

## *Declaration*

This thesis is being submitted for the degree of Doctor of Philosophy at the University of the Witwatersrand, Johannesburg. It is my unaided work under the supervision of Prof. Neil J Coville and Prof. Sabelo D. Mhlanga. This work has not been presented for any degree or examination to any other University.



.....  
David Ofori Kumi

On this ..... day of .....2016

## *Abstract*

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Selective CO methanation (SMET), as an alternative process for cleaning trace content of CO in reformat gas feed for fuel cell applications, has gained increasing attention recently. This is mostly due to the fact that the technique can circumvent the major setbacks experienced in the preferential oxidation (PROX) reaction of CO to CO<sub>2</sub>. The PROX technique is a more established process and has been extensively researched over the years. In this project, we have focused on studying Ru supported on carbon and titania based materials for the selective CO methanation reaction.

A rutile morphology in the form of a novel dandelion like structure was synthesized using TiCl<sub>4</sub>. The rutile dandelion like structure was composed on rutile nanorods which were radially arranged and they had fairly high surface area (61 m<sup>2</sup>g<sup>-1</sup>). Titania rutile was also synthesized by calcining anatase at 900 °C for 10 h. It was observed that the rutile grains had grown larger after the transformation from anatase to rutile and this was accompanied by a collapsed surface area (from 52 to 9 m<sup>2</sup>/g). The two rutile morphologies were employed as Ru catalyst supports and applied in for CO and selective CO methanation reactions. The dandelion like supported catalyst demonstrated higher catalytic performance compared to the thermally prepared rutile supports. This was attributed to the smaller Ru particles sizes which were found to be sinter resistant.

Small RuO<sub>2</sub> nanoparticle sizes supported on carbon nanotubes (CNTs) were obtained by the use of a microwave polyol synthesis. Tuning the microwave temperature generated the different RuO<sub>2</sub> sizes without changing the percentage loading or conventionally heat treating the catalyst. Chemical vapour deposition (CVD) technique was used to synthesize CNTs using a Fe-Co/CaCO<sub>3</sub> catalyst. The microwave polyol synthesized catalysts were compared to a wet impregnated catalyst. It was noted that the impregnated catalyst preparation method showed little control over the RuO<sub>2</sub> particle size distribution. The catalysts were tested in both selective CO and CO methanation. The catalyst with smaller particle sizes, prepared using a short microwave induction time, performed better when compared to the other catalysts. It was also observed that all the catalysts promoted the undesired reverse water gas shift reaction (RWGS) for all the catalyst at temperatures above 260 °C.

The surface of the CNTs were altered by introducing pyridinic nitrogen in an in situ doping process to give nitrogen doped CNTs (N-CNTs). The doping was confirmed by TEM as the CNTs were seen to show bamboo compartments in the tubular CNT structure. A composite of CNT-TiO<sub>2</sub> was prepared by a facile hydrothermal process and used to modify the CNTs. The TiO<sub>2</sub> (anatase) coated CNTs were synthesized using titanium butoxide as anatase source. A solution containing CNTs and the TiO<sub>2</sub> source was reacted in an autoclave. Images from TEM and SEM revealed partially coated anatase N-CNTs and CNTs. Both the doping and the coating of the CNTs resulted in an improved surface area. The coated samples showed significantly improved thermal stability which was attributed to the shielding effect of the TiO<sub>2</sub>. Raman analysis revealed that the N-CNTs had a high defect content compared to the CNTs. When these materials were employed as Ru catalyst supports for methanation reactions, the nitrogen doped CNTs demonstrated superior catalytic activity compared to the CNT supported catalyst. They both promoted the reverse water gas shift reactions. The NCNT-TiO<sub>2</sub> and CNT-TiO<sub>2</sub> catalysts showed higher activity and significantly retarded the reverse water gas shift reaction.

Solid carbon spheres (CSs-H), mesoporous in nature was synthesized *via* the hydrothermal route using sugar as carbon source was functionalized by acid treatment. The data were compared to an un-functionalized CSs-H used as a Ru catalyst support. Raman data suggested a high defect content for the functionalized spheres and the carbons had a slightly higher surface area when compared to the un-functionalized spheres. Two catalysts were prepared from the functionalized solid carbon spheres; a microwave irradiation prepared catalyst and a wet impregnation prepared catalyst. The microwave prepared catalyst, with slightly smaller Ru particles, performed slightly better in both CO and selective CO methanation reactions than the impregnated catalyst. In the CO<sub>2</sub> only methanation reaction almost similar activity was obtained for both catalysts which implied the preparation method did not have much effect on the reaction. The un-functionalized supported catalyst performed poorly in both the reactions due to the poorly dispersed Ru nanoparticles which had sintered. Despite the poor performance, the catalyst did not promote the undesired RWGS reaction. This was attributed to the absence of oxygenated functional groups such as OH.

## *Dedication*

*I dedicate this work to my wonderful family;*

*Dr. Seth Kumi, Dr. Alexander Kumi, Dr. Yvonne Kumi, Dr. Fredrick Kumi.*

*To my mom! You have been my spiritual fortress.*

*To my sister Hannah who was always my second mom and Joshua my brother.*

*Without such a family I would not have come this far!!!!*

*If I have seen further than others, it is by standing upon the shoulders of giants. Isaac Newton*

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---

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## ***PUBLICATIONS AND PRESENTATIONS***

### **PUBLICATIONS**

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T.N. Phaahlamohlaka, **D.O. Kumi**, M.W. Dlamini, L.L. Jewell, N.J. Coville, Ruthenium nanoparticles encasulated inside porous hollow carbon spheres: A novel catalyst for Fischer-Tropsch synthesis. Catalysis Today, (2016). In press.

### **PRESENTATIONS**

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## *List of abbreviations*

|                               |                                                                     |
|-------------------------------|---------------------------------------------------------------------|
| AFC                           | Alkaline Fuel Cell                                                  |
| BET                           | Brunauer-Emmett-Teller                                              |
| C <sub>2</sub> H <sub>2</sub> | Acetylene                                                           |
| CaCO <sub>3</sub>             | Calcium carbonate                                                   |
| CaO                           | Calcium oxide                                                       |
| CCVD                          | Catalytic chemical vapour deposition CVD Chemical vapour deposition |
| CNFs                          | Carbon nanofibers CNS                                               |
| CNTs                          | Carbon nanotubes                                                    |
| CO <sub>2</sub>               | Carbon dioxide                                                      |
| Co                            | Cobalt                                                              |
| CS                            | Carbon sphere                                                       |
| EM                            | Electron microscopy                                                 |
| Fe                            | Iron                                                                |
| GC                            | Gas chromatography                                                  |
| GHSV                          | Gas hourly space velocity                                           |
| h                             | Hour                                                                |
| H <sub>2</sub>                | Hydrogen                                                            |
| HNO <sub>3</sub>              | Nitric acid                                                         |
| H <sub>2</sub> O <sub>2</sub> | Hydrogen peroxide                                                   |
| mL/min                        | Millilitre per minute                                               |
| N <sub>2</sub>                | Nitrogen                                                            |
| N-CNT                         | Nitrogen doped carbon nanotubes                                     |
| nm                            | Nanometre                                                           |
| PEMFC                         | Polymer Electrolyte Membrane Fuel Cell                              |
| PROX                          | Preferential Oxidation                                              |
| PXRD                          | Powder X-ray Diffraction                                            |
| Ru                            | Ruthenium                                                           |
| RWGS                          | Reverse water gas shift                                             |
| SMET                          | selective methanation                                               |
| t                             | Time                                                                |
| TCD                           | Thermal conductivity detector                                       |
| TEM                           | Transmission electron microscopy                                    |
| TGA                           | Thermogravimetric analysis                                          |
| TPR                           | Temperature programmed reduction                                    |
| WGS                           | Water gas shift                                                     |
| wt. %                         | Weight percentage                                                   |



# *Chapter 1*

## **I.0 Synopsis**

This chapter briefly describes the need for renewable energies, an outline of chapters of the individual topics in this thesis, the problem statement for this project, the motivation, the aim and objectives of this study.

Chapter two captures a detailed review of fuel cells and their operation. Attention was focused on the proton exchange membrane fuel cell (PEMFC), its source of fuel, and the major draw backs related to CO contamination in the fuel sources on the PEMFCs operation. Several CO removal techniques were discussed with emphasis on selective CO methanation, and why it was chosen to be studied in this projects based on the advantages it offers. Mechanisms for CO and CO<sub>2</sub> methanation have been included in this chapter. Factors that affect catalytic studies of selective CO methanation such as catalyst types, catalyst supports (focusing on TiO<sub>2</sub> and carbon based materials), catalyst preparation (focusing on microwave polyol preparation, impregnation and deposition-precipitation by urea) have also been reviewed.

Materials and methods employed in this study were discussed in chapter three.

The fourth chapter describes the synthesis of different rutile morphologies and their application as supports for Ru nanoparticles. The rutile catalysts prepared by wet impregnation and deposition-precipitation using urea were applied for CO methanation and selective CO methanation reactions with excess CO<sub>2</sub> in the feed. A manuscript from this chapter has been submitted the RSC journal ‘Catalysis Science and Technology’.

In chapter five, the synthesis of carbon nanotubes (CNTs) employing chemical vapour deposition (CVD) followed by deposition of Ru nanoparticles different sizes on the CNT support was described. Varying RuO<sub>2</sub> nanoparticle sizes were achieved by a microwave polyol synthesis. Some microwave conditions were manipulated to achieve desired particle sizes. These catalysts were studied in CO and selective CO methanation reactions. This work has been prepared in a manuscript to be submitted to the journal, ‘Catalysis Letters’.

Chapter six involved modifying carbon nanotubes by doping them with nitrogen, and partially coating the CNTs with anatase titania using a facile hydrothermal method. Ru was supported on the CNT, NCNT, CNT-TiO<sub>2</sub> and TiO<sub>2</sub> supports. The effect of these supports was studied in CO, CO<sub>2</sub> and selective CO methanation in the amid of CO<sub>2</sub>. A manuscript has been prepared from this chapter and will be submitted to the 'Int. Journal of Hydrogen Energy'.

The seventh chapter comprises of a study on mesoporous solid carbon spheres as Ru catalyst supports. The spheres were prepared from sucrose using a hydrothermal approach. A catalyst was prepared from a functionalized solid sphere by wet impregnation, whilst another catalyst containing Ru on a support was prepared via microwave polyol synthesis. These two catalysts were compared to a Ru catalyst supported on un-functionalized solid carbon spheres.

Chapter eight covers general conclusions for the project and highlights some recommendations for future work.

## **1.1 Renewable energies**

Natural resources have greatly been depleted with little or no consideration to the environmental impact of this process and the consequence of their possible exhaustion since the advent of industrialization. Global warming remains the biggest effect of using fossil fuels. Global warming is able to elevate a sea level worldwide which poses a danger to seaside cities. Warming could also cause many other natural disasters such as forest fires, floods and hurricanes. These environmental problems can be solved by the long-term potent action of sustainable development. In connection with this, renewable energy resources seem to be regarded as one of the most possible effective solutions. Sources which includes, solar energy, wind power, tidal energy, hydro power, biomass energy, geothermal energy and fuel cells are referred to as clean renewable energies. These technologies are fast developing though they have been dogged by several challenges. This project was focused on one solution to the problem – the use of fuel cell technology [1-3].

## **1.2 Problem statement**

Commercializing a low temperature proton exchange membrane fuel cell for transportation and stationary power generation applications has been hindered by the inability to generate “nearly free CO”  $H_2$  gas feed [4]. The reformat gas feed contains about 0.5-1% of CO after the steam reforming process has been subjected to a secondary  $H_2$  generation process usually referred to as the water gas shift process. Also present in large amount is  $CO_2$  which forms nearly 23% of the reformat gas feed. More than 10 ppm concentration of CO in a reformat gas feed fed into the PEMFC deactivates the Pt anode electrode [5, 6]. Preferential oxidation of CO to  $CO_2$  has been the main trace removal technique for CO that has been used over the past years but the process has severe challenges associated with it that makes the process costly and cumbersome. Selective CO methanation (SMET) has gained interest as an alternative technique to the PROX since it can avoid the major challenges experienced in PROX. Further, fine tuning is needed to improve the selective CO methanation reaction in order to bring about the use of PEMFCs in mainstream power generation. This includes developing a suitable methanation catalyst which is more selective towards CO at lower temperatures to avoid huge  $H_2$  losses through  $CO_2$  methanation and to retard the reverse water gas shift reaction.

## **1.3 Project motivation**

In the SMET technique both reactants are found in the gas reformat feed, implying less cost is involved unlike observed for other CO removal techniques. Due its less exothermic nature, SMET can easily be controlled compared to PROX. Ruthenium supported on  $TiO_2$ , and the use of shaped carbons as model supports affords the facile study of different parameters in selective methanation at the laboratory scale.

## **1.4 Aim and objectives of this study**

This project is focused on using the selective CO methanation reaction. The aim is to examine the effect the different supports have on activity and selectivity of CO methanation,  $CO_2$  methanation and selective CO methanation in CO/ $CO_2$  mixtures. Attention was focused on carbon based supports; namely, nitrogen doped carbon nanotubes (N-CNTs), undoped carbon nanotubes (CNTs) and, titania anatase coated CNTs (CNTs- $TiO_2$ ). Other supports

investigated were titania based supports, which included different morphologies of titania i.e. rutile and Degussa P-25 titania (80% anatase and 20% rutile). These studies were done to investigate any correlations that existed in the activity and behavior of the different catalysts on CO hydrogenation and selective methanation of CO in CO/CO<sub>2</sub> mixtures.

Different catalyst preparation techniques were employed in this study to see their effect on the catalyst activity in the CO methanation reaction. Microwave radiation was employed to synthesise Ru nanoparticles on some of the supports; likewise, wet incipient impregnation and deposition precipitation using urea were explored as different catalyst preparation techniques in this study.

The set of objectives to achieve the aim of this project were:

1. To synthesize CNTs and N-CNTs using a bimetallic catalyst (Fe-Co/CaCO<sub>3</sub>), with acetylene as carbon source via a chemical vapour deposition (CVD) route.
2. To purify/functionalize the synthesized CNTs and N-CNTs using nitric acid (HNO<sub>3</sub>).
3. To coat the CNTs and N-CNTs with anatase using a simple hydrothermal route.
4. To prepare crystalline rutile titania nano rods using a hydrothermal technique with TiCl<sub>4</sub> as titania source.
5. To prepare supported Ru metal nanoparticles with metal loading of 5 wt% using a microwave assisted polyol synthesis method, a wet incipient impregnation method and a deposition precipitation method using urea. The prepared catalysts were to be tested after calcination.
6. To characterize the prepared catalysts by using techniques such as transmission electron microscopy (TEM), , *ex-situ* and *in-situ* powder X-ray diffraction (PXRD), temperature programmed reduction (TPR), chemisorption and nitrogen adsorption-desorption at the temperature of liquid nitrogen (BET technique).
7. To analyze and compare the activity and selectivity of the synthesized catalysts in the CO methanation in a CO/H<sub>2</sub> gas mixture, the methanation of CO<sub>2</sub> in a CO<sub>2</sub>/H<sub>2</sub> gas mixture and the selective methanation of CO in a CO/CO<sub>2</sub>/H<sub>2</sub> gas mixture at different temperatures (100 °C to 360 °C).

## 1.5 Main ideas

The main ideas developed from this study include;

- i. We have proposed that the morphology of rutile, used as catalyst support, influences the particle sizes of Ru thereby improving catalytic performance. Again, a dandelion-like rutile support can be applicable for high temperature reaction studies due to its sinter resistance.
- ii. A quick but desired variation of RuO<sub>2</sub> with narrow size distribution was achieved by using the microwave polyol synthesis. This was achieved on carbon nanotubes (CNTs) as support.
- iii. Catalytic performance was improved by doping CNTs with nitrogen or covering the CNTs and N-CNTs partially with anatase TiO<sub>2</sub>. The presence of the TiO<sub>2</sub> covering on CNTs inhibited the undesired reverse water gas shift reaction.
- iv. Acid functionalization improved the specific pore volume and surface area of the support. The dispersion of Ru catalysts were better and were found to have a higher catalytic ability on functionalized mesoporous solid carbon spheres (SCs) than on un-functionalized SCs. Un-functionalized SCs does not promote the RWGS reaction, even though they perform poorly as CO and CO<sub>2</sub> methanation catalyst supports.

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# Chapter 2

## 2.0 Background and literature review

### 2.1.0 Fuel cells

The world's energy demand is escalating. Continual and rapid depletion of energy sources coupled with increases in the concentration of green-house gases (GHGs) at an alarming has revamped the quest for enormous scale research into developing substitute and much greener sources of energy. Fuel cells are known to be one of the cleanest sources of energy with very minimal or possibly zero emission of GHGs (e.g.  $\text{SO}_x$ ,  $\text{NO}_x$  and  $\text{CO}_2$ ).

Fuel cells have attracted the attention of researchers in recent years because of their non-polluting nature and efficiency, as well as providing much higher energy densities in comparison to other current and conventional systems [1-4]. The prime focus of researchers has been to develop a low cost, high performance and durable material for fuel cells. Currently, most fuel cells have fairly poor durability and high intrinsic cost. A number of possibilities have been explored aiming at reducing cost and enhancing the performance of fuel cells. On-going research involves the following [5-10]:

- i. Minimizing the amount of electrocatalysts loaded on fuel cell electrodes.
- ii. Using nanometre scale electrocatalysts.
- iii. Improving dispersion by employing novel fabrication methods in the synthesis of the electrocatalysts.
- iv. Reducing or completely replacing Pt as an electrocatalyst by developing metallic alloy (binary or ternary alloys).
- v. Enabling better catalyst dispersion and utilisation by developing membrane electrode assembly (MEA) fabrication methods.
- vi. Employing novel procedures to enhance mass-transport at the fuel cell electrode surface.
- vii. Exploring and enhancing carbonaceous and non-carbonaceous (including novel non-carbonaceous) electrocatalyst support materials.
- viii. Eliminating or reducing electrocatalyst poisons (e.g. CO) in  $\text{H}_2$  for fuel cells.

### 2.1.1. Fuel cell technology

Fuel cells are devices that generate electrical energy through the direct conversion of chemical energy with water and heat as by-products [11]. They are open thermodynamic systems which consume reactants from an external source via electrochemical reactions [12, 13]. A fuel cell has four major components; the external circuit, an electrolyte layer, the cathode and the anode. The chemical characteristic or composition of the electrolyte account for different types of fuel cells [12].

Hydrogen is oxidised at the anode into protons and electrons, while on the cathode, oxygen is reduced to oxide species, which react to form water. Protons or oxide ions are transported across an electrolyte (which is an ion-conductor but electron-insulator), and this depends on the chemical composition of the electrolyte. Electrons are forced to travel through an external circuit to deliver electric power [13]. Equation (2.1) and Figure 2.1 show the electrochemical reaction and a simple PEM fuel cell diagram.



hydrogen + oxygen  $\rightarrow$  water + (electric power + heat)

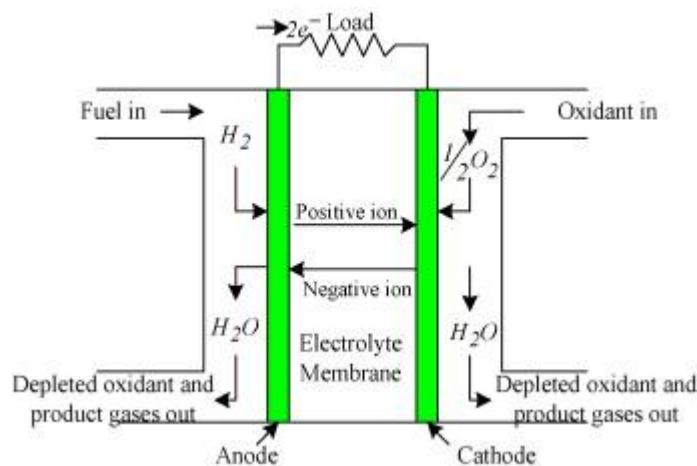


**Figure 2.1.** Schematic diagram of a fuel cell and the chemical reactions occurring in the cell [14].

Christian Friedrich Schönbein, a Swiss scientist is credited with basic principle of a fuel cell in 1838. Sir William Grove is credited for discovering the first operational fuel cell in 1839.

