of Ruthenium Decorated Catalysts by Poly-Ol Process

The GO produced by the modified Hummers process along with alumina nanopowder were used as the support material for the synthesis of the catalysts. Ruthenium metal was decorated on these supports using a nickel (cation) activation process. The overall process is known as the Poly-ol process because ethylene glycol is used as a primary reducing agent. A similar procedure was repeated to synthesize all the catalysts Ru-GO, Ru-Al₂O₃, Ru-(GO+Al₂O₃). A synthesis protocol for the poly-ol process is listed below.
Poly-ol Process Using the Ni-Ion Activation Method

1. A 0.04 M Nickel chloride in ethylene glycol solution was made by weighing 0.305 g of nickel chloride and was put in 32 ml of ethylene glycol, which was kept under constant stirring. This is a light green colored solution.

2. About 0.1 g of GO was taken in a 50 ml beaker and 32 ml of the prepared 0.04 M nickel chloride in ethylene glycol solution was added to it, and it was sonicated for about 7 minutes for even distribution of the sample in the solution.

3. After 7 minutes, this was placed in a silicone oil bath which was heated to 150°C, and the solution was maintained for 4 hours under this temperature.

4. The obtained mixture was filtered using a vacuum filter and then washed with ethanol to remove all the ethylene glycol. This filter cake was dried overnight under vacuum at 50°C.

5. The solid content obtained after the drying was then re-dispersed in 32 ml ethylene glycol solution and 0.3 g of the ruthenium precursor i.e., ruthenium chloride hexahydrate (RuCl$_2$.6H$_2$O) was added to this solution. This was again sonicated for 7 minutes so that the ruthenium precursor was dispersed uniformly along with the reduced GO. This is a yellowish-green colored acidic solution with a pH closer to 2.5.

6. The pH of this solution has to be adjusted to ~8 so that the reduction of the functional groups on the surface of the support and the simultaneous replacement of the ruthenium metal would be easier in a slightly basic medium. Hence, the pH was adjusted to 8 using 1 M sodium hydroxide (NaOH) solution and by continuous monitoring of the pH with the help of a pH meter. Care has to be taken while approaching the pH closer to 7 as even a little (1ml) addition of NaOH would result in a very big change of pH.
7. This adjusted solution was then heated to 118°C in a silicone oil bath and maintained at this temperature for at least 30 minutes so that the moisture present in the solution was evaporated and then the temperature was instantly raised to 160°C and was maintained for 4 hours.

8. The final sludge obtained was again filtered under vacuum and washed with ethanol several times to remove all the chloride ions present in the sample. Removal of chloride ions from the sample is important as it might interfere during the reaction. Presences of chlorides only reduce the performance of the catalyst. Hence to remove all the chlorides, it was washed several times with ethanol. A clear filtrate solution was observed when there were no chlorides in the sample. This color change of the filtrate from yellow to white showed that the chlorides were removed completely.

9. The product obtained after the filtration was dried in vacuum and the final dried catalyst sample was characterized using different techniques.

As listed in the objectives, four different catalysts were synthesized i.e., Ru/GO, Ru/Al₂O₃, the chemically mixed Ru/ (GO+ Al₂O₃) and the physically mixed Ru/GO+ Al₂O₃ with the same process and same initial mass. The term chemically mixed involves the introduction of alumina at the initial stage of the Poly-ol process and physically mixed is the introduction of alumina at the ruthenium decoration stage in the Poly-ol process.

3.2 Catalyst Characterization

The synthesized catalysts were first characterized by FESEM and TEM to identify the ruthenium metal areal density, i.e. dispersion on the GO support, and the Ru particle size. EDS and XPS in elemental survey mode validated Ru presence and chemical state. By TGA the total
amount of ruthenium present in the catalyst sample was calculated. The instruments used and the sample procedures are given below for each technique.

3.2.1 Electron Microscopy and Field Emission Scanning Electron Microscopy (FE-SEM)

To obtain the high-resolution images of the catalyst samples, Field Emission Scanning Electron Microscopy (FE-SEM) and Transmission Electron Microscopy (TEM) were used. FESEM provided surface images of the sample, as did TEM but at the nano level. Detailed information regarding the instruments is given below.

SEM is a non-destructive method of analyzing the sample topography in which the surface features of the sample are observed by electrons scattering off the surface (in so-called “backscatter” mode). Sensors collecting the electrons form an image of the object on the screen. The instrument used for this analysis is a FE-SEM Leo 1530 (Zeiss Inc). The Leo 1530 is a fully software-controlled high-resolution SEM. The sample was mounted on a stage using a two-side copper tape. High resolution images were collected and processed by the software in between the operating voltages of 1 keV and 14 keV. Depending on the catalyst sample, the operating voltages were adjusted for images of best contrast without compromising the resolution. The specially designed GEMINI column in the SEM features a beam booster that facilitates rapid image acquisition, thereby reducing beam sensitivity to stray magnetic fields at lower operating voltages (<5 keV).
3.2.2 Transmission Electron Microscopy (TEM)

To calculate the particle size, dispersion and the metal density of the ruthenium at the nano level, TEM was used. TEM gives a detailed view of catalyst morphology as the Ru metal had a nanoparticle resolution (as observed from FESEM).

Sample Preparation

For TEM analysis, the sample needs to be supported on TEM grids. In this case a lacy carbon TEM grid was used to support the sample. A Small quantity of the catalyst sample (~0.01µg) was deposited in a small vial and about 10 ml of ethanol was added to it. This mixture was sonicated for 15 minutes giving a uniform dispersion of the catalyst sample in the ethanol. This solution was then dropped on the lacy carbon grids using a 1 ml dropper and was left to open air for the evaporation of ethanol. This natural drying of the grids allows the sample to stick on the surface of the grids, aided by capillary action.

The TEM instrument was a Philips (FEI) EM420T (Tungsten Emitter) operated at an accelerating voltage of 120 kV. The objective lens with a point-to-point (Scherzer) resolution of 0.34 nm and a spherical aberration coefficient of 3 mm and a 5-nm probe size was used in convergent beam mode. The tilt angle for the objective lens was maintained at 0° which could be changed up to ±60° depending on the sample orientation on the grid. A single tilt sample holder was selected among the various sample holders that were available to place the sample TEM grids into the instrument. Depending on the sample, the magnifications were varied between 40k and 120k to collect the images.
After the TEM analysis, the images collected were analyzed by an ImageJ, freeware/shareware software tool to calculate the particle size distribution. Several particles were analyzed for size and statistics were calculated.

3.2.3 Energy Dispersive X-Ray Spectroscopy (EDS/EDX)

Energy Dispersive Spectroscopy (EDS) is a standard procedure for identifying and semi-quantifying elemental composition of sample areas as small as a few cubic micrometers. Characteristic X-rays that are produced when the sample is bombarded with high energy electrons in an electron beam instrument (in this case a transmission electron microscope (TEM)) Detection of these X-rays can be accomplished by an energy dispersive spectrometer, a solid state device that discriminates among characteristic X-ray energies.

The EDS instrument was attached to the Phillips 420 TEM. To use the EDS, the sample holder was rotated to 30° so that the EDS instrument could collect the X-rays that would be emitted from the sample. By detecting these characteristic X-rays, a plot was generated in the DTSA software package which identifies and quantifies the individual elements.

3.2.4 Thermo-Gravimetric Analysis (TGA)

To determine the content of Ruthenium (Ru) present on the GO, thermo-gravimetric analysis (TGA) was used. Thermal gravimetric analysis is the act of heating a mixture to a high-enough temperature in the presence of an oxidizing gas (typically air or oxygen) so that one of the components completely decomposes. It is a process that utilizes heat and stoichiometric ratios to determine the percent by mass ratio of a solute. If the compounds in the mixture that remain are known, then the percentage by mass can be determined by taking the weight of what is left in the mixture and dividing it by the initial mass. Knowing the mass of the original mixture
and the total mass of impurities liberated upon heating, the stoichiometric ratio can be used to calculate the percent mass of the substance in a sample.

The instrument used to perform the TGA measurements was a TA Instruments model SDT Q600. It is designed on a horizontal furnace-and-balance system with a dual-beam balance. The balance sensitivity is as low as 0.1 µg, giving accurate measurements even for the lowest of the masses that could be burned off in the instrument. Alumina sample pans were used for the analysis in which the samples were placed. Approximately half of the volume of the pans (40 µL) was filled with the catalyst sample. The mass for each of the catalyst samples differed as Ru-GO was less dense when compared to the other catalyst (Ru-Al$_2$O$_3$, Ru-(GO+Al$_2$O$_3$)). The furnace operations were controlled by software in which the sample conditions were entered manually. Table 3.2.4.1 shows the operation conditions for the TGA analysis.