His discovery was accidental and discovered while he was conducting electrolysis of water experiments. He disconnected the battery from the electrolyzer in his experiment, and connected the two electrodes together and saw a current flowing in the opposite direction, using up the hydrogen and oxygen. This was the reverse of water electrolysis [15]. Francis Bacon demonstrated the first 5 kW alkaline fuel cell in 1950 at Cambridge University [16]. International Fuel Cells research unit developed a 12 kW alkaline fuel cell for NASA's space shuttle orbiter in 1970 to avoid having to use any backup power sources, such as batteries. Research in the mid-1960s focused on developing different fuel cells for applications like stationary power supplies and in transportation [12]. The high cost of installation was a major drawback in fuel cell development. Due to this, many countries only commenced fuel cell research and development fifty years after the USA, Canada and Japan had significantly developed the technology [12]. More recently, intensive research has been channelled into developing a more cost effective fuel cell [13] and a number of fuel cells have thus been developed. These are given below [16]:

- (i) Alkaline fuel cell (AFC),
- (ii) Proton exchange membrane fuel cell (PEMFC),
- (iii) Phosphoric acid fuel cell (PAFC),
- (iv) Molten carbonate fuel cell (MCFC),
- (v) *Direct methanol fuel cell (DMFC)*,
- (vi) Solid oxide fuel cell (SOFC).

The fuel cells are further group based on the operating temperatures. Low temperature fuel cells operate within the range of 50-250 °C. These include the PEMFC, AFC, DMFC and PAFC. High temperature fuel cells such as SOFC and MCFC operate within a temperature range of 650-1000 °C. The work in this thesis will focus on challenges relating to the PEMFC and a more detailed discussion of this fuel cell follows [17, 18].

### *2.1.2. Polymer electrolyte fuel cell*

PEMFCs operate between 60 and 100 °C. They have a rapid start-up (fast in producing electric power) and are light weight compact systems. Due to the solid nature of the

electrolyte, PEMFCs have electrodes that are easier to seal compared to other types of fuel cells. They are hence cheaper to manufacture and enjoy a longer lifetime [14, 19-21]. Due to the above mentioned properties, the PEMFC technology is competitive in transportation (fuel cell cars), stationary power supplies (e.g. generators) and portable devices (e.g. laptop computers, mobile phones and bicycles). However, among all the applications of PEMFCs, transportation is the most feasible application, due to the fact that the fuel cell provides a continuous electrical energy supply and power density [22].

A basic PEMFC (Figure 2.2) consists of a bipolar plate and membrane electrode assembly (MEA, a Teflon-like membrane). The MEA comprises of the membrane, carbon cloth or gas diffusion layer and dispersed catalyst layer. The catalyst oxidises hydrogen fuel to produce proton ions and release electrons at the anode. The membrane transports protons from the anode to the cathode and blocks the passage of electrons and reactants. The electrons are forced to run through an external circuit and generate electricity [12, 20, 21]. Equations 2.2 and 2.3 represent the chemical reactions that occur at the different electrodes and Equation 2.4 form the overall reaction.

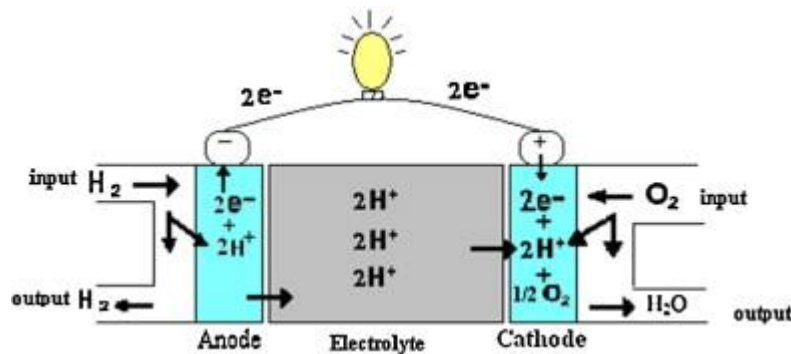
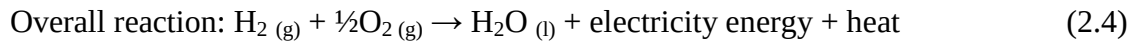


**Figure 2.2.** A proton exchange membrane fuel cell (PEMFC) [23].

In spite of its promising nature, the PEMFC also has major drawbacks, which include a relatively low operating efficiency (55-65 % but its energy output can be as high as 250 kW), hydrogen storage and the use of expensive platinum (Pt) catalyst. The Pt catalyst is also intolerant to poisoning by carbon monoxide (CO) [24].

### *2.1.3. Hydrogen fuel for PEMFCs*

Hydrogen, which is the main source of fuel for a PEMFC is known to be one of the cleanest forms of fuel from an environmental point of view. It also does not contribute to the depletion of the ozone layer. In the presence of a suitable catalyst, hydrogen can be very reactive; hence it has become the gas of choice for many applications e.g. fuel cells. Hydrogen based technologies are expected to revolutionize the energy and transportation market based on the above mentioned property [25]. The main source of hydrogen remains fossil fuels. The hydrogen is mostly produced by dehydrogenation and methanol reforming, through gasification technologies and steam reforming of natural gas [26, 27]. In the hydrogen production through steam reforming, a small amount of CO (typically 0.5-5 mol %) is also produced. CO easily poisons (deactivates) the catalyst used in the PEMFC electrode (usually Pt or in some advanced electrodes Pt-Ru or Pt-Zn). These metals coupled with Pt acts as sacrificial metal and tends to reduce the Pt poisoning by absorbing some of the CO present in the reformat feed [28]. A reduction in the PEMFC power output and a detrimental effect on the cell's voltage is observed when the catalyst used in a PEMFC is exposed to a trace amount of CO [28].

Possible commercialisation of PEMFCs depends on reducing the concentration of CO in reformat gas through a viable method and sufficient process. This project focused on purifying reformates gas for a PEMFC through selective CO methanation, which has proven to be a sufficient and effective method in many studies. Selectivity and high activity are critical in selective CO methanation.

### *2.1.4. Hydrogen feed purification for PEMFCs*

The CO concentration in a gas feed stream for a PEMFC needs to be reduced, preferably below 10 ppm [29-31]. Studies show that approximately 10 ppm of CO in the gas feed is enough to result in the deactivation of the catalyst, thereby, reducing the cell performance [32]. In theory, there are several techniques by which the CO can be removed from a H<sub>2</sub> rich fuel stream for PEMFC use [33]. It is practical to isolate hydrogen from CO by diffusion of H<sub>2</sub> through a CO filtering membrane (Pd-Ag membrane). This membrane requires compressors due to the high pressures involved. This technique is expensive due to the nature of the membrane [34]. However, the best option for the removal of the final traces of CO

have been found to be selective CO methanation (SMET) and preferential CO oxidation (PROX) as shown in Figure 2.3.

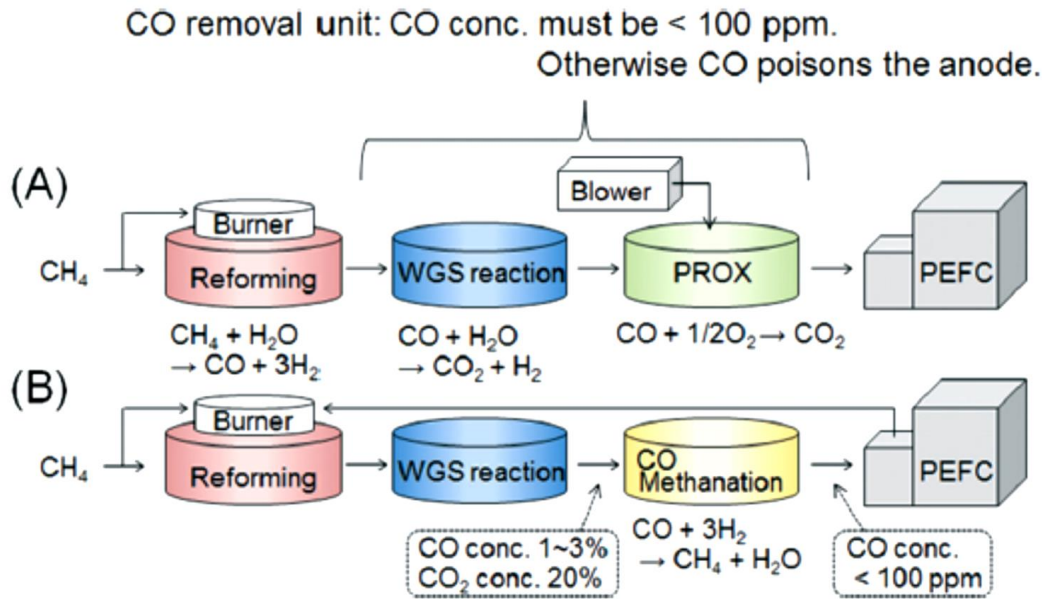
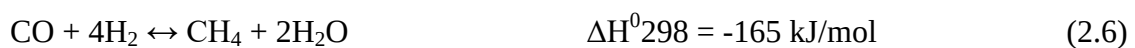
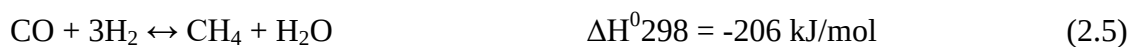


**Figure 2.3.** Fuel processing for PEMFC systems, composing units for (a) preferential oxidation of CO (PROX) and (b) CO methanation [35].

The two techniques use low operating pressures [36]. Due to its ability to remove CO to a very low concentration by raising the oxygen consumption, PROX has been widely explored [37-39]. However, a closely controlled limited supply of oxygen is needed to sustain the lowest possible  $\text{H}_2$  oxidation in this technology. Also, this technique generally operates best over a very narrow temperature window. This complicates and makes the technique more costly and also limits its application in low-power PEMFCs, where a very small flow of oxidant is provided by the use of a mass flow meter [36].

The limitations experienced by PROX can be avoided by selective CO methanation (SMET). Also, CO and  $\text{CO}_2$  methanation (as indicated in the Equations 2.5 and 2.6) are less exothermic than the CO and  $\text{H}_2$  oxidation (Equation 2.7 and 2.8). SMET, unlike PROX, is inherently easier to control.





As indicated in the selective CO methanation equation (Equation 2.5), three moles of H<sub>2</sub> are required to remove one mole of CO, with the by-product being CH<sub>4</sub>. This methane can be reused after the PEMFC reaction *via* re-circulation of the cell's off-gas as feedstock back into the reformer, or for heating. Attached to a PEMFC is an off-gas re-circulation line purposely to recover unreacted H<sub>2</sub> which sometimes forms about 10-20 % of the feed [40]. Therefore, one mole of H<sub>2</sub> is actually lost to water formation in the CO SMET process (meaning 1 mole of H<sub>2</sub> for 1 mole of CO removal) if is 1.0 or 100% methanation selectivity towards CO attained. While in theory, no H<sub>2</sub> is lost in the PROX (Equation 2.7) at 100% selectivity, such efficiencies are not practically feasible. This is due to inefficiencies in the technique over a commercial catalyst and the risk of supplying oxygen at a ratio of O/CO = 1.0 (v/v) even if the catalyst allows for this possibility [38, 41, 42]. Furthermore, there is an inherent fluctuation in a PEMFC which requires an oxygen supply to counter the CO content appearing in the fluctuation. Hence, loss of H<sub>2</sub> via Equation 2.8 prevails in practical PROX. Existing data [38, 41, 42] shows that the loss of H<sub>2</sub> in practical PROX is about one to two moles for a CO removed because the actual PROX reactor generally operates at O/CO ratios of 2-3 (v/v).

Selective methanation of CO is essential, otherwise the methanation of carbon dioxide (likely to be present in e.g. reformat hydrogen gas streams) could occur which would then be a major hydrogen-consuming reaction.

## 2.2. The mechanism for CO methanation

Methanation of CO is widely accepted to occur on the surface of an active metal. The methanation reaction proceeds *via* successive hydrogenation of the resultant surface carbonaceous species after CO has dissociated on a metal surface [43-45]. Methanation of CO in the presence of excess CO<sub>2</sub> (selective methanation condition) is also believed to occur on the surface of the metal. Numerous examples of catalysts used in the methanation reaction have been reported, for example the nature of Ru species on TiO<sub>2</sub> under selective methanation

conditions were thoroughly analysed using *in situ* DRIFTS and TPD techniques by Panagiotopoulou and co-workers [46]. Numerous species were observed under CO only methanation conditions; metallic Ru with bridged and linear CO ( $\text{Ru}_x\text{-CO}$ ), Ru-CO positioned at the metal-support interface ( $(\text{TiO}_2)\text{Ru-CO}$ ) and multicarbonyl species on partially oxidized Ru ( $\text{Ru}^{n+}(\text{CO})_x$ ) were observed. They suggested that the presence of  $\text{Ru}^{n+}(\text{CO})_x$  may indicate dissociative adsorption of CO on the Ru metal (see Equations 2.9-2.11 below).



### 2.3. The mechanism for CO<sub>2</sub> methanation

The methanation of CO<sub>2</sub> over a supported catalyst is generally acknowledged the process occurs *via* CO<sub>2</sub> being adsorbed on the support. The CO<sub>2</sub> reacts with H atom on the surface of the metal to yield methane [35]. Nonetheless, diverging views on the CO<sub>2</sub> methanation pathway exist in literature. Some authors have proposed that the active sites for CO<sub>2</sub> conversion to CO (an important step in CO<sub>2</sub> methanation) is the active metal [44, 47-50], while others propose the sites to occur at the support-metal interface [51, 52]. Ni [49-51, 53] and noble metals such as Ru [52, 54], Rh [48] and Pd [55] have been widely studied to determine the mechanism of CO<sub>2</sub> methanation.

Ni-Al oxide was used to analyse carbon dioxide adsorption and its subsequent hydrogenation over a using *in situ* DRIFTS by Mayo and co-authors [56]. Dosing the DRIFT chamber with CO<sub>2</sub> showed peaks at 2014 and 1844 cm<sup>-1</sup> (Figure 2.4(A-a)) which were assigned to CO adsorbed on metallic Ni. Introducing H<sub>2</sub> alongside CO<sub>2</sub> enhanced the CO peak and revealed the appearance of formate peaks (1601 and 1390 cm<sup>-1</sup>) and a C-H stretch vibration at *ca.* 3000 cm<sup>-1</sup> (Figure 2.4(A-b)). The CO peaks disappeared after H<sub>2</sub> was introduced and the CO<sub>2</sub>/H<sub>2</sub> mixture was switched off, while the C-H and formate vibrations slightly reduced in size (Figure 2.4(A-c, d)). This suggested the conversion of CO<sub>2</sub> to CO occurs *via* adsorption on Ni sites with possibly dissociation to Ni-CO and Ni-O. Extra CO produced through the RWGS reaction of CO<sub>2</sub> adsorbed on Ni sites formed formate species. Carbon monoxide was

dosed on a CO<sub>2</sub>-modified catalyst surface (Figure 2.4(B)) with the aim of identifying the major sites for CO<sub>2</sub> conversion to CO. From Figure 2.4(B-a, b), the CO peak area was observed to have almost doubled and no significant change was observed in the CO adsorbed species when a CO/CO<sub>2</sub> gas mixture was substituted by CO<sub>2</sub> and He. However, the peak red shifted due to the decrease in surface CO coverage or adsorption (Figure 2.4B (b and d)). In spite of the introduction of CO<sub>2</sub> into the chamber, CO was not produced but rather desorbed. Furthermore, no Ni<sup>+</sup>-O peak at ca. 2150 cm<sup>-1</sup> appeared (Figure 2.4B-b) and this implied CO<sub>2</sub> dissociation did not oxidize the Ni surface. This is an indication that CO<sub>2</sub> conversion reaction sites are different from that of CO adsorption. This finding is in agreement with the proposal made by many researchers that CO<sub>2</sub> conversion should occur at the metal-support interface and not on the active metal surface which does not serve as adsorption sites [46, 51, 52, 57-60].

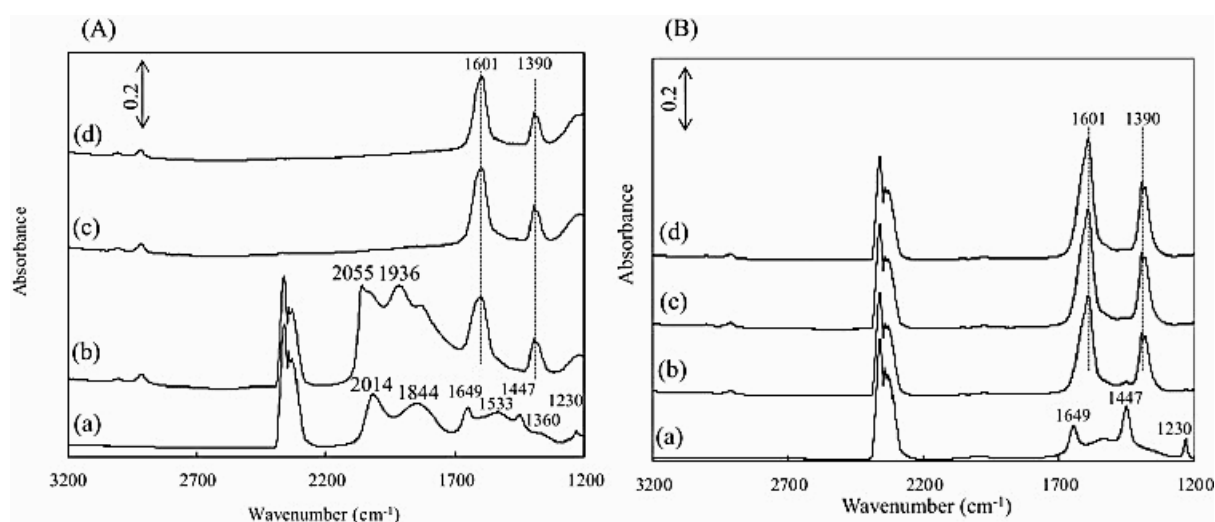


**Figure 2.4.** CO<sub>2</sub> adsorption and hydrogenation over Ni–Al oxide catalyst's FTIR spectra (A) unmodified, (B) RuCl<sub>3</sub> added under flowing (A, a) CO<sub>2</sub>, (A, b) CO<sub>2</sub> and H<sub>2</sub>, (A, c) H<sub>2</sub> for 5 min, and (A, d) H<sub>2</sub> for 30 min, (B, a) CO<sub>2</sub>, (B, b-d) CO<sub>2</sub> and H<sub>2</sub>. These are sequential measurements at 230 °C [14].

A CO<sub>2</sub> methanation mechanistic pathway hinges on the determination and identification of the intermediates involved. One reliable technique employed in such studies is steady state isotope transient kinetic analysis (SSITKA) IR measurements. Eckel and co-workers [61] employed this technique with the aim of studying the CO<sub>2</sub> methanation intermediates (Figure 2.5). They methanated CO<sub>2</sub> over Ru/zeolite and Ru/Al<sub>2</sub>O<sub>3</sub> with a gas mixture of <sup>12</sup>CO<sub>2</sub>/H<sub>2</sub>. The reaction was kept on stream for 1000 min. and the gas mixture was later switched to a mixture with the isotopic labelling isotopomer (<sup>13</sup>CO<sub>2</sub>/H<sub>2</sub>). Formate species containing <sup>13</sup>C

(1550  $\text{cm}^{-1}$ ) gradually appeared while  $^{12}\text{C}$ -containing formates (1590  $\text{cm}^{-1}$ ) somewhat disappeared (Figure 2.5). The C-H and the CO (ca. 3000 and 2000  $\text{cm}^{-1}$  respectively) vibration from  $^{12}\text{C}$ -containing species were replaced with  $^{13}\text{C}$  species. Based on the findings above, the authors concluded that CO could not be derived from the RWGS reaction but rather from  $\text{CO}_2$  dissociation, and that formate species are not intermediate for  $\text{CO}_2$  under selective methanation conditions ( $\text{CO}/\text{CO}_2$  co-existing).