**Table 3.2.4.1 Conditions for TGA**

<table>
<thead>
<tr>
<th>Carrier Gas</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial temperature</td>
<td>30°C</td>
</tr>
<tr>
<td>Final Temperature (for heating)</td>
<td>800°C</td>
</tr>
<tr>
<td>Ramp Rate</td>
<td>20°C/min</td>
</tr>
<tr>
<td>Cooling Gas</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Final Temperature after cooling the furnace</td>
<td>30°C</td>
</tr>
</tbody>
</table>

The weight-loss curve as a gradient of temperature is obtained with the help of the software that monitors the status of the experiment.
3.2.5 X-Ray Photoelectron Spectroscopy (XPS)

The elemental composition on the surface and the state at which the ruthenium was present in the sample was analyzed by XPS. The XPS analysis was done on a Kratos Analytical Axis Ultra instrument which had a 15-nm special resolution, using a monochromatic Al-\(\alpha\) (1486.6 eV) X-ray source operated at ultra-high vacuum conditions (\(10^{-8}\) bar). The instrument is capable of detecting a wide variety of elements ranging from Lithium to Uranium with a sensitivity of 0.01-0.5% (atomic) corresponding to the elements. The sample surface was oriented normal to the analyzer entrance, which had an analysis area of 1mm x 1.5 mm. The instrument sampling depth varied between 0 – 10 nm.

Elemental survey scans were collected at low resolution and the spectra processed by a commercial software package known as CASA-XPS. The elemental identification and the peak assignment were done to identify the different elements that are present in the sample. High-resolution scans were done over carbon C1s and ruthenium Ru3d energy levels to identify the functional groups and the chemical state of ruthenium. This technique can be quantitative, yet with a caveat as some of the elements have overlapping spectral lines. In this case, the Ruthenium and carbon 1s lines have the same binding energy of 284 eV and hence the elemental composition could not be quantified from this technique.

3.2.6 Brunauer-Emmett-Teller (BET)

The BET nitrogen physisorption method is the most common method of measuring surface area and pore volume in catalysis. BET analysis yields the total surface area of the support and the active metal. A Micromeritics adsorption surface analyzer (GeminiTM V-Series) with ultra-pure nitrogen (99.995% N2, from Praxair) as the adsorbate was used. Prior to analysis,
each catalyst sample was evacuated at 80°C under vacuum to ensure that there was no adsorbed moisture and atmospheric gases such as CO₂ on the catalyst surface. The adsorption and desorption isotherms in the evaluation of the BET surface area were obtained at the boiling temperature of liquid nitrogen (-195°C). The data points were collected by spanning the pressure ratio (P/P₀) from 0.1 to 0.2. Measurement in this range of pressure ratio corresponds to a linear region suitable for the BET equation (see equation (3.2.5)). This equation assumes monolayer capacity of adsorbate on the material surface. The catalyst as synthesized was used for this analysis.

\[
\frac{P}{(P₀-P)V} = \frac{1}{CV_m} + \frac{(C-1)P}{C V_m P₀} \quad \text{………… (3.2.5)}
\]

Where,

\[V = \text{volume of gas adsorbed at pressure } p\]
\[V_m = \text{volume of gas adsorbed in monolayer}\]
\[P = \text{gas pressure}\]
\[P₀ = \text{saturation pressure of adsorbed gas}\]
\[C = \text{a constant related exponentially to the heats of adsorption and liquefaction of the gas}\]

### 3.2.7 X-Ray Diffraction Analysis

To determine the crystalline structure of the Ru on the GO, XRD was attempted. X-ray Diffraction is an analytical technique that utilizes the wavelength of the X-ray beam and the physics of diffraction that determine how a beam interacts with organized matter. Classically,
the technique has been applied primarily to well-ordered crystalline materials to determine crystal structures, identify phase composition as well as measure stress, preferred orientation and crystallinity, but the field is rapidly expanding into the characterization of non- or semi-crystalline materials including polymers, nanoparticles, and biological materials.

3.2.8 Inductively Coupled Plasma Spectrometry (ICP) Analysis

To determine the elemental composition of the sample, Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) was used. An inductively coupled plasma spectrometer is a tool for trace detection of metals in solution, in which a liquid sample is injected into argon gas plasma contained by a strong magnetic field. The instrument used in this case is a Perkin-Elmer Optima 5300DV. The ICP-AES and ICP-MS can only be used on solutions. Hence, it is necessary to dissolve solid samples prior to analyses. Two techniques, acid digestion and salt fusion were tried to dissolve the sample. Details regarding the procedure for the digestion and the results obtained are listed in the Appendix A.

3.3 Micro Channel Methanation Reactor

3.3.1 Microchannel Methanation Reactor Assembly

To carry out the hydrogenation activity measurements, a microchannel methanation reactor was used. The reactor design and parts are straight forward, consisting of a tube and compression fittings. Starting with 316 stainless-steel tubular pipe with a channel dimension of 6.5 in x 0.75 in (O.D.) x 0.69 in (I.D.), two Swagelok fittings were attached to each, end providing the inlet for the gaseous mixture and an outlet to collect the product effluent gases after reaction.
CO and H$_2$ reactant gas flows are regulated by mass-flow controllers using separate lines that then merged at the reactor. An additional on/off valve at the CO inlet provides additional control. The reactor was wrapped with a heating tape and a temperature regulator was attached to this heating tape, which maintained the required temperature. An insulation overwrap on this reactor heating tape minimized the heat losses in the reactor and aided temperature stability. The inlet tubing, which preceded reactant mixing, was also covered with the heating tape to separately preheat the gases before entering the reactor. This preheating helped to maintain a constant temperature throughout the catalyst bed. The exit end of the reactor is connected to small stainless-steel tube for periodic gas sampling by tedlar sampler bags for GC measurements.

![Figure 3.3.1.1](image)  

**Figure 3.3.1.1** Photograph showing the methanation reactor

The methanation reactor without the heating element is shown in figure 3.3.1.1. The white lines in the figure show the position of the aluminum foams that were placed in the reactor. The voids after inserting the aluminum foams are filled by glass wool. This packing is important
to ensure that gases flow only through the foams containing catalyst. Apart from the practical consideration of increasing contact time between gases and catalyst, such continuity is presumed for calculations of catalyst activity. The reactor assembly system with all the heating tapes, heating controllers and the gas lines is shown in figure 3.3.1.2.

![Figure 3.3.1.2](image.png) Photograph showing the reactor with the heating element components.

**3.3.2 Hydrogenation Activity Measurements**

The hydrogenation activity tests are performed in the methanation reactor. Initially the reactor was tested for gas leaks through the fittings. Subsequently several tests were made to identify a suitable heating methodology for the reactor, under gas flow, to ensure the optimum parameters for the catalyst activity measurements. Aspects included heating tape coverage, insulation overcoat and pre-heating of reactant gases.
At the start of each test series using a new catalyst (Ru-GO, Ru-Al₂O₃, Ru-(GO+Al₂O₃), Ru-(GO+Al₂O₃ (no Ru))), a pre-treatment was performed by heating the catalyst under flowing H₂ (300 SCCM) at 300°C for 3 hours. Thereafter tests for activity and stability were conducted, at 410°C, during which CO was introduced. The total (gas)-feed flow rate was set to achieve a gas hourly space velocity of 4100 and 16400 h⁻¹. Figure 3.3.2.1 shows the sample collection from the reactor into the Tedlar sample bags just before introducing the CO into the reactor. The samples were collected at intervals of 45 minutes with GC analyses made immediately thereafter for best accuracy. Carbon monoxide, methane and carbon dioxide were the primary products in all tests. The reactant conversion was calculated on the basis of CO consumption. Turnover frequencies were calculated based on the number of moles of CO converted by 1 mole of total ruthenium per unit time.

Figure 3.3.2.1 Image showing the sample collection into the tedlar sample bags
3.4 Catalyst Packing in the Reactor

3.4.1 Duocel Aluminum Foams

Duocel is a true metal skeletal structure which is not a sintered, coated, or plated product and is commercially available from ERG Corp. Figure 3.4.1.1 shows the structure of the Duocel aluminum foams that was used before the catalyst decoration.

![Figure 3.4.1.1](image1.png)

**Figure 3.4.1.1** Photograph showing Duocel aluminum foam.

Duocel foam shares desirable properties such as corrosion resistance, intrinsic strength, electrical and thermal conductivity and can be coated, internally, with ease. Moreover their open-cell structure offers little flow resistance.

![Figure 3.4.1.2](image2.png)

**Figure 3.4.1.2** Magnified image showing the pore and cell structure of the Duocel foam.
Figure 3.4.1.2 shows the pore and the cell structure for the foam. The polygonal opening through each window is termed as a “Pore”. The number of these pores that would subtend to one inch is designated as the foam "pore size or pore density” and is measured in pores per inch (PPI). Aluminum foams with a pore size ranging from 5 to 40 PPI were available as standard materials. In this case, a 40 PPI was used to support the catalyst. As the PPI value increases, the foam appears less coarse and less open which in turn increases the specific surface area of the foam. The specific surface area is a measure of surface area per volume of the foam. The specific surface area increases with an increase in PPI. For the 40 PPI foam, the specific surface area was 48 in$^2$/in$^3$.

**3.4.2 Catalyst Packing in Duocel Aluminum Foams**

After characterization, catalysts were packed in Duocel aluminum foams to further increase the contact area of the input gases with the catalyst. A thin film formed within the foam. This is accomplished by performing vacuum impregnation. The catalyst samples were first dissolved in 10 ml of ethanol. This mixture was sonicated for 10 minutes, sufficient for thick slurry to form. This was immediately applied on the foams with the assistance of a vacuum filter setup. The foam was mounted on the filter top and an anodic filter was placed at the bottom so to collect the excess material (valuable catalyst) that emerged from the foam. The foam was centered in a wax paper that retained the slurry upon the foam sides rather than flow from them. This was repeated until all the material was distributed evenly across four foams. These foams were weighed initially before the start of the impregnation process and at the end of the process to give the exact amount of catalyst infiltrated into each of the foams.
3.5 Gas Analysis by Gas Chromatography (GC)

The gas mixture from the methanation reactor was collected within one-liter Tedlar gas sampler bags purchased from Supelco Inc. A GC equipped with a thermal conductivity detector (TCD) was used in this case to analyze the gas samples. The GC was a Shimadzu-17, equipped with a flame ionization detector (FID) and TCD detectors. It was operated under computer control using the software called “GC REAL TIME ANALYSIS” for monitoring detector status and for controlling the GC parameters. The control program is selected in the software with the analysis uploaded onto the GC. As hydrocarbons such as methane cannot be detected by FID, only the TCD was used for analyses. After the gas samples were collected in the Tedlar bags, they were injected into the GC using a 500-µL syringe. A 15’ × 1/8” stainless-steel-packed-bed column containing 60/80 mesh Carboxen 1000® (carbon molecular sieve particles, Supelco Inc.) separated the gas mixture into its components: H₂, N₂, CO, CO₂ and CH₄. Helium served as a carrier gas and reference gas. Detailed operating conditions of the GC are given in Table 3.5.1.

**Table 3.5.1** Operation conditions for G.C

<table>
<thead>
<tr>
<th>Carrier Gas (Helium)</th>
<th>30 ml/ min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference Gas (Helium)</td>
<td>30 ml/min</td>
</tr>
<tr>
<td>Injector port temperature</td>
<td>200°C</td>
</tr>
<tr>
<td>Detector temperature (TCD)</td>
<td>200°C</td>
</tr>
<tr>
<td>Detector signal</td>
<td>25 mV - 800 mV</td>
</tr>
</tbody>
</table>

In order to elute the products in a discernable and timely manner, a pre-specified temperature program was utilized as shown in Table 3.5.2. The program was set only to 23
minutes as there was no TCD signal beyond that point indicating absence of C₂ or higher molecular hydrocarbons.

**Table 3.5.2** Conditions of the temperature program of the GC.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>RATE (°C/min)</th>
<th>Hold Time (min)</th>
<th>Total Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>-</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>200</td>
<td>20</td>
<td>2.5</td>
<td>18.25</td>
</tr>
<tr>
<td>200</td>
<td>-</td>
<td>5</td>
<td>23.25</td>
</tr>
</tbody>
</table>

The TCD response (peak area) of the GC was calibrated using a custom standard gas mixture obtained from Supelco Inc. This standard mixture was first analyzed in the GC before introducing the sample gas. Table 3.5.3 shows the composition of the Scotty-certified calibration gas used. After the signal was collected over a period of time, the analysis with GC was done with offline software called “GC POST ANALYSIS”. The corresponding peaks are automatically calculated by the software and the respective peak areas corresponding to the gas components are integrated. These peak areas can be converted to volume % by reference to a calibration gas standard and measured injection volume.
Table 3.5.3 Composition of the calibration gas mixture.

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>CONCENTRATION (Vol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide</td>
<td>5</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>5</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>4</td>
</tr>
<tr>
<td>Oxygen</td>
<td>5</td>
</tr>
<tr>
<td>Methane</td>
<td>5</td>
</tr>
<tr>
<td>Helium</td>
<td>72</td>
</tr>
</tbody>
</table>

Procedure for the GC Analysis

1. The temperature program conditions as listed in table 3.6.2 is first loaded in the GC Real Time Analysis software.

2. A batch file is then created for the data collection from the GC which included details of various parameters such as the number of runs, sample ID, type of detector that can be used.

3. The analysis starts with a blank run, a standard run using a standard gas mixture for calibration, followed by the sample run to be analyzed.

NOTE: A blank run always is performed prior to the start of the analysis because it cleans up (i.e. sweeps out) unwanted species that are present in the column from the previous run and also serves to stabilize the base line.
4. The gases of interest are H₂, CO, CO₂ and CH₄. The area occupied by these gases for the standard mixture is for quantification of later analyses.

5. The sample gas is then injected with the spectrum collected over the same temperature program. As described, the peak areas are calculated for each individual species of interest with the aid of the GC Post Run Analysis software.

6. These measured areas are ratio’ed against those of the standard to obtain the species concentration in the mixture.
CHAPTER 4

RESULTS AND DISCUSSIONS

The results obtained from the experimentation are divided into various sections detailing each step of catalyst preparation in the context of catalyst performance measurements thereof. This chapter begins with oxygen functional group characterization, the starting point for the catalyst decoration by the Poly-ol process. Its effectiveness is then gauged by the dispersion of the Ru catalyst. The metal nanoparticle distribution upon the catalyst contributes to activity and can impact selectivity. Both metrics are studied by the methanation of CO for yield and selectivity. Catalyst longevity was studied to characterize stability and durability under reaction conditions. As outlined previously, varied catalyst formulations were studied for testing the hypotheses, with those results presented here. An overview of the sections include:

4.1 Role of Oxygen Functional Groups
4.2 Ruthenium Nanoparticle Dispersion
4.3 Ruthenium Content in the System
4.4 Hydrogenation Activity Measurements
4.5 BET Surface Area Analysis
4.6 Contribution of Nanopowder Alumina
4.7 Summary
4.1 Role of Oxygen Functional Groups

The dispersion of the metal particles on the surface of the GO is dependent on the available surface functional groups. During GO synthesis, functional groups including carboxylic, carbonyl and hydroxyl are created on both graphene edge sites and on basal surfaces. The latter facilitate the exfoliation of GO, a critical step in realizing high surface area for catalyst support. Upon GO sheet separation, these functional groups, particularly the carboxylic and carbonyl, promote the adsorption of metal ions to serve as nucleators for Ru metal decoration

4.2 Ruthenium Nanoparticle Dispersion

High-resolution SEM and TEM was applied to verify ruthenium nanoparticle dispersion on the catalyst support (GO or Al₂O₃ or mixed) as detailed in sections 4.2.1 and 4.2.2.

4.2.1 Field Emission Scanning Electron Microscopy (FE-SEM)

FE-SEM images were collected to observe catalyst and support topography. Figure 4.2.1.1 shows the high-resolution images of Ru/GO sample. The ruthenium particles are the tiny specks on the surface and the entire surface is GO. Images were collected at a magnification of 147K X and 452K X at a working distance of 1.4 mm.
Figure 4.2.1.1 FE-SEM images of (a) & (b) Ru/GO at different locations on the sample.
Figure 4.2.1.2 FE-SEM images of (a) & (b) Ru/ (GO+Al₂O₃) at different locations on the sample.

Figure 4.2.1.2 shows the FE-SEM images of the mixed catalyst. The tiny specks are the ruthenium particles and the bigger (white appearing) particles are the alumina particles that are...
supported on the GO surface. The images were collected at a different location in the sample and are representative of a broader survey. The resolution of the images is 30 nm and 20 nm respectively. To attempt better visualize the Ru on alumina, a higher beam current was applied.

Figure 4.2.1.3 FE-SEM images of (a) & (b) Ru-\(\text{Al}_2\text{O}_3\) at different locations on the sample.
Figure 4.2.1.3 shows the FE-SEM images of the ruthenium on an alumina catalyst. The ruthenium particles are difficult to identify by contrast. Though of lower atomic number, Z, the Al content of the alumina dwarfs the amount of deposited Ru. Moreover the small size of the Ru particles yields minimal electron backscattering.

4.2.2 Transmission Electron Microscopy (TEM)

TEM was chosen as the other technique to characterize the Ru nanoparticle dispersion on the catalyst support. Finer particle detail could be observed with TEM as its resolution is 1 nm. Figure 4.2.2.1 shows TEM images of the Ru on Al₂O₃. We can see the Ru nanoscale particles on the spherical Al₂O₃ surface.

![TEM image of Ru- Al₂O₃ catalyst.](image)

Figure 4.2.2.1 TEM image of Ru- Al₂O₃ catalyst.