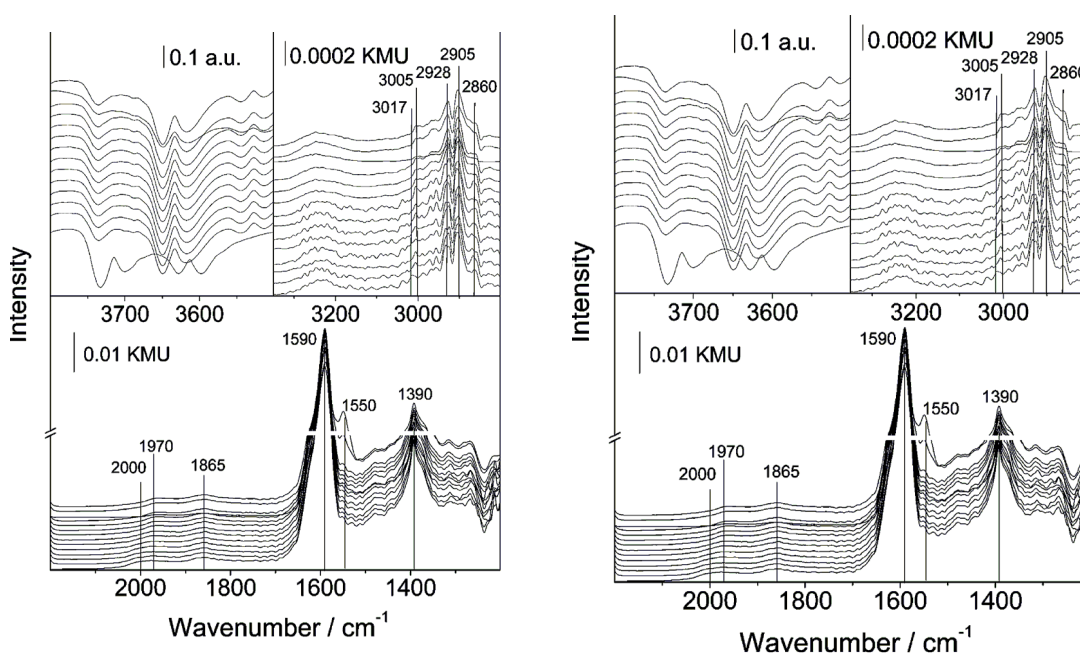
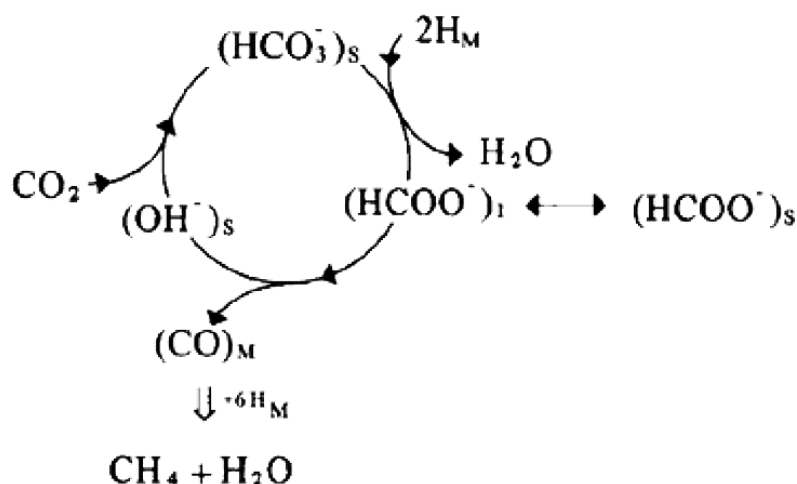


**Figure 2.5.** 1000 min on stream at 190 °C DRIFT spectra recorded (equilibration of surface species) over the Ru/zeolite (top panels) and Ru/ $\text{Al}_2\text{O}_3$  catalysts (bottom panels) in  $\text{CO}_2$ -rich reformat which was afterward changed to  $^{13}\text{CO}_2$  containing reaction atmosphere: from bottom to top: 0, 1, 2, 3, 5, 6, 7, 10, 15, 20, 25, 30, 35, 45 min. [61].

The main intermediates species that are predicted based on computational chemistry for  $\text{CO}_2$  conversion to CO, are hydrocarboxyl species (HOCO) [62, 63], HCOO to make formate species [64-66], while no intermediates were proposed for CO dissociation [64]. This prediction introduces debates on the intermediates formed  $\text{CO}_2$  conversion to CO.

Marwood and co-authors suggested a mechanism for  $\text{CO}_2$  methanation over Ru/ $\text{TiO}_2$  in which they employed the DRIFT technique [52]. Scheme 1 represents the  $\text{CO}_2$  methanation

pathway they suggested, involving hydrogen carbonate ( $\text{HCO}_3$ ) which generated formate species ( $\text{HCOO}^-$ ). The metal-support interface served as an adsorption point for the formate species which decomposed to  $\text{H}_2$  and hydroxyl groups.



**Scheme 2.1.** scheme showing  $\text{CO}_2$  methanation on  $\text{Ru}/\text{TiO}_2$  catalyst. Abbreviations of M, S, and I indicate, metal, support and metal–support interface, respectively [52].

Tada and co-authors compared formate and carbonate hydrogenation rates using a  $\text{Ru}/\text{CeO}_2$  catalyst [59]. A plot (Figure 2.6) of the ratios of the peak areas ( $A/A_0$  where A and  $A_0$  were defined as the peak areas after the desired reaction and initial peaks respectively) as a function of time-on-stream, after switching a gas mixture from  $\text{CO}_2/\text{H}_2$  to  $\text{H}_2/\text{Ar}$ . Peaks at 1580, 1530, 1470, 1370, and 1290  $\text{cm}^{-1}$  were correlated with different species. A similar rapid reduction rate was observed for the peaks at 1580 and 1330  $\text{cm}^{-1}$ . The authors attributed this to the disappearance of bidentate species on the  $\text{CeO}_2$ . Interestingly, the ratios of the rates for 1530, 1470, and 1370  $\text{cm}^{-1}$  almost overlapped. They all registered a decline in the ratio from 1 to 0.6 in an hour and then remained almost unchanged. The 1370 and 1530  $\text{cm}^{-1}$  peaks were attributed to the C-H in plane bending vibration of formate species and O-C-O asymmetric stretches respectively, which the 1470  $\text{cm}^{-1}$  band was ascribed to monodentate carbonate [67]. They further explained the drop in ratios as a result of desorption of some formate species that remained and did not react with  $\text{H}_2$ . In their investigation of the thermal stability of formate and carbonate species under a  $\text{N}_2$  atmosphere, they reported that the carbonate peaks at 1580 and 1330  $\text{cm}^{-1}$  gradually disappeared but peaks for the formate species at 1540 and

1390  $\text{cm}^{-1}$  remained unchanged. They made the following deduction: a) the formate and carbonate species reacted with  $\text{H}_2$  b) at high temperatures (200  $^{\circ}\text{C}$ ), the carbonate species desorbs from the Ru/CeO<sub>2</sub> c) the thermal stability of the formate species at 200  $^{\circ}\text{C}$  is intact.

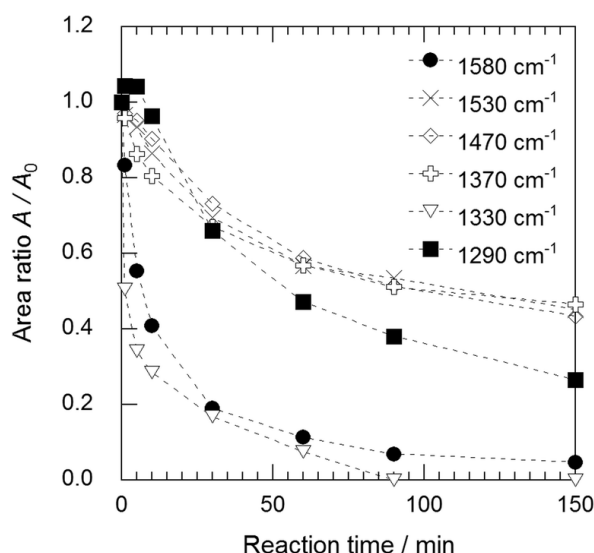
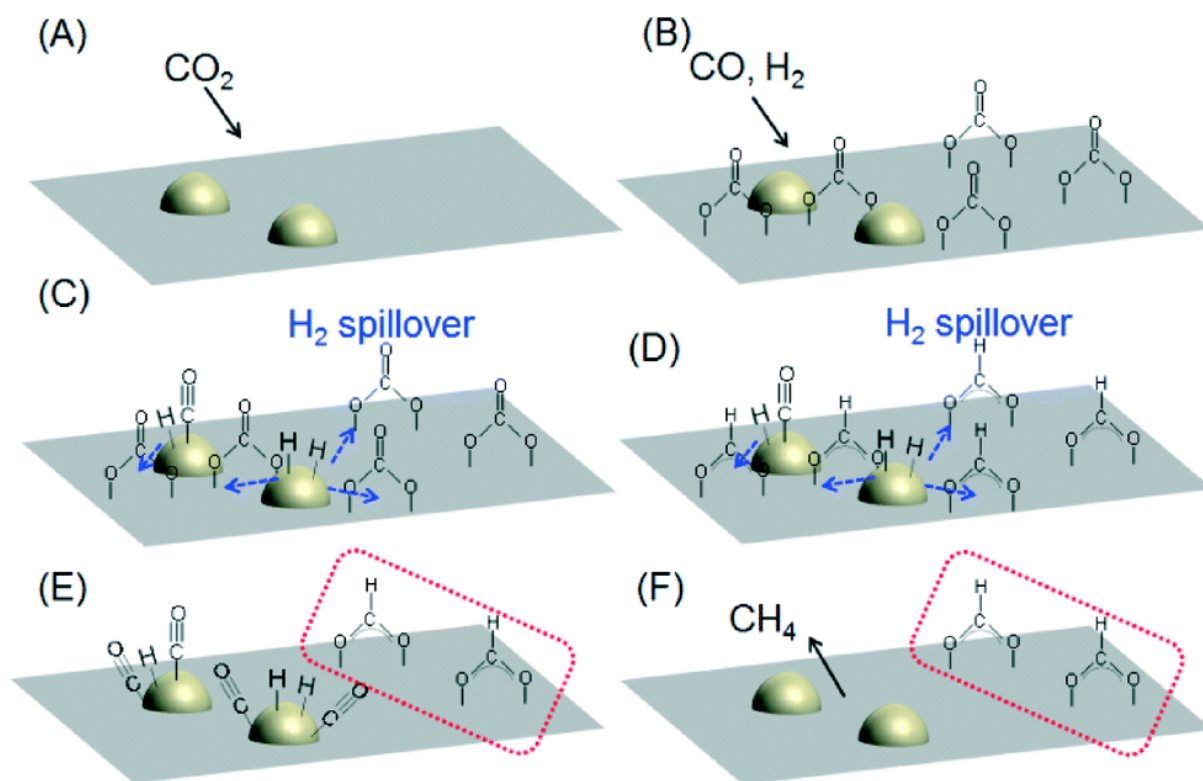


**Figure 2.6.** A function of reaction time to decrease in FTIR peak area ratios to the initial peak area at the respective wavenumbers under 5%  $\text{H}_2/\text{Ar}$  flow at 200  $^{\circ}\text{C}$  as. The results were recorded after a switch from the model gas mixture ( $\text{CO}_2/\text{H}_2 = 1/9$ ) to 5%  $\text{H}_2/\text{Ar}$ . Catalyst: 2% Ru/CeO<sub>2</sub> [59].

In a review by Tada and Kikuchi [35] the reaction scheme for  $\text{CO}_2$  methanation over a supported catalyst was suggested (scheme 2.2). The scheme summarized the phenomena that had been observed.

Carbon dioxide firstly adsorbed on the support which led to carbonate species formation on the support (scheme 2.2(A and B respectively)).  $\text{CO}$  and  $\text{H}_2$  adsorbed on the surface of the active metal as shown in scheme 2.2C. The carbonate species were then converted to formate species *via* a hydrogen spillover phenomenon (scheme 2.2D). Some reports indicate formate species are formed through a carbonate reaction with gas-phase  $\text{H}_2$  [52]. The formate species bordering the active metal are then decomposed into  $\text{CO}$  within the metal-support interface leaving the residual species shown in the dotted square in scheme 2.2E.  $\text{CO}$  adsorbs on the active metal surface and finally reacts with  $\text{H}_2$  to form  $\text{CH}_4$  (scheme 2.2F).



**Scheme 2.2.** Possible CO<sub>2</sub> methanation mechanism of over supported metal catalysts under selective methanation (CO and CO<sub>2</sub> coexisting) conditions [35].

## 2.4 Catalyst preparation

Catalyst preparation methods are known to have a strong bearing on catalytic activity [68]. Generally, numerous techniques exist for catalyst preparation, amongst them are:

- Impregnation methods
- Co-precipitation methods
- Sol-gel methods
- Deposition-precipitation methods
- Plasma methods
- Colloidal methods
- Microemulsion
- Solvated metal atom dispersion methods
- Chemical vapor deposition methods

### ➤ Microwave assisted polyol synthesis

Despite the numerous techniques available for catalyst preparation, the impregnation and deposition-precipitation process remain the most widely used compared to other techniques such as ion exchange and vapour phase deposition [68]. In this project, three techniques were employed, which were the microwave assisted polyol synthesis, impregnation and deposition-precipitation methods.

#### *2.4.1. Impregnation method*

The impregnation method, also known as the incipient wetness method is the simplest and least expensive and most used method to prepare supported metal catalysts. The metal loading is usually achieved *via* contact between a liquid solution containing dissolved metal ions (at the desired loading) and the support surface. Prior to that, the pore volume of the support is identified by wetting the dry support with water, while observing the exact volume of water added. A capillary-type force or diffusional effects drives the active metals into the interior of the support. The liquid remaining is removed by drying in an oven and in the process, the metal salt (typically a metal-nitrate or metal-chloride) is crystallized onto the surface or into the walls of the pores of the support material [69, 70]. The catalyst is then calcined at a desired temperature to form a metal oxide on the support and also remove other unwanted species. Some of the drawbacks in this method is that the metal complexes that are left in the solution can migrate significantly and sometimes the metal precursor does not interact strongly with the surface of the support [71].

#### *2.4.2. Deposition-precipitation method*

This technique exploits the deposition and precipitation of metal ions from a liquid medium [72]. The advantage of the precipitation method relates to particle size control and size distribution. The method also reduces the chances of forming bulk mixed compounds on the support alongside the active phase [73, 74]. In the deposition-precipitation method, the active metal usually derived from a salt is dissolved along with excess urea (1:5 moles) in deionized water. A homogenous solution is formed by slow addition to the support material to form a slurry while stirring. The slurry is heated to 90 °C to hydrolyse the urea and precipitate the

metal on the support. After drying and calcination, the metal oxides are formed on the surface of the support material.

#### *2.4.3. Microwave polyol method*

The microwave assisted method requires microwave irradiation to reduce the metal. This technique is considered as green and novel. This is expected to give a good control over the morphology and particle sizes which are key parameters that define the activity in catalysis [75-77]. There are some advantages that the microwave assisted technique offers this include; a more rapid thermal induction period, uniform heating, localized high temperature at sites of reactions which improves the metal ion reduction rate, and superheating of solvents above their boiling points over the whole liquid as result of the dissipation heat due to the microwave [77-79].

### **2.5 Catalyst supports**

The main purpose of a catalyst support is to increase the dispersion and surface area of the active catalyst species. Furthermore the support stabilizes the active metal against sintering, improves heat and mass transfer in diffusion-limited reactions and can improve the catalyst's mechanical strength [80-82]. Poisoning can sometimes be reduced as a result of supporting the catalyst. The right choice of catalyst support is critical in the performance of the catalyst. There are several available commercial catalyst supports and these include;  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{CeO}_2$ , etc [83-86] and most recently carbon nanostructures such as carbon nanofibres (CNFs) carbon nanospheres (CNSs) and carbon nanotubes (CNTs) [71, 87-90].  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  are the most widely used supports in many catalytic reactions. These traditional oxidic supports have experience some drawbacks when it is used to support some metals such as cobalt. These drawbacks include the formation of very strong metal support interaction leading to the formation of mixed compounds which are only reducible at very high temperature. Thus limits accessible active sites on the metal. Carbon materials form no spinel phases and may moderately interact with metal catalysts, making them more attractive than the oxidic supports [68, 91]. As such, new materials are being continuously tested to yield one that would overcome the limitations of the traditional oxide supports, and amongst these new materials are carbon nanomaterials.

A good support ideally should possess a good catalyst-support interaction, large surface area, good electrical conductivity, and good corrosion resistance and in some cases these leads to easy regeneration of the active catalyst species [92, 93]. Amongst the many catalyst supports, carbon nanotubes (CNTs) have been explored in recent years for use as a catalyst support because of the large surface area [92], good electrical conductivity and good corrosion resistance [94].

### *2.5.1. Carbon supports*

Carbon materials e.g. (carbon black and activated charcoal) have been employed as supports for various catalytic reactions [95]. In recent years, attention has been geared towards other nano carbon materials such as carbon fibres, carbon nanotubes, carbon nanofibres and carbon nano spheres [96].

Carbon materials used as supports in hydrogenation reactions gasify into methane at temperatures above 430 °C and also gasify into CO<sub>2</sub> in the presence of oxygen at temperatures above 230 °C [97]. Despite these shortcomings of carbon based materials, they possess some unique properties that are not present in most catalyst supports. These valuable characteristics are [95]:

- ✓ Structural stability over a wide temperature range.
- ✓ Their surface areas are resistant to basic or acidic media.
- ✓ They are cheap compared to other supports.
- ✓ Through controlled combustion of a carbon support, the active phase can easily be recovered especially when the active phase is a precious metal.
- ✓ Pore sizes needed for specific applications can be achieved by tailoring the pore structure.
- ✓ Polarity of the support can be regulated by modifying the chemical composition.

These properties of carbon materials make them applicable in various catalytic reactions including Fischer-Tropsch [98], hydrogenation [99-102] and oxidation [102, 103] reactions. Carbon nanostructures have been explored lately as possible alternatives to other carbon materials like activated carbon to solve the issue of low reproducibility and microporosity which has hindered the development of the use of carbon supports [84]. Pure carbon that is

$sp^2$  hybridized is able to form incredible structures in the form of fullerenes (0D), graphite (3D), graphene (2D) and nanotubes (1D) [104].

CNTs have gained much interest in heterogeneous catalysis due to their high purity [71, 105], electrical conductivity, lack of microporosity, good mechanical strength. CNTs also enjoy some levels of flexibility for dispersion of active metals due to the ease with which it can be functionalised [106, 107]. Active metals can be deposited in the inner cavity or the outside wall of a CNT [108]. Also, its chemical composition is easily altered by doping with heteroatoms (e.g. nitrogen or boron). CNTs have successfully been used as a catalyst support in many chemical reactions [109, 110].

### 2.5.2. $TiO_2$ as support

Titanium dioxide, also referred to as titania, was discovered in 1821 and mined in the form of rutile and ilmenite (a mixture of iron, titanium and oxygen) [111]. Over the years,  $TiO_2$  has been used for durability and whiteness in paint. Several applications for  $TiO_2$  include its use in coatings, plastics, papers, inks etc. Titania in the sintered form has found very limited use due to its cooperatively poor mechanical properties [111, 112]. There are several polymorphic phases of titania that exist at different pressures. The main polymorphs known and that have been studied are anatase, rutile and brookite. Anatase and rutile have significant industrial application. Anatase results from the kinetic reaction of titanium and oxygen while rutile is the thermodynamically stable phase which cannot be transformed to any other polymorph [113, 114]. Owing to its relatively low cost and availability,  $TiO_2$  has found useful applications in the following scientific and industrial areas [115] as

- a support for catalyst materials
- a photocatalyst for the splitting of water
- a photocatalyst for decomposition of organic molecules into carbon dioxide and water
- a pigment in paints and cosmetics
- an UV absorption agent in suntan lotions
- a gas sensor
- a semi-conducting substrate and light scatterer in dye-sensitised solar cells
- a treatment surface for self-cleaning surfaces (using photocatalytic properties) [115].