Figure 4.2.2.2 shows TEM images of Ru upon GO. The small dark speckles on the images are the ruthenium particles. At a higher magnification shown in figure 4.4.2 (b), the clear
decoration of the ruthenium particles on the GO surface could be observed which is not so clear in the image 4.2.2.2 (a).

Figure 4.2.2.2 TEM image of Ru-GO catalyst.

Figure 4.2.2.3 shows the TEM images of a Ru-(GO+ Al₂O₃) catalyst. The effect of starting both materials together in the Poly-ol process can be seen in the resulting product; the effect of the mixing of alumina during the start of the process can be observed. The tiny speckles are ruthenium particles and the bigger particles in the images are the alumina particles. The dispersion of the alumina particles between the sheets of GO can be seen in these images. In the magnified image of figure 4.2.2.3 (b), we can see that there is decoration on the alumina particles as well, suggesting that alumina was also decorated along with GO during the Poly-ol process.
Figure 4.2.2.4 shows the TEM images of the Ru-(GO+ Al₂O₃) termed the “physically mixed” catalyst. To study the effect of the alumina in separating the GO sheets, a change in the Poly-ol synthesis process was made to prepare this kind of catalyst. The alumina was introduced into the mixture after the nickel-ion activation step that was performed on the GO. The images clearly show that the alumina particles were not dispersed evenly across the surface of the GO as compared with that of the “chemically mixed” Ru-(GO+ Al₂O₃) catalyst. There were lumps of alumina formed on the surface of the GO and from the figure 4.2.2.4 (b), it is clear that there is no ruthenium present on the surface of the alumina. Such differences
illustrate the superior dispersion by solution dispersion rather than by physically mixing the materials dry.

Figure 4.2.4 TEM images of Ru-(GO+ Al₂O₃ (no ru)) [or physically mixed]

4.2.3 Energy Dispersive Spectroscopy (EDS OR EDX)

EDS was performed on all the catalyst samples to verify the presence of ruthenium decorated by the Poly-ol decoration process. Figures 4.2.3.1- 4.2.3.4 show the EDS spectra of Ru-GO, Ru- Al₂O₃, Ru-(GO+ Al₂O₃) and Ru-(GO+ Al₂O₃ (no Ru)) as collected on the Phillips 420. The elements of interest in these EDS spectra are carbon, ruthenium, oxygen and aluminum. The presence of copper in all the spectra arose from the copper mesh within the Lacey carbon TEM grid, supporting the catalyst particles.
Figure 4.2.3.1 TEM-EDS spectra as collected for Ru-GO.

Figure 4.2.3.2 TEM-EDS spectra as collected for Ru-Al₂O₃.
Figure 4.2.3.3 TEM-EDS spectra as collected for Ru-(GO+Al₂O₃)

Figure 4.2.3.4 TEM-EDS spectra as collected for Ru-(GO+Al₂O₃) physical mixture catalyst
4.2.4 X-Ray Photoelectron Spectroscopy (XPS)

Elemental analysis was done over the samples to verify the elemental state of ruthenium. Figures 4.2.4.1 to 4.2.4.4 show the spectra obtained from the survey analysis over the catalyst samples. Figure 4.2.4.1 is the elemental survey of GO only. Only the carbon and the oxygen peaks are evident.

![Image of a graph showing the survey analysis of GO](image.png)

**Figure 4.2.4.1** Elemental survey for GO
4.2.4.2 Elemental survey for Ru-GO

Figure 4.2.4.3 Elemental survey for Ru-\text{Al}_2\text{O}_3
Figures 4.2.4.2- 4.2.4.4 shows the elemental survey for Ru-GO, Ru- Al₂O₃, Ru- (GO+ Al₂O₃) catalysts. The presence of ruthenium along with carbon and oxygen in all the spectra can be observed. Small sodium contamination was evident for all the catalyst samples. There was no presence of nickel in all samples suggesting its role was only to serve as nuclei. These elemental surveys cannot, however, be used to quantify the relative contents of ruthenium and carbon as the C1s and Ru3d transitions have considerable overlap. Deconvolution based upon nominal transition wavelengths yields uncertain semi-quantitative values given unknown shifts in experimental peak transitions.
4.2.5 Particle Size Measurement

Catalyst particle size is relevant to its activity and selectivity. To quantify the ruthenium metal nanoparticle size (distribution), the freeware software package ImageJ was applied to TEM images showing the Ru nanoparticles upon the different catalyst supports. Multiple areas, from different selected images were selected as representative and individual ruthenium particles within those areas analyzed for size. The software couldn’t perform an automatic analysis for all the particles for their sizes as there was insufficient contrast between the metal particles and the background. Hence, an average was taken for at least 100 particles, analyzed individually. Table 4.2.5.1 gives the average number that was obtained after the analysis for the different catalyst systems.

**Table 4.2.5.1** Average particle size as calculated from ImageJ

<table>
<thead>
<tr>
<th>CATALYST</th>
<th>Ru AVERAGE PARTICLE SIZE (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-GO</td>
<td>1.9</td>
</tr>
<tr>
<td>Ru- Al₂O₃</td>
<td>1.9</td>
</tr>
<tr>
<td>Ru-(GO+ Al₂O₃)</td>
<td>2.2</td>
</tr>
</tbody>
</table>

4.2.6 Discussion

By inspection of the SEM and TEM images, it can be inferred that the functional groups on the surface of the GO enhanced the adsorption of activating metal ions and subsequently deposition of the metal nanoparticles in the reduction process. Therein the surface concentration
of carboxylic sites controls the concentration of the metal nanoparticles on the surface\textsuperscript{77, 78}. Absent porosity or interior mass, GO is then primed as support for metal nanoparticle decoration.

The Poly-ol process introduces a catalytic nucleation center for the preparation of the metal decorated GO\textsuperscript{79}. When nickel ions are reduced in ethylene glycol, the surface of the GO is coated with small nickel (atom) clusters that do not grow (further) into nanoparticles at the relatively low temperature of 150\textdegree{}C which is sufficient for ruthenium. Hence these clusters serve as nucleation centers for the heterogeneous growth of ruthenium nanoparticles. The EDS and the XPS analyses show no Ni content, indicating the Nickel nucleation being limited to small clusters on the surface of the GO. Also the average Ru particle size produced by the Poly-ol process is listed in table 4.2.5.1. This is a key factor in the activity measurements\textsuperscript{80}.

This Poly-ol process begets an additional advantage when synthesizing the mixed catalyst Ru-(GO+ Al\textsubscript{2}O\textsubscript{3}). When alumina was added at the start of the process, the alumina particles were also dispersed in between the sheets of GO, providing a uniform separation of the GO sheets. To validate this, a fourth catalyst, Ru-(GO+ Al\textsubscript{2}O\textsubscript{3} (no Ru)) was made in which the alumina was added only after first doing the nickel-ion activation step. From the TEM images it was clear that there was no proper dispersion of the alumina in between the GO sheets and instead it formed particle clumps on the surface of the GO. Also, there was no ruthenium on the alumina, which suggested that the nickel-ion activation stage is really important for the growth of the ruthenium particles on the surface.
4.3 Ruthenium Content in the System

In order to determine the ruthenium content on the support, the metal-supported catalysts were subjected to TGA analysis. Figure 4.3.1 shows the weight-loss curve for the Ru-GO catalyst. The ruthenium-decorated catalysts were heated to 800°C in air and the observed weight loss was equivalent to the mass of GO. The complete decomposition of carbon in air is observed between 600-800°C. The metal ruthenium content was then back calculated from the generated TGA residue which is presumed to be ruthenium oxide (RuO₂).

![Figure 4.3.1 Weight-loss curve obtained from TGA for Ru-GO catalyst.](image)
Figure 4.3.2 Weight-loss curve obtained from TGA for Ru- (GO+ Al₂O₃) catalyst

Unfortunately this procedure cannot be used to determine the ruthenium content on alumina as alumina is stable and does not decompose at 800°C.

A similar procedure was used to calculate the ruthenium in the mixed catalyst. Figure 4.3.2 shows the weight-loss curve for the Ru-(GO+ Al₂O₃) catalyst. For the Ru- (GO+ Al₂O₃ (no Ru)) catalyst, the ruthenium present on the support is assumed to be the same as that of Ru-GO as there was no decoration of ruthenium observed on alumina. Table 4.3.1 shows the amount of ruthenium in the system for each of the catalysts used.
Table 4.3.1 Ruthenium content as calculated.