Titania is widely used as a solid catalyst support and has demonstrated good catalytic performance [116-119], allowing catalyst activity modulation for a number of reactions, which include the water gas shift [120], dehydrogenation [117, 118], hydrodesulphurization [119] and thermal catalytic decomposition. In spite of this, major drawbacks exist using  $\text{TiO}_2$  as a catalyst support in heterogeneous catalysis. These limitations include its small surface area, small quantum efficiency, and low adsorption abilities [119, 120]. Quite significant studies have focused on  $\text{TiO}_2$  as a support material despite these drawbacks. The electronic effect and bifunctional mechanism are the main effects  $\text{TiO}_2$  supports offer as an advantage in heterogeneous catalysis [121].  $\text{TiO}_2$  as a support can enforce an electronic effect on a catalyst when the presence of a hypo-d-electronic  $\text{T}^{3+}$  promotes electrocatalytic features of hyper-d-electronic noble catalyst surface atoms [122]. On reaction with CO the presence of  $\text{Ti}^{3+}$  can decrease the CO intermediate adsorption energy, while the mobility of CO groups can be enhanced. Also, OH species adsorption on  $\text{TiO}_2$  tends to convert toxic CO to  $\text{CO}_2$  catalytically, thus enhancing the durability of the catalyst [123, 124]. Both scenarios indirectly disperse and anchor the active metals supported on  $\text{TiO}_2$  [123].

### *2.5.3. CNT- $\text{TiO}_2$ composite as support*

The catalytic activity of  $\text{TiO}_2$  support as well as its durability can be improved by modifying it by doping or forming a composite with another material [125]. There has been great research interest to combine CNT's and other inorganic nanomaterials i.e., metal oxides to exploit the synergetic property which the individual components will possess. While many composites exist, CNT- $\text{TiO}_2$  composites have recently attracted much attention for research due to its potential application and unique properties in photocatalysis. This has for example been achieved by adding CNTs to  $\text{TiO}_2$  to extend the light adsorption of  $\text{TiO}_2$  to the visible region [126-132]. This is said to significantly increase photocatalytic efficiency. Figure 2.7 summarizes several of the photocatalytic enhancements based on CNT- $\text{TiO}_2$  composition that have been proposed in the literature.

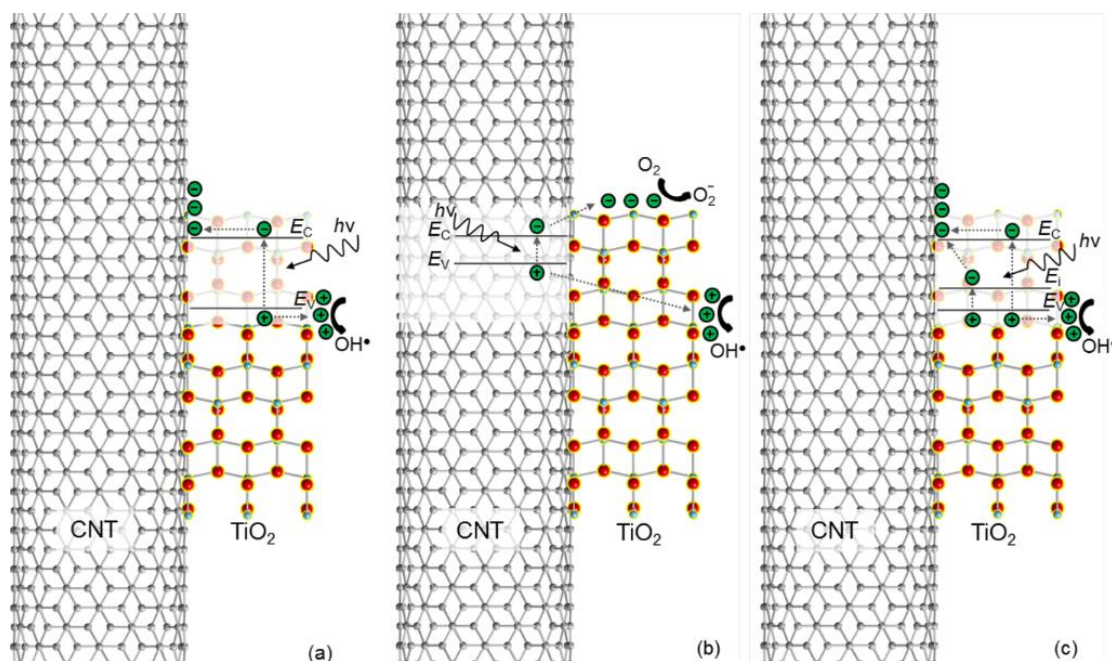


**Figure 2.7.** Mechanisms showing the efficiency enhancement using CNT–TiO<sub>2</sub> nanocomposites for photocatalysis (a) electrons generated in TiO<sub>2</sub> are scavenged by CNT, resulting in excessive holes on the surface for redox reactions. (b) CNT functions as a photosensitizer and releases electrons and holes into TiO<sub>2</sub> for redox reactions. (c) CNT introduces energy states in the band gap of TiO<sub>2</sub> which can convert long wavelength photons to electrons and holes [133].

## 2.6 Methanation catalyst

Due to the dissociative adsorption of CO and H<sub>2</sub>, on Group 8-10 elements they are known to be very active metals for CO<sub>x</sub> hydrogenation reactions [134]. The most active metals for CO hydrogenation include Rh, Co, Ru, Ni, and Fe [135-138]. For selective methanation reactions, Ru, Rh and Ni, have widely been employed. Nickel on Al<sub>2</sub>O<sub>3</sub> was initially considered as the traditional methanation catalyst, but it has been found to interact with CO at relatively low temperatures to yield mobile nickel subcarbonyls which easily deactivate the Ni catalyst [139]. Ruthenium on the other hand has shown higher activity for both CO methanation [51, 140], and CO<sub>2</sub> methanation when deposited on metal oxides even at low temperatures [141, 142], Ru is also known to be active for selective CO methanation [51, 143, 144]. The CO methanation activity is said to be determined by the breaking of a C-O bond and the stability of the individual species on the surface of the active metal used [145, 146].

A volcano-shaped curve is observed when a catalyst's activity for particular reaction is plotted as a function of a parameter which relates to the catalyst surface ability to form chemical bonds with either, products, reaction intermediate or reactants [147-149]. This relation is helpful in searching for new catalysts [150, 151].

Bligaard and co-authors [145] described the activity of some metal catalyst and correlated it with the chemisorption energy of surfaces of the active metals. The reaction energy for dissociative CO chemisorption is plotted as function of activity of some supported metals is shown in Figure 2.8. The volcano plot indicates that the far right metals had high dissociative CO adsorption energies with the rate of methanation limited by the high resistance to CO dissociation. They concluded that these catalysts were not good for CO methanation. However, the group on the left in Figure 2.8 had lower dissociative CO adsorption energies and the reaction rate was limited by the high binding energy of the adsorbed C and O species. They concluded that they would not be good catalysts either. The metals in the middle of Figure 2.8 (e.g. Ru) had optimum chemisorption energy in the region of  $-150 \text{ kJmol}^{-1}$  and this could explain why Ru had a higher activity than all the other group 8-10 elements in the methanation reaction. Rh, Ni and Co also have a good activity.

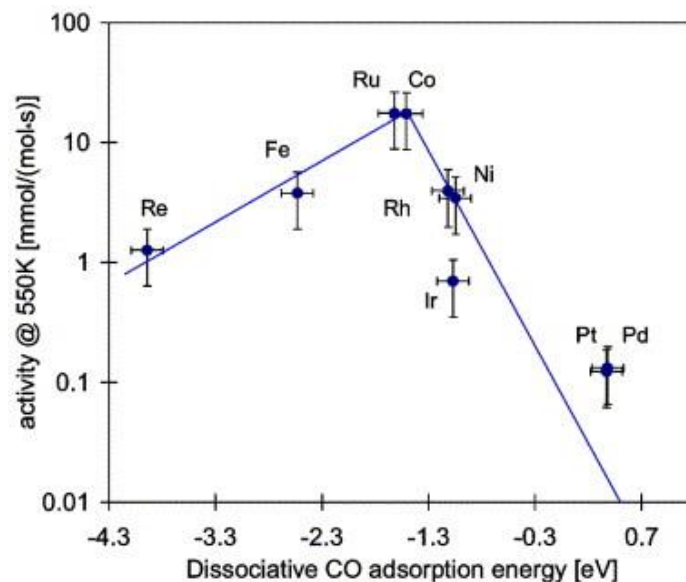


**Figure 2.8.** Activities of different supported transition metals are plotted as a function of the reaction energy for dissociative CO chemisorption [145].

## 2.7 CO methanation

Several studies by various research groups have been done to select suitable catalysts for the selective methanation of CO. Most platinum group metals (PGMs) have been studied and they include Ru [152, 153], Rh [154], Pd [138, 155], Ir [138], and Pt [156, 157].

Camila Galleti et al. [158] studied the total CO removal in hydrogen rich fuel using CO-selective methanation over Ru based catalyst supported on a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. Their study was limited to a gas stream with a small CO content (0.5% CO which is less than the actual reformat content). The catalysts were prepared using the conventional impregnation method with loadings of 3%, 4%, and 5% Ru. They tested CO removal (using the catalyst prepared) by using powder level bed reactor with a reformat gas mixture of 0.5% CO, 40% H<sub>2</sub>, 18% CO<sub>2</sub> and 15% H<sub>2</sub>O in He. They concluded that complete conversion of CO was achieved by 4% Ru-  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (residual outlet concentration lower than 2 ppm, the analytical detection limit) in a narrow temperature range with CO<sub>2</sub> methanation also kept at low level and with a negligible reverse water gas shift reaction.

Takenaka et al. [159] reported that Ru and Ni based catalysts were the most efficient catalysts for selective CO methanation according to their studies. They observed that Ni/ZrO<sub>2</sub> and Ru/TiO<sub>2</sub> gave optimal catalytic activity among the various catalysts studied. CO levels were reduced from 0.5 vol% to 12 ppm, with a low CO<sub>2</sub> conversion in the presence of 25 vol% CO<sub>2</sub> but over a narrow temperature range.

Aihua et al. [160] reported superior CO selective methanation with H<sub>2</sub> in a reformat gas using 1 wt% Ru on Ni-Al mixed oxides. They used a solution-spray plasma technique in synthesising the catalyst. Their studies showed that, the best catalyst could reduce CO levels from 1 vol% to 13 ppm at a temperature of 210 °C with 80% selectivity. They concluded that Ru did not only improve CO formation on the nickel (active sites) on the surface of NiAl<sub>2</sub>O<sub>4</sub> (by reduction with spill-over hydrogen), but also enhanced the selectivity by suppressing CO<sub>2</sub> dissociation on nickel metal sites.

Several attempts have been made to design a catalyst which will selectively convert CO in reformat gas into methane with high activity and selectivity. Most catalysts have been reported to use relatively expensive supports (e.g. CeO<sub>2</sub>, NiAl<sub>2</sub>O<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub>) and require longer preparation times (e.g. impregnation method). They are able to convert a low CO

concentration (0.5% CO instead of 8% CO) as reported by Galletti et al. [158] for reformat gas streams.

## 2.8 Particle size and dispersion effect

Generally, the degree of dispersion defines the activity of supported active metals [161-163]. The size of the active metal particles is inversely proportional to its dispersion i.e. the smaller the particle sizes the greater it is dispersed and vice versa. Catalytic activity is said to increase with increased dispersion, which implies an increase a metal surface area or a decreased crystallite size [162].

The size and structure of metal particles plays a vital role in CO<sub>x</sub> hydrogenation (e.g. selective methanation) this is due to the structure-sensitivity of the reaction. From density functional theory (DFT) calculations, the dominant step in CO hydrogenation (CO dissociation) occurs at the step-edge sites of the active metal e.g. Ru [164-166], Rh, and Ni. Some aspects of CO<sub>x</sub> hydrogenation are still under debate. Hence no consensus has been reached on the optimum particle size [49, 167-169]. This is mainly because of the effects that experimental conditions have on it (dependent) and the nature of the methanation catalyst used.

Dagle and co-authors used an impregnation method to prepare Ru supported on Al<sub>2</sub>O<sub>3</sub> and focused on the metal loading effect, crystallite size and the preparation technique on the selectivity of the CO methanation reaction [143]. The Ru crystallite sizes were grown through multicycle impregnation and the use of pre-reduction temperatures under H<sub>2</sub>.

Figure 2.9 shows a remarkable shift in conversion (both CO and CO<sub>2</sub>) as the temperature is increased and as the particle size increased (single-step impregnation = 10.9 nm and multiple-step impregnation = 304.2 nm respectively). This implied a decrease in activity with growth of the crystallite in the methanation reaction. Their work revealed CO methanation was preferred to CO<sub>2</sub> methanation as the particles grew bigger, and that the CO<sub>2</sub> activity decreased with size as shown in Figure 2.9.

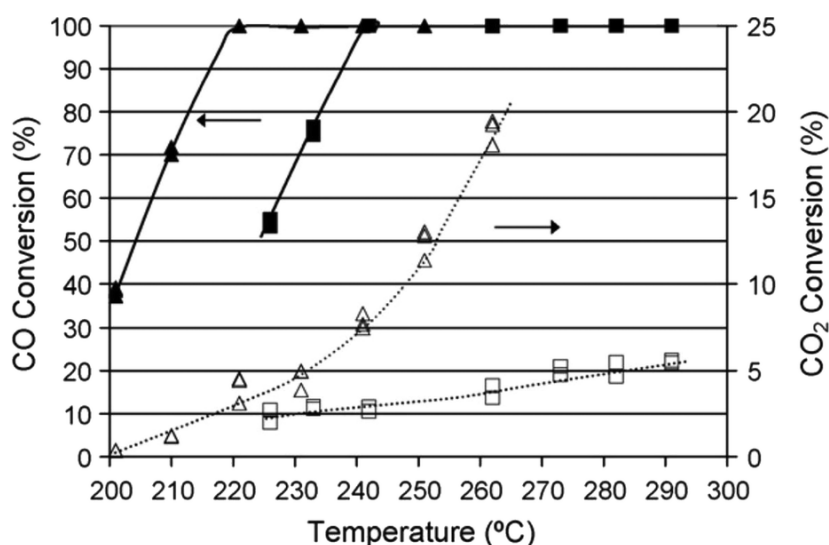


**Figure 2.9.** The crystallite size effect of a 3% Ru over  $\text{Al}_2\text{O}_3$  catalyst on CO and  $\text{CO}_2$  conversion (feed composition: 0.9% CO, 24.5%  $\text{CO}_2$ , 68.9%  $\text{H}_2$ , 5.7%  $\text{H}_2\text{O}$ ,  $\text{SV} = 13500 \text{ h}^{-1}$ ). Crystallite size of Ru: (■, multiple-step impregnation) = 34.2 nm, (▲, single-step impregnation) = 10.9 nm. CO conversion (filled),  $\text{CO}_2$  conversion (open) [143].

Tada and Kikuchi used a hemispherical model in an attempt to interpret these effects [35]. As represented in Figure 2.10, the authors assumed all the metal oxide particles were spherical, with uniform volume, particle size and density. The total metal surfaces were denoted as  $S_{\text{tot}}$  and  $L_{\text{tot}}$  for the total length of metal-support interface and estimated from the equations below:

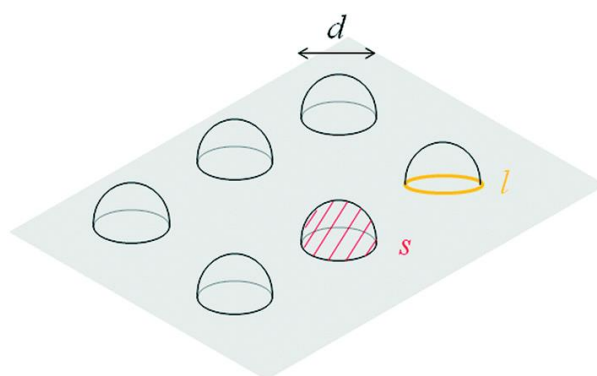


Figure 2. 10. Metal oxides supporting a hemispherical model of metal particles [35].

$$S_{tot} = n \times s \quad (2.12)$$

$$L_{tot} = n \times s \quad (2.13)$$

$$l = \pi d \quad (2.14)$$

$$s = \frac{\pi d^2}{2} \quad (2.15)$$

$$n = \frac{w}{v \times \rho} \quad (2.16)$$

$$v = \frac{\pi d^2}{l2} \quad (2.17)$$

where  $n$  is the number of particles per unit mass of the catalyst,  $l$  is the parameter of a particle,  $s$  is the surface area of the metal particle,  $d$  is the size of the particle,  $w$  is the loading,  $v$  is the volume of the metal particle and the density of the metal particle is  $\rho$ .

The equations above shows  $L_{tot}$  and  $S_{tot}$  ought to be proportional to  $d^2$  and  $d^1$  respectively and this points to the fact the particle growth adversely affects the diminution of  $L_{tot}$  compared to a decrease in  $S_{tot}$ . This implies a decrease in CO<sub>2</sub> methanation activity can be faster than that observed for CO methanation with regards to an increase in particle size, thus if the methanation of CO and CO<sub>2</sub> occurs on the metal surface and along the metal-surface interface respectively. Their assumption is in agreement with Dagle's [143] experimental data as mentioned above. This suitable catalyst for high CO selectivity can be achieved by controlling the metal support interface.

## 2.9 Reference

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# Chapter 3

## 3.0 Materials and experimental Methods

### 3.1. Chemicals

Sigma-Aldrich or Merck chemicals were the source of chemicals (solid and liquid) used in this study. No further purification was done before usage. Both distilled and deionised water generated in the School of Chemistry was used in this study.

### 3.2 Gases

African Oxygen (AFROX) supplied all the gases used in this study. Certificates indicating the expiry date, and the level of purity of the gas mixtures and the gas compositions accompanied each gas cylinder. The premixed gases with different compositions [(1% CO, 10% N<sub>2</sub>, 89% H<sub>2</sub>, purity: 99.999%), (1% CO, 20% CO<sub>2</sub>, 10% N<sub>2</sub>, 89% H<sub>2</sub>, purity: 99.999%), (20% CO<sub>2</sub>, 10% N<sub>2</sub>, 89% H<sub>2</sub>, purity: 99.999%)] were used for in the solo CO methanation, selective CO methanation and solo CO<sub>2</sub> methanation studies respectively.

The gas feed composition chosen for this study (as shown above) was a mimic of the reformat gas feed usually fed into the PEMFC. It was difficult to incorporate steam. This was due to technical challenges, hence a dry gas feed was employed for this studies. It was recommended that future studies include steam.

### 3.3 The horizontal CVD reactor

A horizontal chemical vapour deposition (CVD) reactor (Figure 3.1) was used to synthesize both CNTs and N-CNTs used in this project. The CVD setup was designed in the School of Chemistry, University of the Witwatersrand [1-3]. A similar CVD setup has been reported in literature over the years [4]. The equipment consists of a quartz glass tube reactor which can resist a high temperature up to 1200 °C. The tubes have an internal diameter of 19 mm and lengths varying from 300 mm to 600 mm depending on the furnace used to provide controllable heating in a steady manner. The setup was equipped with adapted connectors

which allowed different gases to flow into the reaction chamber, while a thermocouple fitted to the temperature controller was positioned inside the furnace to monitor the heating rate. A quartz tube boat (50 nm length and 8 nm width) was used as the catalyst bed inside the reactor. Acetylene gas was used as the carbon source while acetonitrile served as the nitrogen source in the nitrogen doping experiments.

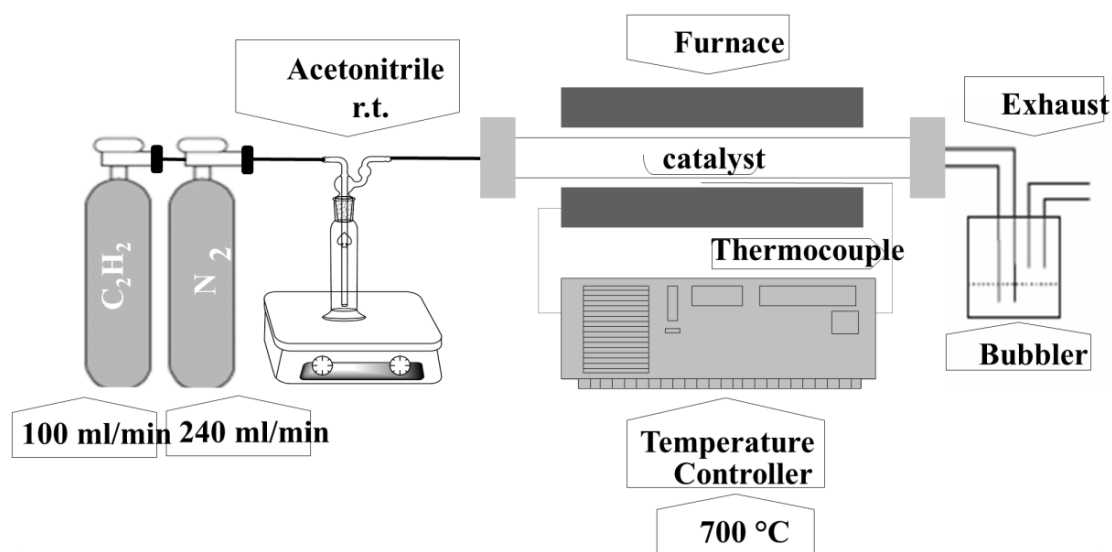


**Figure 3.1.** Schematic diagram of the chemical vapour deposition (CVD) reactor setup.

### 3.4 Hydrothermal synthesis of carbon spheres

The hydrothermal technique was carried out in a 100 ml autoclave to synthesize CNTs coated with  $TiO_2$  and solid carbon spheres (CSs). The autoclave was heated at rate of 1 °C/min till the required temperature was reached. The CNT- $TiO_2$  composite were made at 200 °C and the reaction was run for 16 h using titanium butoxide as the titania source. For the CSs, the reaction was done at 190 °C for 4 h with sucrose as the carbon source.

### 3.5 Methanation in a single micro reactor system

Figure 3.2 shows a scheme of the rig and reactor system used in the study. The reactor was made of steel and was a tubular fixed bed reactor (FBR). The gases for the methanation

reactions were supplied from a gas cylinder. Pressure regulators were used to monitor gas output pressures. The setup had pressure gauges fitted between the shut off valve and the reactor. Another regulator was placed between the trap and the Gas Chromatographs (GC-TCD and GC-FID).

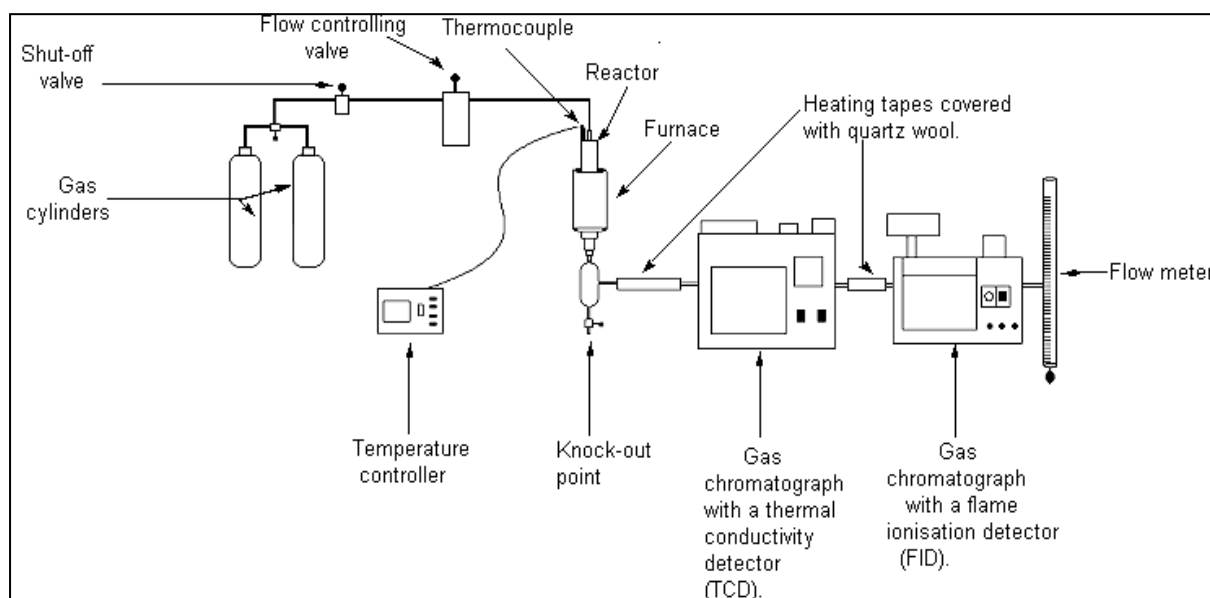


**Figure 3.2.** Schematic diagram of the single fixed-bed methanation micro reactor system set up (not to scale).

The quantity of gas entering the reactor was regulated by use of a soap bubble meter (to vent). The gas lines were maintain at 150 °C and the cold trap at ambient temperature. The GCs (GC-TCD and GC-FID) were connected in series online with the gaseous products directed through the GCs for analysis. The gas lines in the setup consisted of 1/4” and 1/8” stainless tubing fitted with Swagelock connectors where necessary. The signals generated from both the TCD and FID were made readable with the Clarity ® software.

### 3.6 Micro-fixed bed reactor design

All the methanation experiments were conducted in a stainless steel micro single tubular fixed bed micro reactor (FBR) as shown in Figure 3.3. The height of the micro-reactor was 250 mm, with an internal diameter of 16 mm and 4.5 mm as it thickness. A sieve plate with pore diameter of 0.5 mm, serving as a catalyst bed was positioned 162 mm beneath the top of the reactor tube. The tube was filled with steel balls (1mm) to maintain a constant temperature in the reactor. The FBR was inserted into a heating jacket equipped with a heating element of 700 Watt which provided a uniform temperature along the length of the

reactor. The reducing gases as well as the methanation gases entered the FBR from the top (near atmospheric pressure), while unreacted gases and products exited at the bottom.

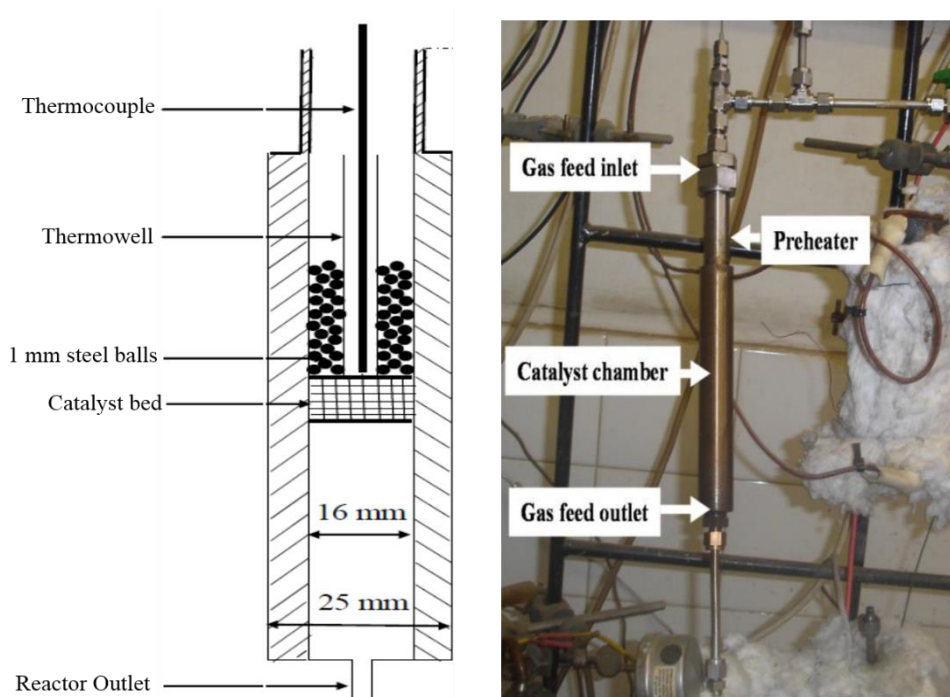


**Figure 3.3.** Schematic diagram of fixed bed reactor and a digital image (right) of a stainless-steel fixed bed reactor.

Table 3. 1: Specifications of the gas chromatographs employed

| <b>Online gas chromatograph 1</b> |                                                     |
|-----------------------------------|-----------------------------------------------------|
| Model type                        | PYE Unicam (Series 204)                             |
| Detector                          | Thermal conductivity detector (TCD)                 |
| Column type                       | Packed, stainless steel, 2m x 2.2mm, O.D = 1/8"     |
| Stationary phase                  | Carboxen-1000, 60-80 mesh                           |
| <b>Online gas chromatograph 2</b> |                                                     |
| Model type                        | Hewlett Packard 5890                                |
| Detector                          | Flame ionization detector (FID)                     |
| Column type                       | Packed, stainless steel, 1.5 m x 2.2 mm, O.D = 1/8" |
| Stationary phase                  | Porapack q, 80/100 mesh                             |

### 3.7 Methanation measurements

#### 3.7.1 Blank test

Before the methanation runs were performed, blanks were run. This was achieved by allowing the reaction gases to flow through the reactor chamber without any catalyst. The unreacted gases were detected by the GC-TCD. This acted as a reference for calculating CO and CO<sub>2</sub> percentage conversions.

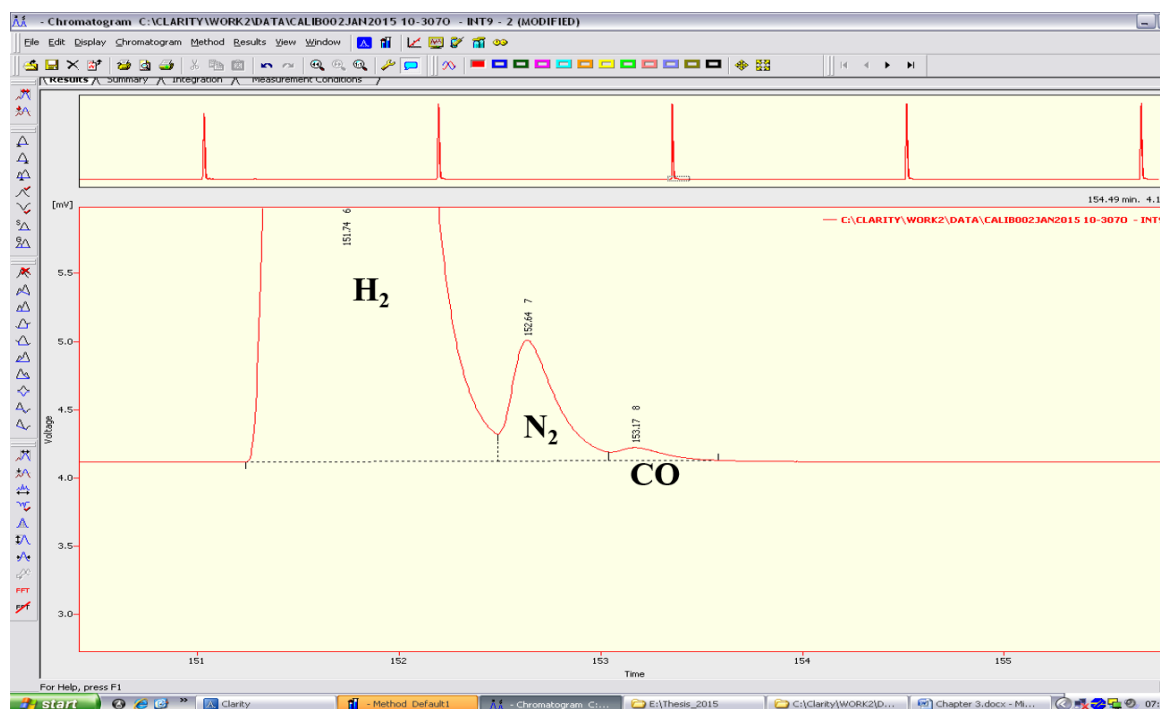


**Figure 3.4.** TCD graph of methanation gases (1% CO, 10% N<sub>2</sub>, 89% H<sub>2</sub>, purity: 99.999%) using argon as a carrier gas.

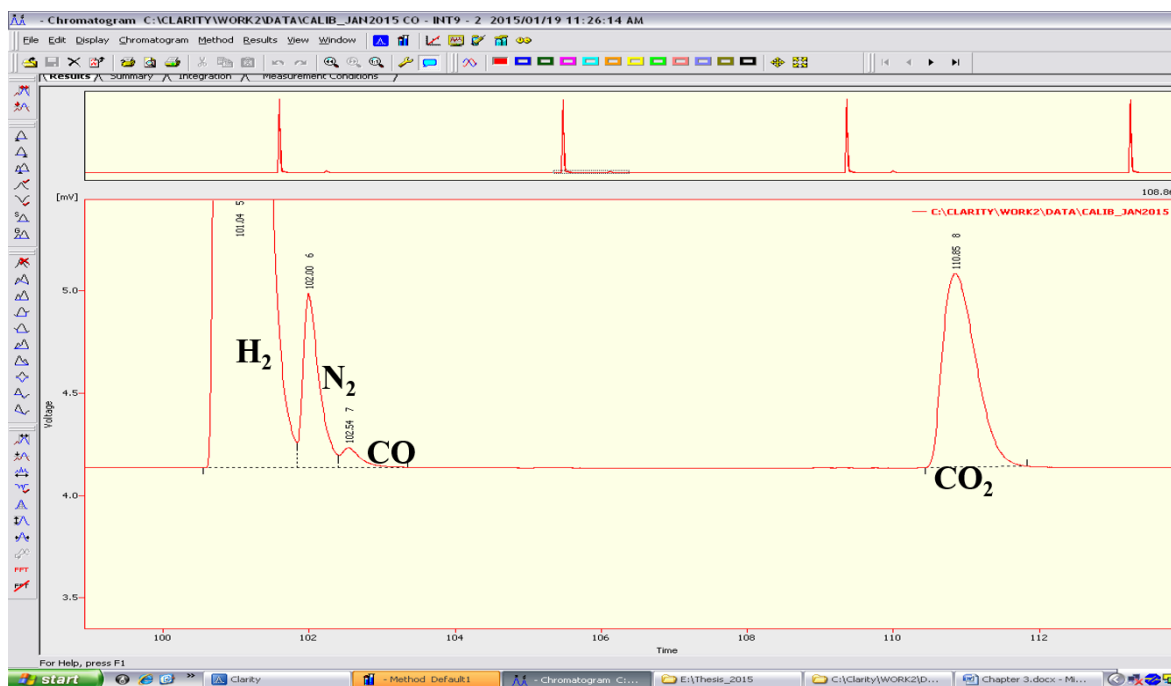


**Figure 3.5.** TCD graph of methanation gases (1% CO, 20 % CO<sub>2</sub>, 10% N<sub>2</sub>, 89% H<sub>2</sub>, purity: 99.999%) using argon as a carrier gas.

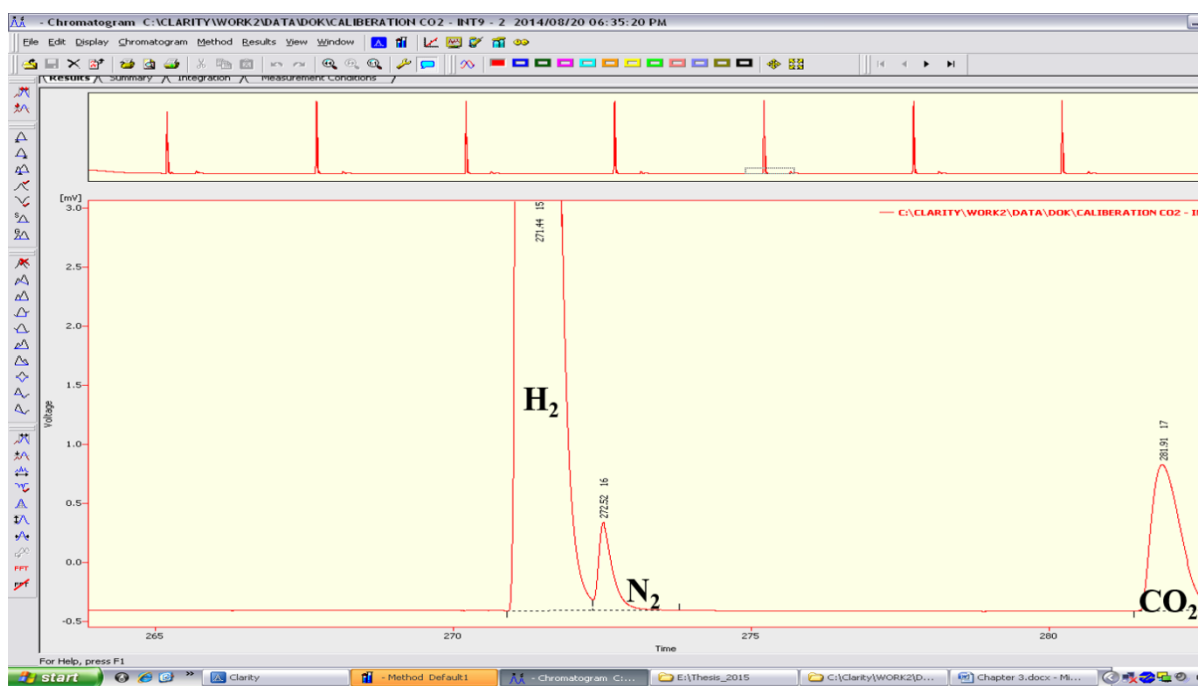


**Figure 3.6.** TCD graph of methanation gases (20 % CO<sub>2</sub>, 10% N<sub>2</sub>, 89% H<sub>2</sub>, purity: 99.999%) using argon as a carrier gas.

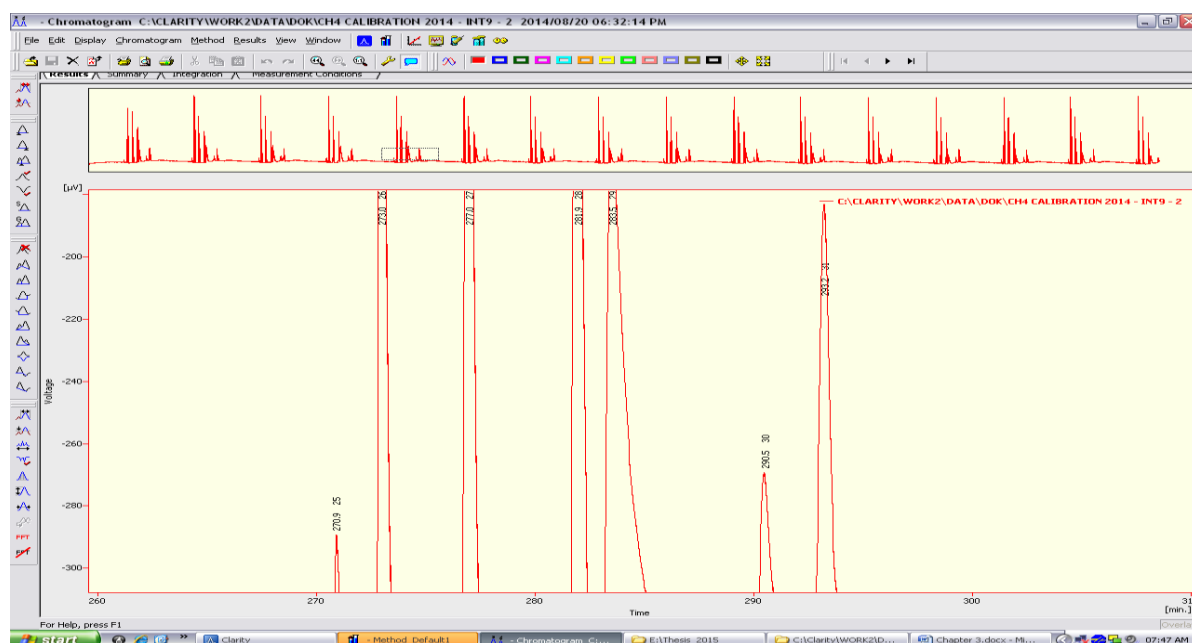


**Figure 3.7.** TCD graph of calibration gases using argon as a carrier gas.

### 3.7.2 Methanation experiments

In a typical reaction, 0.5 – 1.0 g of fresh catalyst was placed into the FBR and reduced in-situ with  $H_2$  at a constant heating rate of  $5\text{ }^{\circ}\text{C}/\text{m}$  at a flow rate of  $60\text{ ml}/\text{min}$  for a period of 2-4 hours at between  $250\text{ }^{\circ}\text{C}$  -  $400\text{ }^{\circ}\text{C}$ . The reactor was allowed to cool to room temperature with  $H_2$  passing. The methanation gases were introduced to study solo CO or  $CO_2$  methanation and selective CO methanation with premixed gases with compositions of (1% CO, 10%  $N_2$ , 89%  $H_2$ , purity: 99.999%), (1% CO, 20%  $CO_2$ , 10%  $N_2$ , 89%  $H_2$ , purity: 99.999%), (20%  $CO_2$ , 10%  $N_2$ , 89%  $H_2$ , purity: 99.999%) and flow rates between 90-100 ml/min (depending on the study). The reactor was heated to the desired reaction temperature ( $100\text{ }^{\circ}\text{C}$  -  $360\text{ }^{\circ}\text{C}$ ) at a similar heating rate as used in the reduction process and run for 5 h.