<table>
<thead>
<tr>
<th>CATALYST SYSTEM</th>
<th>% Ru on the support</th>
<th>Ru mass (mg) per foam element</th>
<th>Total Ru mass (mg)</th>
<th>Total catalyst mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-GO</td>
<td>27.74</td>
<td>20.4</td>
<td>81.5</td>
<td>0.29</td>
</tr>
<tr>
<td>Ru-(GO + Al₂O₃)</td>
<td>22.14</td>
<td>18</td>
<td>72.0</td>
<td>0.33</td>
</tr>
<tr>
<td>Ru-(GO + Al₂O₃ (no Ru))</td>
<td>27.74</td>
<td>26.1</td>
<td>104.4</td>
<td>0.38</td>
</tr>
</tbody>
</table>

4.4 Hydrogenation Activity Measurements

The catalyst performance was determined by the extent of CO conversion to methane. The methanation conditions that were used across the various catalysts are given in the table 4.4.1. The inlet gas flow was changed depending on the CO and H₂ concentrations.
Table 4.4.1 Reaction Conditions for Methanation

<table>
<thead>
<tr>
<th>CATALYST</th>
<th>REDUCTION CONDITION</th>
<th>TEMPERATURE (°C)</th>
<th>GAS HOURLY SPACE VELOCITY (GHSV hr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-GO</td>
<td>310°C, 300 SCCM H₂</td>
<td>(409±5)</td>
<td>4100-16400</td>
</tr>
<tr>
<td></td>
<td>for 3 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru- Al₂O₃</td>
<td>310°C, 300 SCCM H₂</td>
<td>(409±5)</td>
<td>4100-16400</td>
</tr>
<tr>
<td></td>
<td>for 3 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru-(GO+ Al₂O₃)</td>
<td>310°C, 300 SCCM H₂</td>
<td>(409±5)</td>
<td>4100-16400</td>
</tr>
<tr>
<td></td>
<td>for 3 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru-(GO+ Al₂O₃ (no Ru))</td>
<td>310°C, 300 SCCM H₂</td>
<td>(409±5)</td>
<td>4100-16400</td>
</tr>
<tr>
<td></td>
<td>for 3 hours</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Catalyst metric of conversion (yield) and selectivity were calculated based on the percentage change in the CO concentration after the single-pass through the reactor. Catalyst performance was measured as a function of time, CO concentration, residence time, and different molar ratios of the inlet H2/CO gas mixture. The equations 4.3.1-4.3.4 were used to calculate specific values for these parameters.

\[
GHSV = \frac{V_R}{V}
\]  
Equation 4.3.1

\[
Residence\ time\ (t) = \frac{V}{V_R}
\]  
Equation 4.3.2
Conversion \((X(CO))\) = \(\frac{[CO_{in}] - [CO_{out}]}{[CO_{in}]} \times \frac{V_{exit}}{V_{in}} \times 100\) \hspace{1cm} \text{Equation 4.3.3}

\[CH_4\text{ selectivity}\left(S(CH_4)\right) = \frac{[CH_4]}{[CO_{in}] - [CO_{out}]} \times \frac{V_{exit}}{V_{in}} \times 100\] \hspace{1cm} \text{Equation 4.3.4}

where

- \(V_R\) = Volume of the reactor (in this case, the volume of the metal foams)
- \(V\) = Total volume of the gas flowing into the reactor
- \(V_{in}\) = Total flow rate of the input gas mixture
- \(V_{exit}\) = Flow rate of the product gas mixture
- \([CO_{in}]\) = Concentration of CO in the inlet gas stream
- \([CO_{out}]\) = Concentration of CO exiting the reactor
- \([CH_4]\) = Concentration of methane formed

### 4.4.1 Conversion Over Time – Catalyst Aging

CO conversions plotted as a function of time for the four catalysts are shown in figure 4.4.1.1. The conversion was highest for the Ru-(GO+ Al\(_2\)O\(_3\)) catalyst followed by the physical mixture catalyst Ru-(GO+ Al\(_2\)O\(_3\) (no Ru)). The initial conversion for the Ru- Al\(_2\)O\(_3\) was quite high but as the time progresses, the conversion dropped gradually to 91 percent and thereafter was stable. The Ru-GO had a variable conversion starting at 91 percent, reaching a maximum conversion of 98 percent at a time of 60 minutes, and then reverted back to 95 percent. From
such conversion over time data, catalyst efficiency was determined reactant gas conversion. By inspection of the conversion data presented in figure 4.4.1.1, of the catalysts are ranked in the following order for conversion efficiency: Ru-(GO+ Al₂O₃) > Ru-(GO+ Al₂O₃ (no Ru)) > Ru-GO > Ru- Al₂O₃.

![Time Profile for CO Conversion](image)

**Figure 4.4.1.1** Conversion of CO over time.

### 4.4.2 Effect of Molar Ratio on Yield

CO conversion plotted against different molar ratios of H₂/CO is shown in figure 4.4.2. Based on the data, at the molar ratio of 3, Ru-GO has the highest conversion, but as the molar ratio increased the conversion of CO for the Ru-(GO+ Al₂O₃) increases to the overall highest value of 99 percent. Similarly the conversion for all the catalysts Ru-GO, Ru-(GO+ Al₂O₃), Ru-
(GO+ Al₂O₃ (no Ru)) is also maximum at this particular molar ratio. The underlying reason for this uniform behavior is that, in the presence of excess hydrogen, the methanation reaction favors forward direction yielding higher conversion of CO to methane and water, by LeChatlier’s principle.

![CO Conversion vs. Molar Ratio](image)

**Figure 4.4.2.1** Conversion of CO over different (H₂/CO) molar ratio for the four catalysts.

### 4.4.3 Interplay between CO Concentration and Residence Time

Figures 4.4.3.1 and 4.4.3.2 show the effect of the CO concentration and residence time upon CO conversion. The conversion was highest for the Ru-(GO+ Al₂O₃) catalyst, and not surprisingly dependent on the total (gas) flow rate into the reactor. As CO concentration increases, the total flow in the reactor also increases. With decreased residence time for the
gases in the catalyst bed CO conversion decreases, as observed from the graphs. The mixed (support) catalyst exhibited better performance than the pure GO support, with the performance gap becoming evident and increasing with increasing space velocity (flow rate).

Figure 4.4.3.1 Conversion of CO plotted against change in CO concentration.
Figure 4.4.3.2 Conversion of CO with space velocity (total flow rate) of the input gas.

Results obtained for conversions and selectivity of the different catalyst systems are listed in table 4.4.1
Table 4.4.1 Conversion and Selectivity of the Listed Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Gas Hourly Space Velocity (hr(^{-1}))</th>
<th>(H2/CO) ratio</th>
<th>CO Conversion (%) ± 1%</th>
<th>Methane Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-GO</td>
<td>4100</td>
<td>6</td>
<td>98</td>
<td>99</td>
</tr>
<tr>
<td>Ru-GO</td>
<td>4686</td>
<td>3</td>
<td>97</td>
<td>99</td>
</tr>
<tr>
<td>Ru-GO</td>
<td>5857</td>
<td>4</td>
<td>94</td>
<td>99</td>
</tr>
<tr>
<td>Ru-GO</td>
<td>7028</td>
<td>3</td>
<td>98</td>
<td>99</td>
</tr>
<tr>
<td>Ru-GO</td>
<td>9372</td>
<td>3</td>
<td>94</td>
<td>98</td>
</tr>
<tr>
<td>Ru-GO</td>
<td>16400</td>
<td>6</td>
<td>89</td>
<td>99</td>
</tr>
<tr>
<td>Ru-Al(_2)O(_3)</td>
<td>4100</td>
<td>6</td>
<td>92</td>
<td>99</td>
</tr>
<tr>
<td>Ru-Al(_2)O(_3)</td>
<td>4686</td>
<td>3</td>
<td>95</td>
<td>99</td>
</tr>
<tr>
<td>Ru-Al(_2)O(_3)</td>
<td>5857</td>
<td>4</td>
<td>94</td>
<td>98</td>
</tr>
<tr>
<td>Ru-Al(_2)O(_3)</td>
<td>7028</td>
<td>3</td>
<td>94</td>
<td>96</td>
</tr>
<tr>
<td>Ru-Al(_2)O(_3)</td>
<td>9372</td>
<td>3</td>
<td>89</td>
<td>98</td>
</tr>
<tr>
<td>Ru-Al(_2)O(_3)</td>
<td>16400</td>
<td>6</td>
<td>86</td>
<td>92</td>
</tr>
<tr>
<td>Ru-(GO+ Al(_2)O(_3))</td>
<td>4100</td>
<td>6</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Ru-(GO+ Al(_2)O(_3))</td>
<td>4686</td>
<td>3</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Ru-(GO+ Al(_2)O(_3))</td>
<td>5857</td>
<td>4</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Ru-(GO+ Al(_2)O(_3))</td>
<td>7028</td>
<td>3</td>
<td>98</td>
<td>100</td>
</tr>
<tr>
<td>Ru-(GO+ Al(_2)O(_3))</td>
<td>9372</td>
<td>3</td>
<td>95</td>
<td>99</td>
</tr>
<tr>
<td>Ru-(GO+ Al(_2)O(_3))</td>
<td>16400</td>
<td>6</td>
<td>99</td>
<td>99</td>
</tr>
<tr>
<td>Ru-(GO+ Al(_2)O(_3) (no Ru))</td>
<td>4100</td>
<td>6</td>
<td>99</td>
<td>99</td>
</tr>
<tr>
<td>Ru-(GO+ Al(_2)O(_3) (no Ru))</td>
<td>5857</td>
<td>4</td>
<td>95</td>
<td>99</td>
</tr>
<tr>
<td>Ru-(GO+ Al(_2)O(_3) (no Ru))</td>
<td>9372</td>
<td>3</td>
<td>94</td>
<td>98</td>
</tr>
<tr>
<td>Ru-(GO+ Al(_2)O(_3) (no Ru))</td>
<td>16400</td>
<td>6</td>
<td>89</td>
<td>96</td>
</tr>
</tbody>
</table>
4.4.4 Activity Normalized Per Mass of Catalyst