## 3.8 Mass balance and data analysis

The mass balance calculations adopted in this study has been used in previous studies by Bahome [5], Ngwenya [6] and Motchelaho [7]. All the mass balance calculations were carried out under steady state conditions for about 5 h.

### 3.8.1 Mass balance equations

Measurements were done every hour to monitor the outlet gas flow rate ( $F_{out}$ ) using a bubble flow meter. This was used to calculate the inlet gas flow rate ( $F_{in}$ ) assuming the gas flow in and out of the reactor is equal. Nitrogen was employed as an inert internal standard during all the methanation reactions. The relation below was used to express the total molar inlet gas flow (from the total molar outlet gas flow).

$$F_{in} \times X_{N_2_{in}} = F_{out} \times X_{N_2_{out}} \quad (3.1)$$

$$\text{This implies } F_{in} = \frac{F_{out} \times X_{N_2_{out}}}{X_{N_2_{in}}} \quad (3.2)$$

where:

$F_{in}$  = Total molar flow rate entering the reactor.

$F_{out}$  = Total molar flow rate exiting the reactor (calculated at atmospheric pressure and 298 K).

$N_{2(in)}$  = Mole fraction of  $N_2$  in the stream entering the reactor.

$N_{2(out)}$  = Mole fraction of  $N_2$  in the stream exiting the reactor.

The percentage CO and  $CO_2$  conversions were calculated by calculating the amount of CO in the outlet stream.

The peak areas determined from (peak integration Clarity (v. 2.5) package) was used to calculate the molar percentage of any component gas  $\Phi$  in the outlet stream.

Thus:

$$\% \Phi_{gas} = \left[ \frac{A_{\Phi_{gas}}}{A_{\Phi_{cal}}} \right] \times \% \Phi_{cal} \quad (3.3)$$

where:

$\% \Phi_{gas}$  = mole percentage of compound  $\Phi$  in the sampled gas.

$\% \Phi_{cal}$  = mole percentage of compound  $\Phi$  in the calibration gas.

$A_{\Phi_{gas}}$  = Integrated area of compound  $\Phi$  obtained from the GC peak using the Clarity software.

$A_{\Phi_{cal}}$  = Integrated area of compound  $\Phi$  in the calibration gas obtained from the GC peak using the Clarity.

The compounds without direct calibration data from the calibration mixtures were obtained by use of a reference compound present in the gas mixture and their relative molar response factor. Molar response factors from Hydrocarbon product references were employed [5-7]. The following expression was used:

$$\% \Phi_{gas} = \left[ \frac{A_{\Phi_{gas}}}{A_{\Phi_{cal}}} \right] \times \% \theta_{cal} \times RF_{\Phi\theta} \quad (3.4)$$

where:

$RF_{\Phi\theta}$  = Response factor of compound  $\Phi$  relative to reference compound  $\theta$ .

$\% \theta_{cal}$  = Integrated area of reference compound in the calibration gas obtained from the GC peak using Clarity software.

### 3.8.2 The percentage CO and CO<sub>2</sub> conversions

$$\% CO_{conversions} = \left[ \frac{X_{CO_{in}} - X_{CO_{out}} \times \left( \frac{X_{N_2_{in}}}{X_{N_2_{out}}} \right)}{X_{CO_{in}}} \right] \times 100 \quad (3.5)$$

where:

$X_{CO_{in}}$  = Mole fraction of CO entering into the reactor.

$X_{CO_{out}}$  = Mole fraction of CO exiting the reactor.

$$\left( \frac{X_{N_2_{in}}}{X_{N_2_{out}}} \right) = \text{contraction factor.} \quad (3.6)$$

The percentage CO<sub>2</sub> conversion was calculated using the following equation:

$$\%CO_{2conversions} = \left[ \frac{X_{CO_{2in}} - X_{CO_{2out}} \times \left( \frac{X_{N_{2in}}}{X_{N_{2out}}} \right)}{X_{CO_{2in}}} \right] \times 100 \quad (3.7)$$

Where:

$X_{CO_{2in}}$  = Mole fraction of CO<sub>2</sub> entering the reactor.

$X_{CO_{2out}}$  = Mole fraction of CO<sub>2</sub> exiting the reactor.

The selectivity of hydrocarbon products were calculated as follows:

$$S_{\phi_i} = \left[ \frac{nC_{\phi_i}}{\Sigma nCO_{\phi_i}} \right] \times 100 \quad (3.8)$$

where:

$nC_{\phi_i}$  = Total moles of carbon in compound in the product stream.

$S_{\phi_i}$  = selectivity of product  $\Phi_i$ .

### 3.9 Synthesis and characterization techniques

Several synthesis techniques were employed in study, they include, CVD synthesis, hydrothermal synthesis, microwave polyol technique, impregnation, deposition-precipitation using urea. Detailed description of all the synthesis can be found in results Chapters (4, 5, 6 and 7). The supports and synthesised catalysts were thoroughly characterized using the following techniques; Transmission electron microscope (TEM), scanning electron microscope (SEM), In-situ and Ex-situ Powder X-ray analysis (PXRD) Raman spectroscopy, Brunauer–Emmett–Teller (BET), CHNS analysis, Thermogravimetric analysis (TGA), Temperature programmed reduction studies (TPR) and Chemisorption studies. The results Chapters (4, 5, 6 and 7) show detailed description of all the procedure for all characterization studies.

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# Chapter 4

## SELECTIVE CO METHANATION OVER RU CATALYSTS SUPPORTED ON DIFFERENT TITANIA RUTILE MORPHOLOGIES

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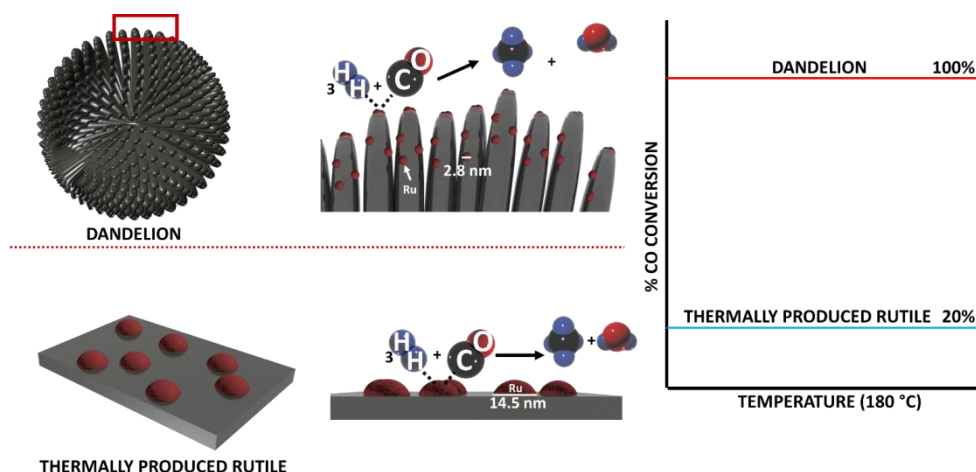
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### ABSTRACT

A ruthenium-based catalysts have been assessed in the selective methanation of carbon monoxide for possible application in the purification of reformat gas streams for feeding to polymer electrolyte membrane fuel cells where the CO content must be reduced to very low values. A rutile dandelion-like structure was synthesized and showed a higher surface area ( $61 \text{ m}^2\text{g}^{-1}$ ) than a thermally produced rutile catalyst ( $9 \text{ m}^2\text{g}^{-1}$ ). Ru/rutile catalysts were synthesized with different Ru particle sizes (1.4 nm – 8.1 nm) and the Ru/dandelion-like rutile showed smaller particles that when compared to the thermally produced rutile catalyst. The dandelion-like supported Ru (prepared by either impregnation or deposition precipitation by urea) revealed a superior catalytic activity over the thermally produced rutile supported catalyst in both CO methanation and selective CO methanation in the presence of excess  $\text{CO}_2$ . Almost similar CO conversions were recorded for both P-25 ( $d_{\text{Ru}} = 3.1 \text{ nm}$ ) and the dandelion-like supported catalyst, indicating the important role of the Ru particle size in the reaction. The sinter resistance studies of the Ru/dandelion catalysts (*in situ* PXRD studies) give an indication that they are very well suited for high temperature use.

## Graphical Abstract



## KEYWORDS

Ruthenium; rutile support; dandelion-structure; CO methanation; reformat gas; CO<sub>2</sub> methanation

## 4.1 Introduction

The need to develop fuel processors capable of generating hydrogen from carbonaceous fuels has resulted in renewed interest in the methanation reaction [1]. Since Sabatier and Senderens discovered this reaction, it has been widely used in a number of major chemical industries. These include the Haber process as a means for removal of carbon oxides from the inlet feed, and for the purification of reformat gas for fuel cells and other processes related to Fischer-Tropsch synthesis [2, 3]. Studies in fuel cell technology especially polymer electrolyte membrane fuel cells (PEMFCs), have shown that CO concentrations in a hydrogen-rich gas feed stream of 10 ppm and above can easily poison the pure Pt anodes [4, 5].

The preferential CO oxidation (PROX:  $\text{CO} + (\frac{1}{2})\text{O}_2 \leftrightarrow \text{CO}_2$ ;  $\Delta H_{298}^\circ = -284 \text{ kJ/mol}$ ) reaction is a known established technique for the reduction of CO concentration to tolerable levels. However, there are some severe limitations that have generated interest in finding alternatives to this process. These limitations include the challenge of supplying the appropriate amount

of oxygen (or air) needed from external sources into the PROX chamber, a cooling system, and an oxygen (or air) and hydrogen-rich gas mixer component making the technique complicated and costly. The addition of oxygen (or air) gives rise to hydrogen dilution, which restricts the operation parameters of the PEMFCs further, hampering its application in the transportation industry [5-9].

The above mentioned limitations in PROX can be avoided through the selective CO methanation process ( $\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}$ ;  $\Delta H^\circ_{298} = -206 \text{ kJ/mol}$ ). The necessary reactants (CO and  $\text{H}_2$ ) for the methanation reaction are present in the reformat gas feed. Besides, methane generated in the process is inert and can be utilized in the afterburner [6, 10, 11]. However, it is imperative to develop a suitable catalyst that promotes selective CO methanation, suppressing all undesired reactions capable of running parallel which include  $\text{CO}_2$  methanation ( $\text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ ;  $\Delta H^\circ_{298} = -165 \text{ kJ/mol}$ ) which results in huge  $\text{H}_2$  losses causing runaway of the reactor (catalyst) temperature, and the reverse water gas shift reaction (RWGS,  $\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$ ;  $\Delta H^\circ_{298} = 41 \text{ kJ/mol}$ ) which also tends to add CO to the  $\text{H}_2$ -rich gas outlet stream [12, 13].

Selective CO methanation is a temperature sensitive reaction. This is because both  $\text{CO}_2$  methanation and the RWGS reaction can be retarded at low temperatures. Due to this, several catalysts have been developed to achieve higher CO activity at low temperatures and Ru-based catalysts have been found to be the most active catalysts for CO methanation [4, 7, 10, 13, 14]. The nature of the support used is also known to impact on the activity and selectivity of the catalyst. This is due to several factors that include the metal-support interaction and the morphology (e.g. pore distribution) of the support. A superior catalyst activity for Ru supported on  $\text{TiO}_2$  compared to Ru supported on other metal oxides has been reported [9, 14]. Panagiotopoulou et al. also showed that Ru on  $\text{TiO}_2$  performed better than Ru supported on YZS,  $\text{SiO}_2$ ,  $\text{CeO}_2$  and  $\text{Al}_2\text{O}_3$  and attained optimal CO conversion in the presence of excess  $\text{CO}_2$  [15].

It has been reported that the different polymorphs of  $\text{TiO}_2$  (anatase and rutile) exhibit different levels of activity when used separately as a support for Ru.[16] Anatase is usually preferred as a catalyst support material for heterogeneous metal catalyst relative to rutile  $\text{TiO}_2$ , due to its good support interaction with metal nanoparticles and its relatively high surface area [17, 18]. Rutile is mostly employed as a model catalyst support for surface science studies due to its thermodynamic stability and higher crystallinity [19, 20]. The phase

transition from anatase to rutile (which occurs above 500 °C) has been connected to its crystal size growth and collapse of the pore structure, which results in a drastic reduction of the specific surface area. Furthermore, anatase and rutile differ in their ability to anchor active metal species on their respective surfaces which in turn is believed to relate to different metal-support interactions exhibited by the oxides [19, 21]. This consequently influences the catalytic activities of anatase- and rutile-supported systems.

However, a few studies have reported the superior activity of rutile as a catalyst support over anatase, such as in the oxidation of toluene, benzene and xylene over Cu supported on rutile [22]. This suggests that modification of the rutile structure could lead to further enhanced activity in a reaction. To test this idea in the selective CO methanation reaction, a novel crystalline rutile dandelion  $\text{TiO}_2$  material with an unusual structure was prepared. The multi pore structure of this rutile morphology offers some advantages such as easy accessibility of the pores to reactant materials, diffusion efficiency, a good porous volume and importantly an enhanced surface area due to the presence of both micropores and mesopores [23].

In this study we report for the first time the use of a  $\text{TiO}_2$  rutile dandelion-like structure (Figure 4.1) as a Ru catalyst support for the catalytic selective CO methanation reaction in the presence and absence of excess  $\text{CO}_2$ . This catalyst was compared to Ru supported on  $\text{TiO}_2$  Degussa P-25 and to Ru supported on the traditionally formed rutile phase of  $\text{TiO}_2$ .

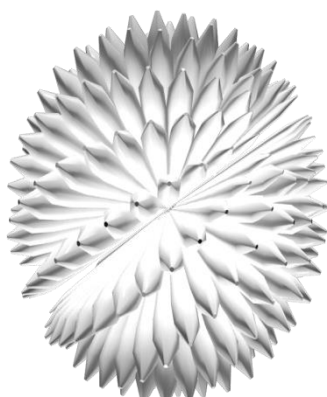


**Figure 4.1.** Schematic structure of the dandelion rutile  $\text{TiO}_2$  structure.

## **4.2 Experimental**

### *4.2.1 Preparation of the dandelion rutile TiO<sub>2</sub> support*

A round bottom flask was filled with deionised water (100 mL) and placed in an ice bath, a desired amount of TiCl<sub>4</sub> (Sigma Aldrich with 98% purity and above) was added to the flask. The solution was refluxed for 24 h at 200 °C. The solution was to cool to ambient temperature. The resulting TiO<sub>2</sub> precipitate was obtained by centrifuging at 4000 rpm followed by washing several times with deionised water. The residual rutile TiO<sub>2</sub> with a dandelion morphology was dried in an oven at 110 °C overnight [24].

To obtain thermally produced rutile, anatase was firstly synthesised using the hydrothermal method [25]. In this method, a desired amount of titanium isopropoxide was added to isopropanol and the solution sonicated for 30 min. Diethylamine (2 mL) was added to catalyse the decomposition process. The solution was transferred into an autoclave and left to react for 16 h at 200 °C to give TiO<sub>2</sub> nanoanatase [25]. This TiO<sub>2</sub> material was calcined at 900 °C for 10 h to ensure total transformation of the anatase to rutile.

### *4.2.2 Catalyst preparation*

The Ru/TiO<sub>2</sub> catalysts were made by two different procedures. For the impregnation method (IMP), an aqueous solution of RuCl<sub>3</sub> (Sigma Aldrich) was used to obtain a 5 wt.% Ru loading on the dandelion, and the thermally produced rutile. In the deposition-precipitation by urea (DPU) synthesis, the Ru particles were made by dissolving a desired amount of RuCl<sub>3</sub> and urea (1.5 mol urea per mol Ru) in 10 mL deionised water and the solution was added dropwise to the supports (the dandelion rutile, the thermally produced rutile and the Degussa P25). The resulting mixture was heated on an oil bath at 90 °C for 12 h while stirring.

The prepared catalysts were dried at 110 °C overnight and then calcined for 3 h at 350 °C to remove of all of volatiles and to form the RuO<sub>2</sub> particles. The catalysts were coded as D, R and P-25 to denote dandelion, thermally produced rutile and Degusa P25 supports respectively. The catalysts were called IMP-D, IMP-R, DPU-D DPU-R and DPU-P25 to reflect the deposition-precipitation by urea (DPU) or impregnation (IMP) methods used to make the catalysts.

#### 4.4.2.3 Catalyst and support characterization

The structural morphologies of the supports and the catalyst were elucidated by electron microscopy (SEM FEI Nova Nanolab 600 and TEM Tecnai T12). The samples for TEM analysis were dispersed in ethanol and sonicated to create a suspension. A drop of the solution was transferred to a copper grid and dried before analysis. For the SEM analysis, the samples were loaded on a carbon tape and coated with gold-palladium before analysis.

The crystallinity of the support and the mean crystallite size of RuO<sub>2</sub> on the supports were measured on a Bruker D2 diffractometer. A cobalt source (K $\alpha$  radiation; Ni filter) was used in a 0.02° stepwise fashion with a scan range of 10-90° (2 $\theta$ ) to obtain PXRD patterns. The crystallite size  $d_{Ru}$  was calculated using the Rietveld refinement:

$$d_{Ru} = \frac{0.9\lambda}{\beta \cos \theta} \quad (4.1)$$

where  $\lambda$  = X-ray wavelength of Co-K $\alpha$  radiation (0.1789 nm),  $\beta$  = broadening (in radians) of the RuO<sub>2</sub> and  $\theta$  = is the diffraction angle associated with the peak broadening.

The surface area/porosity studies for the supports and catalysts were carried out on a Micromeritics ASAP 3000 apparatus. Prior to the measurements, about 0.2 g sample was outgassed in N<sub>2</sub> at 150 °C for 4 h using a Micromeritics flow Prep 060 degas system. Using the BET method, the surface area and pore volumes were determined *via* N<sub>2</sub> adsorption at -196 °C.

A Micromeritics Autochem 2910 instrument was used for H<sub>2</sub>-TPR experiments. A U-shaped quartz tubular reactor was loaded with about 0.12 g of the catalyst sample. The sample was heated under an Ar gas atmosphere at a rate of 5°C/min to 150 °C for 30 min and cooled to 50 °C under an argon flow. The reduction experiments were done by exposing the samples to a gas mixture (5% H<sub>2</sub>, balance Ar) at a flow rate of 40 ml/min while heating to 900 °C at a rate of 5 °C/min. A thermal conductivity detector (TCD) was used to monitor the change in the amount of hydrogen flowing in both the reactor and the reference.

Hydrogen chemisorption experiments were performed using a Micromeritics Autochem 2910 instrument. All the catalysts were reduced at 350 °C in hydrogen (99.999% purity) for 2.5 h and later cooled to ambient while passing helium through the reactor. Before the reduction, the catalyst was degassed *in situ* at 150 °C for 30 min. The pulsing procedure was done using

a 423  $\mu\text{L}$  sample loop filled with hydrogen (99.9995%  $\text{H}_2$  purity) with argon as a carrier gas. It was injected into the sample which was held at 70  $^\circ\text{C}$ . The  $\text{H}_2$  uptake was used to calculate the percentage metal dispersion assuming an H:Ru stoichiometry of 1:2. The mean crystallite size of the dispersed metal was calculated from hydrogen uptake data, with the assumption that the Ru particles were spherical, using the relation:

$$d_M = \frac{6 \times 10^2 \times \text{MW}}{\rho_M \times \vartheta_M \times 6.022 \times 10^{23} \times D} \quad (4.4.2)$$

where  $d_M$  is the mean Ru crystallite size, MW is the atomic mass for Ru (101.07 g/mol),  $\rho_M$  is the Ru density (12.3 g/cm<sup>3</sup>),  $\vartheta_M$  is the exposed surface area per gram of Ru metal and D is the percentage dispersion of the Ru metal [26].

The Bruker D8 Advance AXS diffractometer equipped with Cu radiation ( $\lambda_{K\alpha} = 0.154084 \text{ nm}$ ) fitted along with a Göbel mirror to produce a pseudo-parallel primary beam was used to do *in situ* experiments. It was operated with 40 Kv and 40 mA. The samples were loaded in an Anton Paar XRK 900 reaction chamber and diffraction patterns were collected. The detector employed was VÅNTEC position-sensitive detector and the reaction was carried out under hydrogen (5% $\text{H}_2$ ,  $\text{N}_2$  balanced) flow. The temperature was ramped from 30 to 600  $^\circ\text{C}$  with an increase of 50  $^\circ\text{C}$  with a scan time of 40 minutes. TOPAS 4.2 (Bruker AXS) software package was used in the Rietveld refinement of the *in situ* PXRD data. Starting structure models and analytical peak shape function were obtained from the Inorganic Crystal Structure Database (ICSD) [27].

#### 4.2.3 Catalytic evaluation

The catalytic evaluation of the prepared samples for the methanation process was achieved using a fixed-bed quartz tubular reactor at near atmospheric pressure. The reaction temperature was measured with a K-type thermocouple placed in the catalyst bed. The catalyst (1 g) was loaded into the reactor and reduced under a hydrogen atmosphere at 400  $^\circ\text{C}$  for 4 h at 1 bar pressure with  $\text{H}_2$  gas (99.995%) and a 60 ml/min flow rate prior to the reaction. Methanation reactions were conducted in the temperature range of 100 - 340  $^\circ\text{C}$  using a feed stream with composition of 1% CO, 10%  $\text{N}_2$  and  $\text{H}_2$  balance and 1% CO, 20%

CO<sub>2</sub>, 10% N<sub>2</sub> and H<sub>2</sub> balance and a flow rate of 100 mL/min. The outlet stream was analysed using an online gas chromatograph (GC) equipped with a Porapak Q and a Carboxen-1000 column coupled to a FID and a TCD respectively. Traces from the GC were recorded by a computer running on Clarity software.

## **4.3 Results and discussion**

### *4.3.1 Support and catalyst characterization*

The TEM images (Figure 4.2) show the synthesized rutile TiO<sub>2</sub> with dandelion-like structure. A microsphere morphology was observed by both TEM and SEM analyses with average sphere diameter between 500 – 1000 nm (Figure 4.2a and 4.2b). It can be seen that the microspheres were composed of densely packed radially arranged (spherically aligned) nanorods. These nanorods are on average between 15-20 nm in diameter. The systematically packed radial nanorods were observed to have nearly square ends due to the preferred growth orientation along the (001) direction [28]. PXRD analysis (see Figure 4.3b) revealed that the nanorods were comprised of rutile. It has been established that the hydrolysis reaction of TiCl<sub>4</sub> is suppressed by the presence of Cl<sup>-</sup> and H<sup>+</sup> ions. The growth along the 001 direction is preferentially promoted by Cl<sup>-</sup> ions while H<sup>+</sup> cations promotes TiO<sub>2</sub> agglomeration and formation of nanorods through heterogeneous nucleation [28-30]. The nano anatase agglomerated after the thermally treating to convert to rutile as shown in Figure 4.2c and 4.2d.

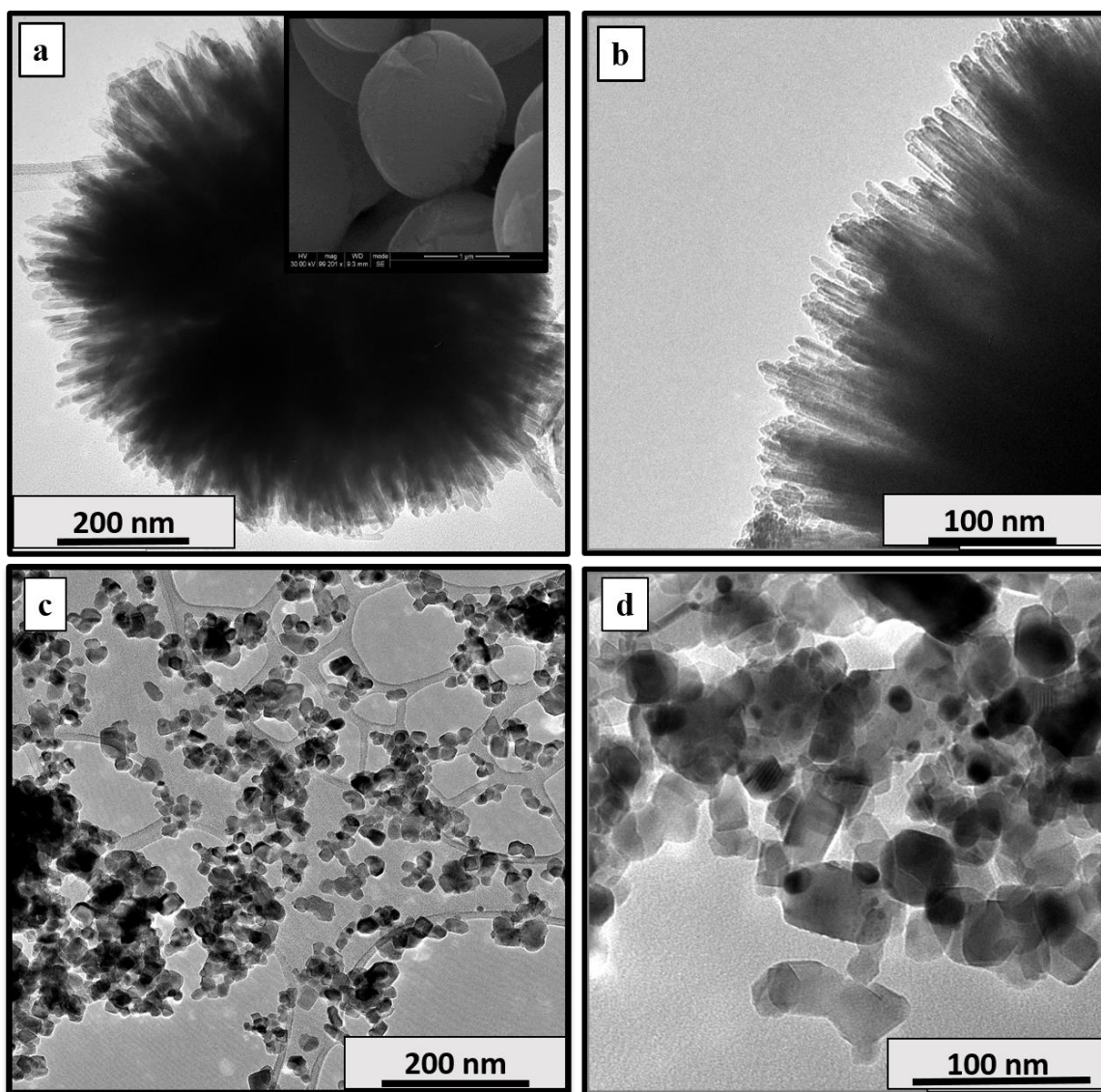


**Figure 4.2.** TEM images of (a) a microsphere dandelion  $\text{TiO}_2$  (with a SEM insert), (b) higher magnification of radially aligned nanorods of the dandelion, (c) hydrothermally synthesised anatase  $\text{TiO}_2$  and (d) rutile  $\text{TiO}_2$  prepared from anatase  $\text{TiO}_2$  by calcination.

The BET and pore analysis data for the different catalysts are summarized in Table 4.1. The results showed that the dandelion rutile structure exhibited the largest surface area ( $61 \text{ m}^2/\text{g}$ ) and this was attributed to the dandelion-like structural morphology of the rutile  $\text{TiO}_2$ . The nanoanatase registered a slightly higher surface in comparison to the P-25 titania (52 and  $48 \text{ m}^2/\text{g}$  respectively). The complete transformation of anatase to rutile usually occurs at high temperature, resulting in enlargement of the  $\text{TiO}_2$  grains coupled with a drastic decrease in the specific surface area of the rutile titania.[31, 32] Indeed in our studies the thermally

produced rutile TiO<sub>2</sub> was found to have a low surface area of < 10 m<sup>2</sup>/g. Incorporation of Ru onto the three supports by both deposition precipitation (DPU) and impregnation showed that the specific surface areas and pore volumes decreased relative to the supports, for all the catalysts (Table 4.1).

Table 4.1. N<sub>2</sub> physisorption data.

| Sample        | Surface area <sub>BET</sub> (m <sup>2</sup> /g) | Pore volume (cm <sup>3</sup> /g) |
|---------------|-------------------------------------------------|----------------------------------|
| Anatase (A)   | 52                                              | 0.211                            |
| Dandelion (D) | 61                                              | 0.273                            |
| Rutile (R)    | 9                                               | 0.081                            |
| P-25          | 48                                              | 0.213                            |
| IMP-D         | 39                                              | 0.154                            |
| DPU-D         | 42                                              | 0.121                            |
| IMP-R         | 7                                               | 0.091                            |
| DPU-R         | 6                                               | 0.045                            |
| DPU-P-25      | 42                                              | 0.167                            |

*P-25: commercial TiO<sub>2</sub>.*

Figure 4.3 show the PXRD patterns of the catalysts prepared by DPU. The patterns are similar to the catalyst prepared by impregnation (Figure 4.S1 and 4.S2). The thermally produced rutile had sharper  $2\theta$  peaks compared to the slightly broader peaks of the dandelion TiO<sub>2</sub>. This confirmed that the rutile grains were larger and more crystalline than the dandelion-like TiO<sub>2</sub>. No diffraction peaks for the oxides of Ru were detected on the dandelion support, whereas RuO<sub>2</sub> was observed on the thermally produced rutile support. This can be explained by the uniformly dispersed and smaller RuO<sub>2</sub> particles that formed on the dandelion rutile support (see below) [33, 34], as result of the TiO<sub>2</sub> morphology and the relatively higher surface area of the dandelion rutile.

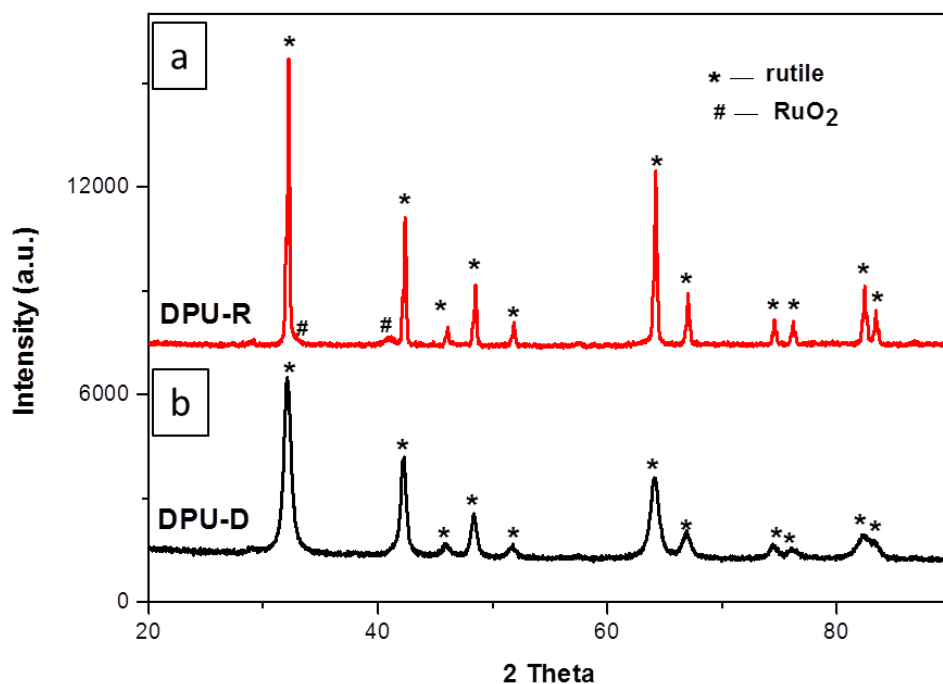


**Figure 4.3.** PXRD patterns of the two rutile supported catalysts, showing rutile and  $\text{RuO}_2$  crystalline phases (a) DPU-R (b) DPU-D.

The morphologies of the catalysts prepared by the different techniques were observed by TEM (Figure 4.4). Small (2.4 and 2.8 nm) and uniformly dispersed  $\text{RuO}_2$  particles were noted on the dandelion support prepared by both the DPU and IMP methods (Table 4.2) confirming data from the PXRD analysis. For the thermally produced rutile support, the particles observed were much larger (10.2 and 14.6 nm) than those seen on the dandelion support. This data also showed that the DPU process yielded slightly smaller  $\text{RuO}_2$  particles which were better dispersed (Figure 4.4c and 4.4d and Table 4.2) independent of the supports used.

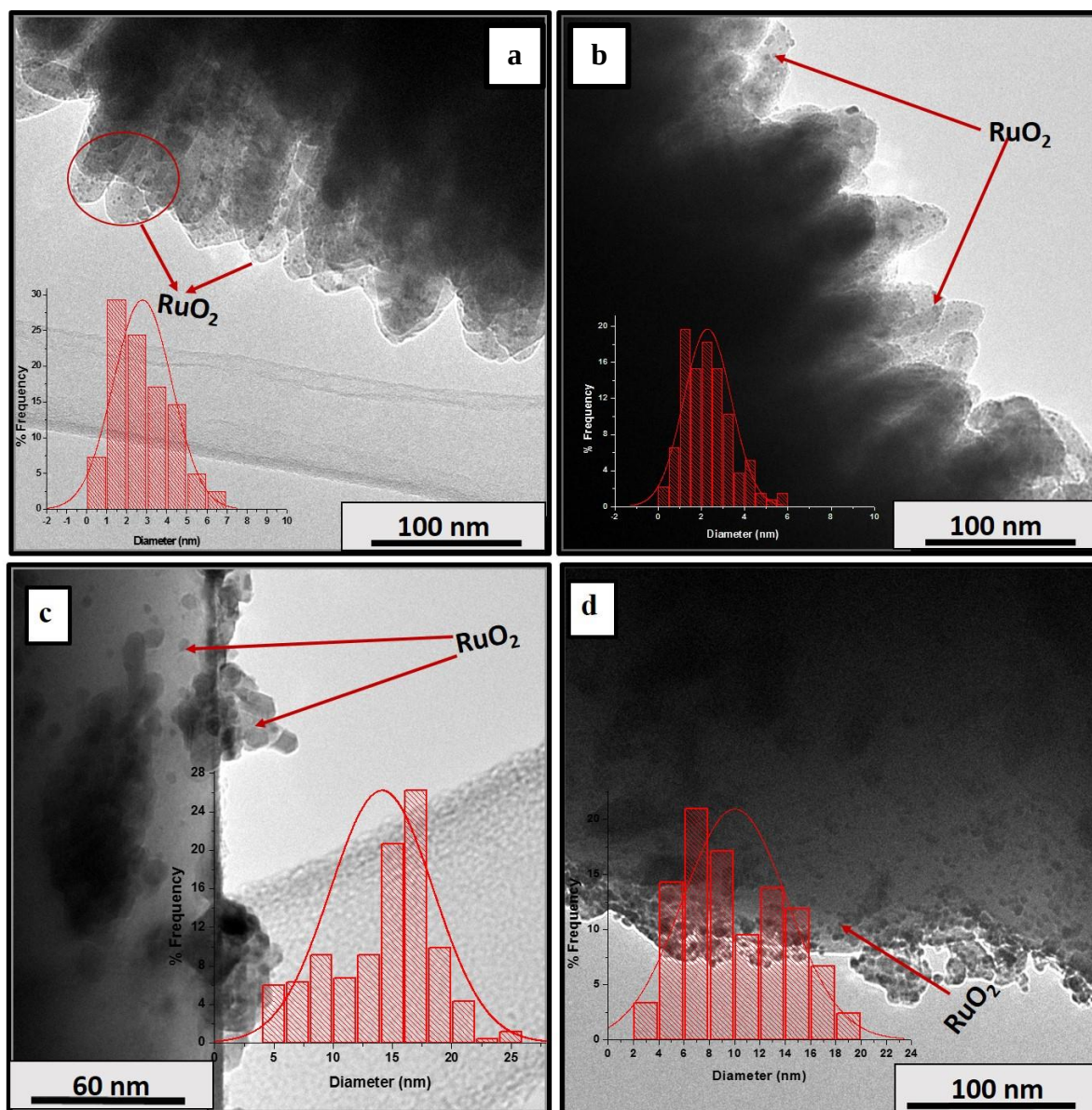


**Figure 4.4.** TEM images of Ru catalysts (a) IMP-D (b) DPU-D (c) IMP-R (d) DPU-R.

Table 4.2 Catalyst properties.

| Catalyst | Ru dispersion<br>(%) | $d_{\text{Ru}, \text{H}_2}$<br>(nm) <sup>a</sup> | $D_{\text{RuO}_2, \text{TEM}}$<br>(nm) <sup>b</sup> | $d_{\text{RuO}_2, \text{XRD}}$<br>(nm) <sup>c</sup> | Active metal<br>surface area<br>(nm <sup>2</sup> ) |
|----------|----------------------|--------------------------------------------------|-----------------------------------------------------|-----------------------------------------------------|----------------------------------------------------|
| DPU-D    | 61                   | 1.4                                              | 2.4                                                 | -                                                   | 240                                                |
| IMP-D    | 56                   | 1.6                                              | 2.8                                                 | -                                                   | 193                                                |
| DPU-R    | 21                   | 6.4                                              | 10.2                                                | 12.9                                                | 77                                                 |
| IMP-R    | 16                   | 8.1                                              | 14.6                                                | 16.7                                                | 58                                                 |

*a* Average diameter of Ru particles measured using H<sub>2</sub> chemisorption technique.

*b* Average diameter of Ru particles obtained from TEM images.

*c* Average crystallite sizes estimated from PXRD using Rietveld refinement.

Table 4.2 summarises information about the catalysts. The dispersion of Ru was measured by chemisorption. The average Ru particles sizes were estimated by assuming spherical particles. The smaller particles observed on the dandelion-like supports were highly dispersed, while the thermally produced rutile with agglomerated particles had a relatively lower dispersion. This agrees with both *ex situ* PXRD, *in situ* PXRD (later discussed) data and TEM analyses.

The H<sub>2</sub>-TPR profiles of the different catalysts are shown in Figure 4.5 and a summary of the reduction temperatures for the different catalysts are given in Table 4.3. The samples revealed similar hydrogen consumption profiles with a peak maximum at temperatures between 91 and 134 °C. The thermally produced rutile supported samples gave peaks that were broader than seen for the dandelion-like supported samples. This relates to the presence of larger particles and a broad range of particle sizes, consistent with the TEM data [35]. The differences in the hydrogen consumption profiles implied that both supports (dandelion-like rutile and rutile grains) and the Ru addition method affected the reduction process. The RuO<sub>2</sub> on the dandelion support reduced at a relatively lower temperature compared to the thermally produced rutile (Table 4.3), an indication of a weaker metal support interaction even though the RuO<sub>2</sub> particles were smaller. This implied that relatively less energy was required to reduce the smaller RuO<sub>2</sub> particles to Ru. In addition, it is suggested that the dandelion morphology (radially arranged rutile nanorods) did not hinder reduction of RuO<sub>2</sub> to Ru, due

to the easy accessibility of the RuO<sub>2</sub> particles on the tips and on the rods to the reducing gas (H<sub>2</sub>). In summary: the thermally produced rutile had a lower surface area which resulted in larger RuO<sub>2</sub> particles and poorer dispersion and hence the higher reduction temperature.