The activity of the three catalysts Ru-GO, Ru-(GO+Al₂O₃) and (Ru-GO) + Al₂O₃ as normalized per mass of the catalyst was plotted against the CO flow rate in the reactor with the same molar ratio of CO/H₂. As observed in the figure 4.4.4.1, the activity of the mixed catalyst (Ru- (GO+Al₂O₃)) was highest and had a 13% enhancement when compared to the activity of Ru-GO and 35% when compared to the physically mixed catalyst (Ru-GO) + Al₂O₃. As the flow rate of CO in the reactor increases, the residence time of the gases in the reactor decreases. At these high flow rates, the variation in the activity of the mixed catalyst (Ru- (GO+Al₂O₃)) further increase in activity can be observed (21% (Ru-GO) and 39% (Ru-GO)+Al₂O₃). This increase in the activity for the mixed catalyst system when compared to the other systems is because of the effective dispersion of the catalyst supports GO and Al₂O₃. When Al₂O₃ was added to the system during the Ni-ion activation stage of the decoration, it assisted in the exfoliation of the GO sheets and because of its varied geometry of the particles, the Al₂O₃ particles distributed uniformly throughout the surface of the GO as confirmed from the TEM images in figure 4.2.2.3. This exfoliation of the GO sheets and the dispersion of the Al₂O₃ support produced an additional increase in the catalyst surface active sites which are now accessible for the gas molecules to react. Hence, higher conversion is recorded for the mixed catalyst system which indicates the effectiveness of the catalyst support dispersion.
Figure 4.4.4.1: Plot showing the activity of the catalysts at various flow rates.

4.5 BET Surface Area Analysis

BET analysis performed using CO was intended to provide catalyst surface areas. Unlike for traditional catalysts with micron and larger sized particles, the BET technique was a failure in determining the total surface area of the nano catalyst. Table 4.5.1 gives the BET surface area information for the three catalysts before and after decoration with ruthenium.
Table 4.5.1 BET surface area as measured.

<table>
<thead>
<tr>
<th>Catalyst Sample</th>
<th>Bet Surface Area Before Ru Decoration (m²/g)</th>
<th>Bet Surface Area After Ru Decoration (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-GO</td>
<td>500</td>
<td>12.24</td>
</tr>
<tr>
<td>Ru- Al₂O₃</td>
<td>40</td>
<td>9.3</td>
</tr>
<tr>
<td>Ru-(GO+ Al₂O₃)</td>
<td>-</td>
<td>60.57</td>
</tr>
</tbody>
</table>

From these numbers it can be inferred that the surface area as measured did not produce satisfactory results in light of the activity measurements for these catalysts. A possible reason is that catalysts that have been impregnated into the foam have undergone an additional step of dispersion that would facilitate breakup of clumps and separation of mutually adhering graphene layers in the foams.

Yet by the data trend the mixed catalyst has nearly 5 times higher surface area than that of the GO catalyst and nearly 7 times the surface area as that of the Al₂O₃ catalyst. This higher surface area is revealing in light of the elevated performance of the mixed catalyst when compared with the other catalysts. By these measurements it would appear that the process of introducing Al₂O₃ along with GO into the initial decoration stages aided separation of the GO layers.

### 4.6 Contribution of Nanopowder Alumina

Alumina nanopowder was added to the carbon-based support (GO) to improve the exfoliation of the GO. With a nominal particle diameter of 50 nm, mixing with GO during the reduction process with ethylene glycol is effective in dispersing the GO layers, as observed by
reduced GO clumping. With (better) exfoliated GO sheets, more graphene area is exposed, thereby increasing accessibility of the supported Ru nanoparticles.

To understand this effect of nanopowder alumina, comparisons were made between the catalysts Ru-GO, Ru- Al₂O₃ which were prepared separately and the Ru-(GO+ Al₂O₃), Ru-(GO+ Al₂O₃ (no Ru)). During the synthesis of Ru-(GO+ Al₂O₃ (no Ru)), alumina was added after the nickel-ion activation process to test the hypothesized role of alumina in separating the GO sheets. The results in the section 4.2.2 showed that there was no ruthenium present (as expected) on the alumina. This also shows that a nickel-ion activation stage in the Poly-ol process is necessary to create the active sites on which the ruthenium can be decorated. As alumina was added later in the process, active sites were not created on the alumina with consequence of no ruthenium decoration.

Alumina is one of the most important support materials for catalysis, especially in the automotive and petroleum industries. Based on its texture properties, surface area, pore volume, pore-size distribution and acid-base characteristics, it is a very useful oxide material. The chemical and the hydrothermal stability of gamma-alumina is a critical point for catalytic applications. The recent studies comparing cobalt-decorated alumina and CNT’s indicated that CNT’s achieved a higher level of activity when compared with that of alumina. For the selectivity of methane, the authors reported an enhancement of the CO conversion of 80 percent when compared with that of the Co- Al₂O₃ which is also a methanation catalyst. The selectivity for the formation of methane (a lighter hydrocarbon) was reported the highest for the Co-CNT’s. The addition of alumina as reported only improved the selectivity of methane in the system.

For technical reasons, analysis of the Ru content of the Ru-Al₂O₃ catalyst was unsuccessful. Absent such data, the supports of GO and Al₂O₃ cannot be evenly compared.
High catalyst dispersion by the Poly-ol process coupled with high surface areas led to comparable performance for the Ru-GO and Ru-Al$_2$O$_3$ catalyst systems. The merit of nanoscale catalysts is manifested in the high conversions for each system.

Relevant to the hypothesis is the performance comparison between the Ru-GO and Ru-(GO + Al$_2$O$_3$ (no Ru)) as outlined in the experimental chapter. As documented by Table 4.4.1, the co-synthesized catalyst showed comparable activity at all test conditions. Such results would seemingly discredit the hypothesis and purported utility of the mixed-catalyst supports. Yet though the physically mixed catalyst supports were deemed equivalent to the co-synthesized support system, judging from the test results, apparently they are not. The co-synthesized system has highest activity with an increasing margin of performance as flow rate increases.

The first conclusion is that the co-synthesized catalyst truly produces the best prevention of support agglomeration. Therein the co-synthesized and physically mixed systems are not equivalent with the first activation step of the poly-ol process apparently responsible, that bating the definable difference between the two catalyst systems. The second conclusion is that at low flow rates, diffusional processes are sufficient to overcome pseudo-porosity created by agglomerated support material. This accounts for the similar performance between the physically mixed and co-synthesized systems at flow rates yielding long residence times. Yet as space velocities increase, mass transport limitations become manifest in lowering catalyst exposure and effective activity. This accounts for the increasing performance gap between the two catalyst systems.

The physical interpretation is that the alumina nanoparticles being somewhat spherical and thicker than graphene are disparate in geometry relative to the graphene sheets and as a result, hinder graphene platelet stacking. There should also be relatively little affinity between
the GO and nanoalumina. This increase in the surface area could be confirmed from the BET analysis showing an increase of 5-7 times in surface area when compared to the individual catalyst (support) systems.

By this support “dispersion” the catalytic Ru nanoparticles deposited on the exterior surface of the GO support will not be physically covered or inhibited (blocked) by GO agglomeration in the presence of alumina particles. Hence, the ruthenium catalyst not fully exposed in the Ru-GO system is now more accessible to the reactant gases. This increase in the accessible catalyst increases conversion and selectivity for methane formation as could be observed in section 4.3, thereby supporting the hypothesis.

4.7 Summary of Results and Discussions

The results obtained from the experiments showed that the presence of alumina nanopowders contributed to GO sheet exfoliation, thereby increasing the ruthenium particles’ exposure (decorating the GO support) and resulting catalyst performance. These nanoscale catalyst systems (Ru-GO and Ru-(GO+ Al₂O₃) demonstrated high activity in the hydrogenation tests, interpreted as reflecting high Ru dispersion on both support systems. The presence of alumina in the Ru-(GO+ Al₂O₃) system proved advantageous in that it helped to prevent GO sheet agglomeration. The nanoalumina addition thus was synergistic in providing a higher surface area than the single component system, (Ru-GO), with a modest enhancement in the conversion and selectivity towards the production of methane that increased with space velocity.
CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

5.1 Conclusions

This study focused on application of GO as the support for Ru catalyst for CO methanation. Attractive features include its high surface area and oxygen-group concentration that provide for relative ease of decoration with metal nanoparticles. Unlike other porous carbons GO is devoid of porosity, a topographical feature that promotes decoration and catalyst exposure without mass transfer limitations during reaction. As a carbon material it also offers chemical inertness and thermal stability, particularly under highly reducing conditions. These factors account for the high activity of the nanoscaled catalyst Ru-GO system. These same considerations of surface area, particle size and porosity absence similarly account for the comparable activity of the Ru/Al₂O₃ using nanoalumina powder as support. Yet nanoscale catalysts can agglomerate, yielding a facsimile of a porous material with attendant complications. Enlargement of pseudo-porosity or even prevention of agglomeration is achieved by co-presence of disparate supports. As measured, the mixed catalyst (Ru-(GO + Al₂O₃)), co-synthesized, exhibited the highest activity and selectivity for reasons as outlined by the hypothesis and demonstrated by the test results.

In a broader context, dispersion is a key factor for catalysis. High exposed surface area maintains exposure. For this reason catalysts are often tested in packed or fluidized beds. Both reactor configurations facilitate mass transport by maintaining macro-scale catalyst dispersion or physical separation, in addition to minimizing local thermal excursions in exothermic reactions. Catalyst agglomeration is prevented, largely by the inert packing or fluidizing material. So too
the (nano)alumina used in these studies serves this same general purpose, but here it is demonstrated on a micro-scale as the alumina is nano-sized and the reactor configuration is already prestructured by virtue of being an open cell foam. A hierarchical reactor offers additional advantages by providing minimal flow resistance compared to a traditional packed bed while yet providing high gas-surface contact and facilitating gas mixing. Moreover it inherently introduces a level of catalyst physical dispersion.

In principle such a hierarchical support should be sufficient to maintain catalyst dispersion but apparently the catalyst support material coating the struts and walls and vertices can become layered or otherwise partially packed. This should not be surprising as graphene has both favorable geometry and π-π bonding attraction to foster platelet stacking. The nanoscale alumina is then appropriately sized to facilitate graphene dispersion whereas traditional inert powders of micron or larger size range would be mismatched in scale. In conclusion the key message of this catalyst-development project is that physical dispersion of a catalyst matters on all length scales. Demonstrated here is the importance of such dispersion for nanoscale catalyst systems.

5.2 RECOMMENDATIONS FOR FUTURE WORK

Two approaches should be pursued to further improve the catalyst system. A technical or scientific approach would be to choose another catalyst system, include a promoter or other additive to extend the hypothesis by testing. The second tack would be an improvement in the hardware depending upon the micro-reactor geometry selected.

5.2.1 Scientific Approach

Based upon the electronic structure of the support, materials should be explored that could enhance this effect. Further insights would be gained by testing the benefits and limitations
using alumina of different particle sizes and shapes. Fumed alumina might be a very logical alternative as its size is commensurate with that of grapheme; therein it could potentially provide the best separation. Other materials, not particularly active for reasons of chemical composition or shape, may be advantageous as physical additives, such as fumed silica, a commercial and very cheap, inert material that will not interact chemically nor electronically with graphene or the Ru nanoparticles. Indeed, for other reactions it is used as an inert support\textsuperscript{77}.

Alkali elements as dopants, well known as promoters in traditional oxide-supported catalysts could contribute added electronic charge, effectively increasing the graphene electronic density of states\textsuperscript{78}. If these energy levels were favorably aligned, i.e. matching those of the supported metal d-band orbitals, catalytic activity could be enhanced, presumably by accelerated CO dissociative chemisorption. Modeling would be an integral tool for both selecting and predicting the best physical size and shape with measurements providing feedback for parameter refinements.

5.2.2 Hardware

Further improvements on hardware would be matching the aluminum foam geometry to the reactor tube. The present system was a compromise between ease of cutting and compressing foams to reach the selected porosity (or reciprocally surface area) and their relative cost. Rectangular pieces are vastly easier to create than cylindrical shapes, and even then each foam section, the cost is ~ $32. Alternatively cylindrical reactors are convenient, requiring no special machining and with a variety of sizes, materials and fittings are available, and are extremely versatile and economical. In these studies a packing material (glass wool) was chosen to fill the
gap between the rectangular foams and cylindrical housings. Rectangular tubing in the future would be the better option with foams then cut to match.
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APPENDIX

FACTORS AFFECTING THE ACTIVITY OF THE CATALYSTS

SULPHUR POISONING

Methanation catalysts are very sensitive to sulphur poisoning. For example, with nickel catalysts, the adsorption of sulphur from the feed gas is almost quantitative which is inactive for methanation. The adsorption of sulphur poisons the catalyst by competing with reactants for active sites on the catalyst surface which results in the loss of active surface area. The simple solution could be to reconstruct the catalyst surface by the addition of additives to the catalyst and by controlling the particle size of the catalyst which can affect the sulphur tolerance levels\(^{19}\).

Cusumano and co-workers have estimated the life of a nickel methanation catalyst by passing H\(_2\)S gas over the catalyst and they estimated that it is adequate for practical process only when the level of H\(_2\)S in the reaction gases does not exceed perhaps 1 ppm. With a supported nickel catalyst a level of 0.05 ppm of H\(_2\)S in the reaction gases resulted in slow deactivation of the initial portion of the catalyst bed but no deactivation further into the bed even after fifty days on stream. A level of 3 ppm of H\(_2\)S in the gases caused very rapid deactivation further into the catalyst bed within six days of operation.

The suggested temperature of most methanation processes is in the range of 300 °C - 450°C and the form of a nickel catalyst does not have much effect on its sulphur tolerance or sulphur capacity. There is no straightforward or economic method to regenerate the sulphur-poisoned nickel catalysts. It may prove possible to regenerate certain metal catalysts used by suspending it in molten metal salts. As stated later in this review, molybdenum and tungsten sulphides are not
poisoned by sulphur, but they are less reactive methanation catalysts than some other materials and require higher reaction temperatures.

**THERMAL STABILITY**

Methanation is highly exothermic and this could be an important factor in considering the techniques for the operation process in any industry. If the reaction temperature becomes too high, not only is the reaction equilibrium adversely affected, but the catalyst life is also reduced by sintering of the metal particles. This process can be operated in two different ways. One could be to keep the reaction temperature as low as possible by process technique, and the other could be the process is operated adiabatically without temperature control, the maximum temperature depending on the conversion limit. Various methods to control the temperature in the first system includes product gas recycle, addition of steam, tube-wall reactor designs, use of a liquid phase heat removal medium and fluidization. Hence, the design limitations appear and it needs to be addressed when dealing with such problems with the temperature control.

Reaction temperature in either method of operation lies between 300 ° and 450°C, at which the care of the catalyst life and activity are prominently required. Improvements to any of these could only be advantageous to the catalyst system. Hence, the catalysts capable of operation at higher temperature are desirable. Within the limits of operation, the higher the temperature at which the heat of methanation is released the more effectively it can contribute to the overall thermal efficiency of the conversion process. Also, sulphur poisoning may be less of a problem at higher temperature because of decreased stability of catalyst metal sulphided under the conditions of operation.
CARBON DEPOSITION

As most of the nickel catalysts are affected by the carbon deposition, the effect of carbon deposition was tested on uncontaminated nickel catalysts operating at up to 450°C with 20 percent to 50 percent mole H₂O in the methanation reactants maintain activity for prolonged periods when the H₂/CO ratio varies from 5.8 to 2.0. Reactive carbon may play an important role in the methanation reaction as it is the source for the carbon deposition. Under certain transient conditions or at higher temperature (or even at 400°C in the absence of added water) bulk carbon in unreactive form as Ni₃C, produced on or in the catalyst, can lead to loss of catalyst activity and fouling of equipment²⁰.

Molmot and Kyle²¹ have determined the conditions for carbon deposition from various gas compositions by considering gas-phase/solid carbon equilibria for the system comprising carbon, hydrogen, oxygen, nitrogen over the range of conditions 500-1500 K, 100 to 2500 kPa, O/H atomic ratios 0.001 to 1000 and N/O atomic ratios 0 to 10. White and others²² have calculated the equilibrium constants of reactions between hydrogen, oxides of carbon, carbon, methane and steam, and described how the deposition of bulk carbon in SNG manufacture can be avoided by control of the water gas shift reaction. However, conditions may arise in which the deposition of unreactive carbon on catalysts cannot be avoided, and attention has been given to its removal. Bernardo and Trimm²³ studied the kinetics of gasification of carbon deposited on nickel foils and nickel-alumina catalysts by steam, carbon dioxide and hydrogen in the temperature range 450°-850°C.

Carbon deposition was effected by passing a mixture of n-hexane (13.5 molar %), hydrogen (25%) and nitrogen (61.5%) over the catalyst at 600°C. Steam was the most effective gasifying agent at atmospheric pressure. Hydrogen was more effective than carbon dioxide
between 400°C and 650°C. Understanding this information can help in the regeneration of catalysts deactivated by carbon deposition but the extent the catalyst would be effective for methanation after carbon removal is unknown.

Most of the recent catalytic methanation research is concerned with these problems, mostly with nickel catalysts, although not to the exclusion of other materials, notably other Group VIII metals. The aims of the research fall broadly into the categories: maintenance of catalyst activity over long periods, resistance to poisoning and improved techniques of catalyst preparation. Attention is being directed also to the mechanism of catalytic methanation and to the assessment of the specific activity of catalysts.

**SEM WORKING PRINCIPLE**

SEM works on the principle that accelerated electrons which carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence-CL), and heat.

Secondary electrons and backscattered electrons are commonly used for imaging samples. Secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). X-ray generation is produced by
inelastic collisions of the incident electrons with electrons in discrete orbitals (shells) of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength which is related to the difference in energy levels of electrons in different shells for a given element. Thus, characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam.

SEM analysis is considered to be "non-destructive" i.e., x-rays generated by electron interactions do not lead to volume loss of the sample. Hence, it is possible to analyze the same materials repeatedly. Figure 2 shows the electron beam impact and the different types of electrons that are released at different points from sample due to the impact.

![Electron beam – sample interaction](image)  
**Figure A.1.** Picture showing the electron beam and sample interaction
DATA FROM OTHER TECHNIQUES

Traditional techniques used to characterize the catalyst samples does not work well for the nano catalysts especially with GO as the support. Techniques such as BET, XRD, and ICP which produced quantitative results with the catalysts that were synthesized over the years did not produce satisfactory results when it was using the nano catalysts. Even though some general valuable information was obtained from these techniques, it could not be quantified to obtain clear results. Some observations from these techniques are listed below.

X-ray Diffraction (XRD)

Traditional XRD was used to infer the crystal structure, chemical composition and physical properties of the material. For this particular catalyst system, XRD failed to identify the crystal structure and the physical properties of the Ruthenium that is supported on the GO and the mixed catalyst.

Figure 5.4.1 shows the XRD pattern collected for the Ru/GO catalyst. The signal collected had a lot of disturbance as the carbon absorbed most of the x-rays. We could see a clear peak in the spectrum at a value of $2\theta = 25^\circ$ which corresponds to the signal obtained from carbon and there are no corresponding peaks for Ruthenium which has its $2\theta$ value closer to $50^\circ$ and $70^\circ$. 
Figure A.2. Plot showing the XRD pattern for Ru-GO catalyst

Figure 5.4.2 shows the XRD pattern for the mixed catalyst. Clearly, there is no evidence of ruthenium from the spectra. We can see a clear indication of carbon and alumina but no ruthenium. The results from the SEM, EDX, TEM and XPS confirmed the presence of ruthenium but with XRD, we cannot identify the ruthenium in the sample.

A possible reason that Ruthenium was not observed on any of the catalysts is because of its particle size (< 5nm). For the particles below 5 nm, the clear identification of the crystal structure is difficult when we have supported it on carbon supports. Other reason could be that most of the X-rays are absorbed by the carbon in GO and hence the signal obtained from the ruthenium is quite low that it does not pass the background. This is clear evidence that the traditional techniques do not clearly give results when working with nano catalysts.
Figure A.3. XRD pattern for Ru-(GO+Al₂O₃)
INDUCTIVELY COUPLED PLASMA SPECTROMETRY (ICP) ANALYSIS

To determine the elemental composition of the sample, Inductively Coupled Plasma Emission Spectrometry (ICP-AES) was used. An inductively coupled plasma spectrometer is a tool for trace detection of metals in solution, in which a liquid sample is injected into argon gas plasma contained by a strong magnetic field. The elements in the sample become excited and the electrons emit energy at a characteristic wavelength as they return to ground state. The emitted light is then measured by optical spectrometry. This method, known as inductively coupled plasma atomic emission spectrometry (ICP-AES) or inductively coupled optical emission spectrometry (ICP-OES), is a very sensitive technique for identification and quantification of elements in a sample. Most ICP-AES instruments are designed to detect a single wavelength at a time (monochromator). Since an element can emit at multiple wavelengths, it is sometimes desirable to detect more than one wavelength at a time. This can be done by sequential scanning or by using a spectrometer that is designed to capture emissions of several wavelengths simultaneously (polychromator). Detection limits typically range from parts per million (ppm) to parts per billion (ppb), although depending on the element and instrument, can sometimes achieve less than ppb detection.

ICP-AES and ICP-MS can only be used on solutions. Hence, it is necessary to dissolve solid samples prior to analyses. There are two dissolution methods available

I. Acid Digestion

II. Salt fusion
I. Acid Digestion

The dissolution of the sample in this process is done using mineral acids such as nitric acid, hydrochloric acid, hydrofluoric acid, per chloric acid either by themselves or in combination with each other to attack and break down the structure of the solid (typically in powder form). This attack is done either in an open dish or a sealed vessel. This type of dissolution is good for ultra-trace determinations since high purity acids can be purchased commercially and it is effective for many metals and alloys. This is a time consuming and labor intensive process. The complete dissolution is difficult to achieve on a broad range of geologic and ceramic materials without specialized procedures. It is element specific as some of the elements can be lost during the digestion process.

II. Salt Fusion Technique

This technique involves heating of the solid sample with a salt at a high temperature results in the breakdown of the structure of the solid, making it easier to dissolve in an acid solution. Typical salts used are lithium metaborate fusion and sodium peroxide fusion. This is a really fast and simple technique. The complete dissolution is achieved on a broad range of geologic and ceramic materials but it is ineffective on metal samples. It is difficult to do ultra-trace analysis work since high purity fusion materials are not available. The Lithium metaborate fusion method was used for the dissolution of the Ru samples as the acid digestion had no effect on the samples since the support material was a carbon based sample.

Lithium Metaborate Fusion

a. About 0.1 gm. of -100 mesh samples was added to a pre-weighed vials containing 1 gm. of lithium metaborate.
b. The vials were shaken gently but thoroughly allowing the two components to be mixed properly.

c. The contents of vials were placed in graphite crucibles and the crucibles were inserted in an oven pre-heated to 900°C.

d. 100 ml of a 5% nitric acid solution was pipetted into a watch glass covered Teflon beaker with a magnetic stirring bar.

e. After ten minutes of heating at 1000°C, the oven was allowed to reach 900°C, the crucibles were taken out and the contents were transferred to the beakers on magnetic stirrers and the contents were mixed from the crucibles to pick up any beads that formed lumps.

f. This was stirred at least for 15 minutes and the contents were transferred into polyethylene bottles for storage.

After the dissolution process, the sample was analyzed in a Perkin-Elmer Optima 5300 instrument to obtain the individual concentrations of the elements that were present in the sample.

RESULTS FROM INDUCTIVELY COUPLED PLASMA (ICP) ANALYSIS

ICP analysis is used to identify the elements that are present in the sample which can have a concentration of metal ions as low as one part in $10^{12}$ (per trillion) but with at least 5 percent of the sample should be present in the mixture. As the dissolution process requires the addition of various chemicals, there might be some additional compounds detected while analyzing the sample. From the table 5.4.2, we can clearly see that there are some impurities (Na2O, SiO2) other than the actual metal of interest. This might be coming from the dissolution process and the glassware that was used during the analysis (presence of SiO2).
The analysis did not produce quantitative results as the dissolution process was difficult. The dissolution of carbon along with other metals is tough to achieve. Moreover, the percentage of ruthenium in the sample is also low (~2.5 percent). To increase the detection of ruthenium, the alumina also increased simultaneously as more amount of metal was added during the dissolution process and this created an abundance alumina region and hence the signal for the ruthenium is lost. Also, the dissolution of ruthenium was a challenge as it takes a lot of time when compared with the other metals in the catalyst. Because of this variable dissolution times, some of the identity of the samples could be lost.

This technique does not work if the any of the metal is attached to carbon. Since carbon cannot be detected by this technique, the signal from the inorganic metals such as ruthenium which are attached to carbon might be lost.

Table A.1. Results from ICP-AES for the three catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al₂O₃ (%)</th>
<th>Na₂O (%)</th>
<th>SiO₂ (%)</th>
<th>Ru (%)</th>
</tr>
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<tbody>
<tr>
<td>Ru-GO</td>
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<td>0.6</td>
<td>1.11</td>
<td>.11</td>
</tr>
<tr>
<td>Ru-( GO+Al₂O₃)</td>
<td>41.3</td>
<td>0.80</td>
<td>1.82</td>
<td>0.32</td>
</tr>
<tr>
<td>Ru-Al₂O₃</td>
<td>16.7</td>
<td>18.1</td>
<td>1.27</td>
<td>0.11</td>
</tr>
</tbody>
</table>