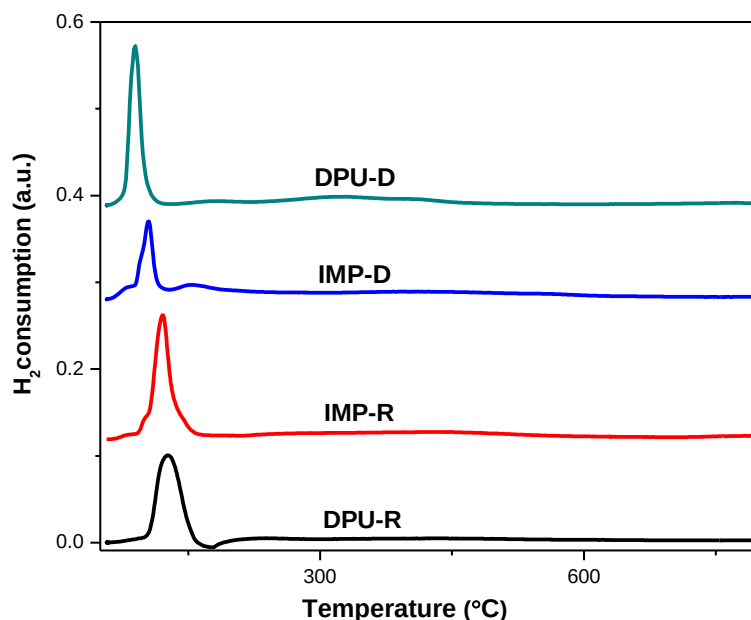


**Figure 4.5.** H<sub>2</sub>-TPR profiles for Ru supported on the different rutiles.

Table 4.3. Summary of the reduction temperatures for all the catalysts.

| Catalyst | Reduction temperature (°C) |
|----------|----------------------------|
| DPU-D    | 91                         |
| IMP-D    | 106                        |
| DPU-R    | 121                        |
| IMP-R    | 127                        |

The different catalysts were subjected to *in situ* PXRD studies to monitor the reducibility of the different catalysts. Figure 4.6 shows *in situ* diffraction patterns of Ru on the rutile supports. It was noted that the RuO<sub>2</sub> phase dominated at lower temperature ( $T < 150$  °C). Again, it is observed that hexagonal Ru [PDF 03-065-1863] indexed as (100) and (002)

corresponding to  $2\theta$  angles of  $38.4^\circ$  and  $42.1^\circ$  respectively appeared at  $T > 500^\circ\text{C}$  and grew with temperature indicating sintering of the Ru particles (Figure 4.6). The absence of the Ru peaks between  $200^\circ\text{C}$  and  $500^\circ\text{C}$ , after the oxide reduction could be explained by the presence of small undetectable Ru crystallites at these temperatures. The reduction behaviour revealed by the *in situ* PXRD data agrees with data from the  $\text{H}_2$ -TPR process. For the dandelion supported catalyst, both the  $\text{RuO}_2$  and Ru remained undetected at  $T < 600^\circ\text{C}$  (Figure 4.S3). This indicates insignificant sintering of the Ru crystallites even at the high temperatures.

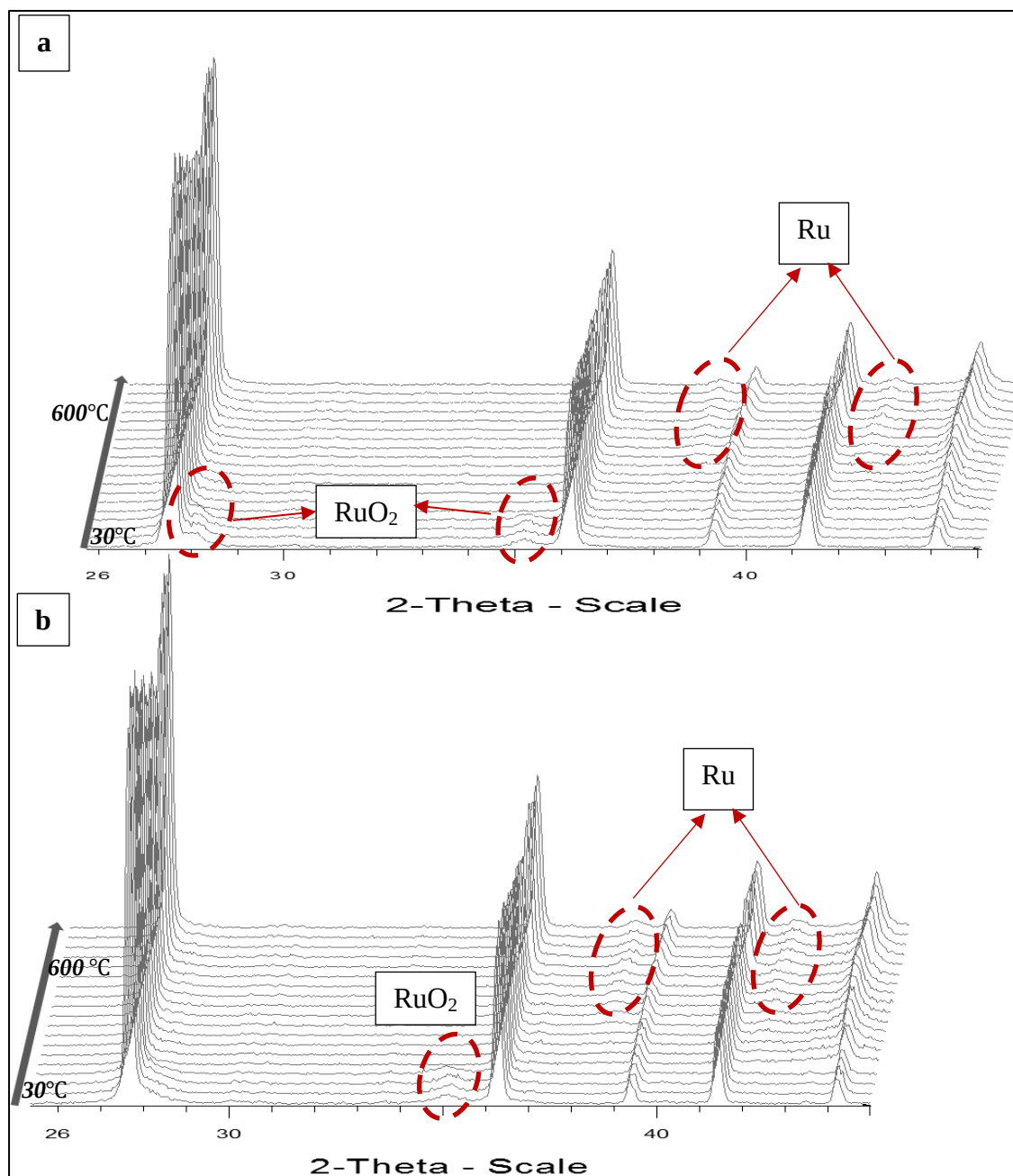


**Figure 4.6.** In situ PXRD pattern of the catalysts (a) IMP-R and (b) DPU-R.

Table 4.4. Crystallite sizes of IMP-R after in situ XRD reduction.

| Temperature (°C) | Crystallite size (nm) | GOF <sup>(a)</sup> |
|------------------|-----------------------|--------------------|
| 350              | 8.4                   | 1.2                |
| 400              | 9.1                   | 1.2                |
| 450              | 14.5                  | 1.2                |
| 500              | 18.1                  | 1.2                |
| 550              | 19.8                  | 1.2                |

*a-* goodness of fit (GOF)

#### 4.4 CO hydrogenation

The effect of the different rutile morphologies as support materials on the catalytic performance was investigated using Ru loadings of 5 wt%. The data were compared to similar studies on the traditional Ru/P-25 DEGUSSA catalyst where the anatase polymorph comprises 80% anatase and 20% rutile. The catalytic reactions were performed in the presence and absence of CO<sub>2</sub>.

Figure 4.7 shows the influence of reaction temperature on the catalytic conversion of CO ( $X_{CO}$ ) on the different catalysts. The CO conversion increased with increasing temperature for all catalysts studied. Both IMP-R and DPU-R catalysts had CO conversions below 4% at temperatures below 140 °C, while the DPU-D, IMP-D and P-25 conversions were higher. The dandelion-like support showed a higher activity, than the P-25 supported catalyst at 160°C and slightly at 160 °C. At about 180 °C, total CO conversion was observed for DPU-D, IMP-D and P-25 while lower conversions were noted for DPU-R (ca. 25%) and IMP-R (ca. 17%). Total conversion in the gas feed occurred at temperatures of about 260 and 280 °C for DPU-R and IMP-R respectively. This difference in activity was attributed to a particle size effect (smaller Ru particles on the dandelion rutile and P-25; see Table 4.2) associated with the differences in surface areas of the different supports.

The DPU-D and IMP-D catalysts were found to be the most active for CO methanation with almost similar activities. The rutile catalysts prepared using the impregnation method showed the lowest activity in this study again suggesting a link to particle size effects.

One of the critical parameters that determine activity of a catalyst is dispersion of the active metal species on the support. The surface area for dandelion-like rutile were observed to be the highest and resulted in an enhanced dispersion (Table 4.2).

Previous studies on methanation using Ru catalyst has shown that the reactions on  $\text{TiO}_2$  (P-25) have a higher activity than when Ru is supported  $\text{Al}_2\text{O}_3$ ,  $\text{CeO}_2$ , YSZ and  $\text{SiO}_2$  [15]. This has been explained in terms of either particle size effects, strong interaction of the active metal and the support and formation of Lewis acid-base complexes between the oxygen the adsorbed CO and anionic vacancies present at the edge of the oxide-metal boundaries [36].

Krishna and Bell have reported that Ru supported on anatase gave a higher activity than over rutile. This was explained to be due to the different levels of dispersion observed on the different  $\text{TiO}_2$  polymorphs [16]. Further studies by Carballo and co-workers [37] reported a superior activity for Degussa P25 titania (80% anatase and 20% rutile) over pure anatase in an FT synthesis reaction. They based their explanation on the complimentary nature of the two  $\text{TiO}_2$  polymorphs and the strong anchoring of Ru onto the rutile part of the P-25 support. Our studies have shown that modifying the morphology of rutile can significantly improve the activity of the Ru/rutile catalyst by improving the surface area which led to smaller metal Ru particles which were well anchored to the support for CO methanation reactions. It was expected that the smaller Ru particles will give higher activities on a catalyst mass basis and that this could rationalize much of the increased activity. Indeed, the Ru supported on Degussa P25 has slightly larger particles ( $d = 3.1 \text{ nm}$ ) and the rate (not included) is slightly lower than that for the Ru supported on the dandelion Ru particles ( $d = 2.8$ ). It is clear that the particle size effect dominates and this suggests dandelion rutile titania could be used in many other reactions in which particle size reduction is important.

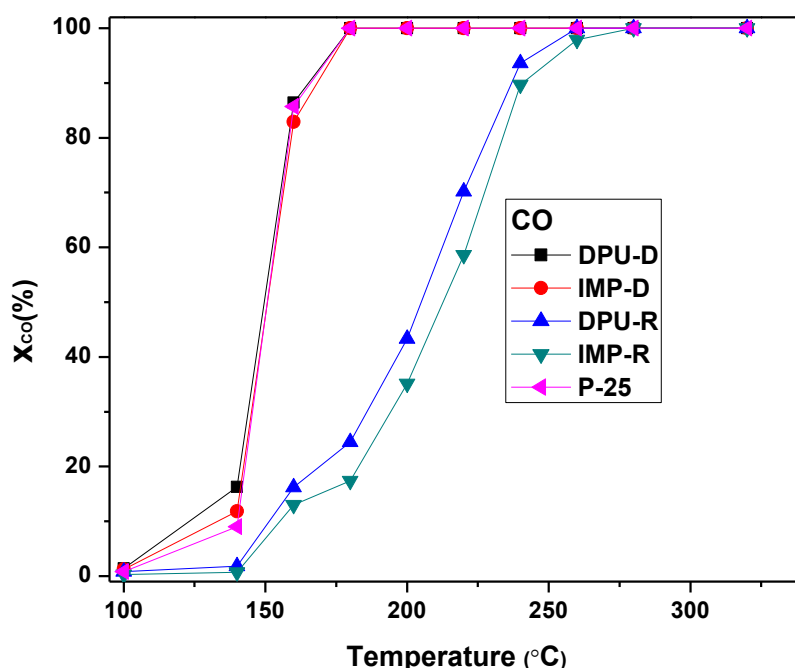


**Figure 4.7.** The effect of the Ru/TiO<sub>2</sub> on the CO conversion ( $X_{CO}$ ) as a function of reaction temperature using 5 wt.% Ru. Experimental conditions: mass of catalyst: 1 g; reactant composition: 1% CO, 89% H<sub>2</sub> (balance N<sub>2</sub>); total flow rate: 100 cm<sup>3</sup>/min.

It should be noted that CO hydrogenation under the reaction conditions also resulted in the production of other higher hydrocarbons besides methane. Figure 4.8 shows results obtained, where hydrocarbon selectivity ( $S_{C_xH_y}$ ) is plotted as a function of temperature for the DPU-R and DPU-D catalysts. The selectivity towards  $S_{CH_4}$  was observed to increase from *ca.* 84% to 100% with increasing temperature from 140 °C to 280 °C and remained constant at the higher temperature. Below 240 °C, the main by-products observed were C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>10</sub>. Less than 5% of C<sub>3</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>10</sub> were formed at 140 °C where they constituted the highest proportions and this was observed for both catalysts. Data for the DPU-D and DPU-R catalysts investigated (not shown), showed similar results. Panagiotopoulou and co-workers reported similar selectivity to higher hydrocarbons, including paraffin and olefins (up to C<sub>3</sub>) in their work with Ru on TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> [15, 38]. There were similarities observed in their data and the small differences noted when compared to our data could be due to differences in experimental conditions such as flow rate.

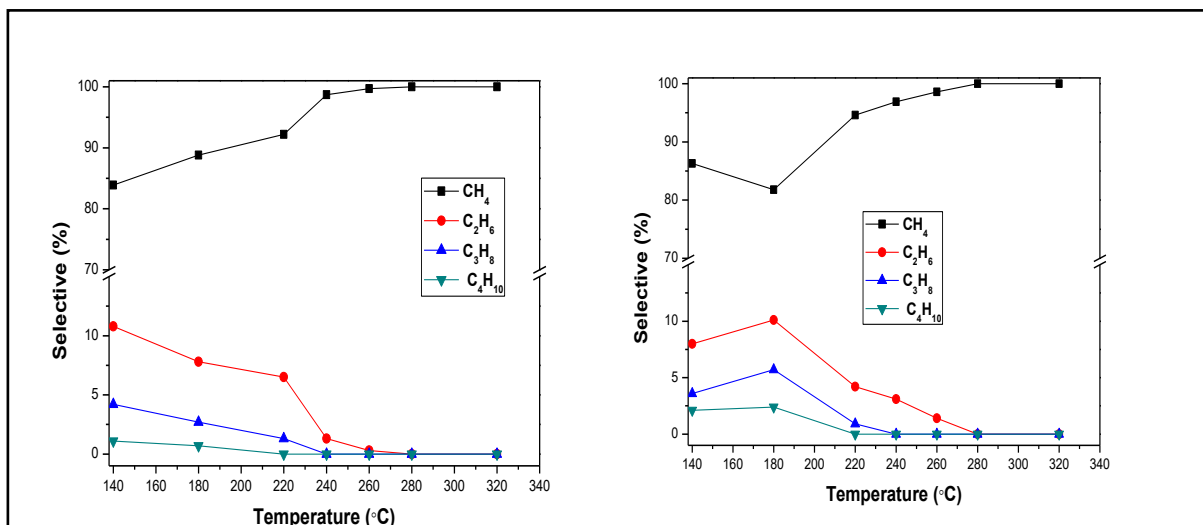


**Figure 4.8.** The effect of temperature on the selectivity of (a) DPU-R and (b) DPU-D catalysts.

#### 4.5 Selective CO methanation

The rutile supported catalysts were investigated for selective CO methanation in CO/CO<sub>2</sub> mixtures. The results obtained are summarized in Figure 4.9. It was noticed that  $X_{CO}$  increased with increasing temperature as observed for the CO hydrogenation data shown in Figure 4.7 but at lower  $X_{CO}$ .

The presence of CO<sub>2</sub> in the mixture shifted the maximum CO conversion for all the catalysts towards higher temperatures. The methanation of CO<sub>2</sub> was insignificant until CO conversions attained maximum values under the experimental condition. The DPU-R and IMP-R catalysts showed relatively low activity with maximum conversion of *ca.* 25% and 17% respectively. Significant CO<sub>2</sub> conversion (5% and above) only occurred beyond 220°C.

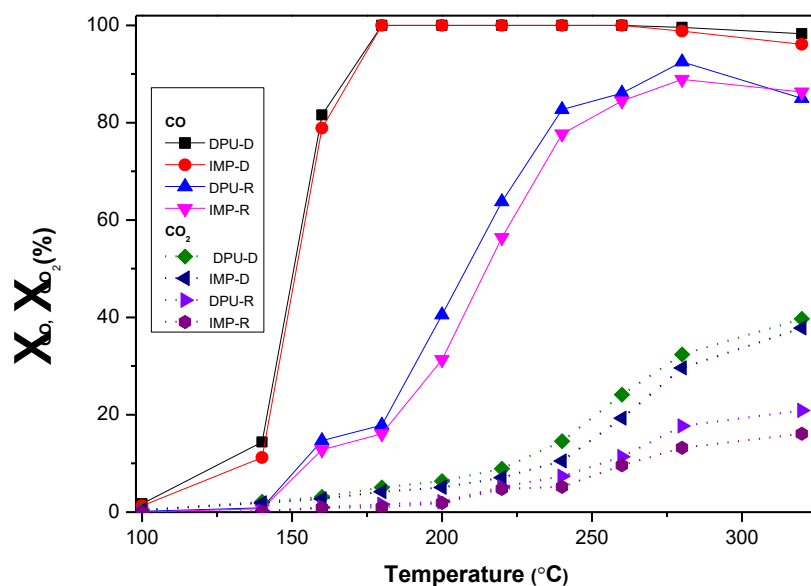


**Figure 4.9.** The effect of support on catalytic performance (a) CO conversion ( $X_{CO}$ ) and (b) selective methanation of CO in the presence of  $CO_2$  ( $X_{CO_2}$ ) as a function of reaction temperature using 5% wt.% Ru. (Solid symbols: CO conversion: open symbols:  $CO_2$  conversion). Experimental conditions: mass of catalyst: 1 g; reactant composition: (a) 1% CO, 89%  $H_2$  (balance  $N_2$ ) and (b) 1% CO, 20%  $CO_2$ , 69%  $H_2$  (balance  $N_2$ ); total flow rate:  $100\text{ cm}^3/\text{min}$ .

The suppression of  $CO_2$  methanation until CO methanation attained maximum conversion is expected to be due to preferential occupation of the surface sites by CO, as CO has a higher adsorption energy than  $CO_2$ . The  $CO_2$  methanation will be suppressed until the CO partial pressure falls below certain levels [5, 39, 40].

The radially aligned nanorutile rods which gave the dandelion-like morphology showed a relatively high surface area, with smaller Ru particles which were well dispersed. This was explained by the fact that the nanorods were separated from each other; this enhanced the spacing and dispersion of the Ru particles. The dandelion-rutile nanorods have been observed to have a defined contact area due to the rutile morphology and also have curvature which helps dock the Ru particles firmly on the supports and could be one of the reasons for the formation of the smaller Ru particles which showed sinter-resistance (from *in situ* PXRD studies). Smaller Ru particle sizes have greater opportunity to achieve a high surface-to-

volume ratio which leads to good and improved catalytic activity [24, 41, 42]. It has been reported that the dandelion structure promotes a facile electron transfer process and makes it superior to other TiO<sub>2</sub> supports when used in photocatalysis [23, 28]. The rutile morphology increases the electron density on the Ru which enhances M-CO back bonding and hence increases the C-O bond cleavage. This results in the improved CO conversion [43]. This could enhance the catalytic activity of the dandelion supported catalyst. The catalyst preparation method did not reveal any significant difference in activity for the DPU-D and IMP-D catalyst in the selective CO methanation. Therefore, the differences in activity observed in this study are dominated by particle size effects.

#### **4.6 Conclusion**

In summary, Ru loaded crystalline dandelion-like rutile structures were synthesized and characterized. It was revealed from *in situ* PXRD studies that Ru particles loaded on the crystalline dandelion-like rutile structures were small (< 3 nm undetected) and experienced no observable agglomeration under the reaction conditions, and were undetected by XRD. This was attributed to their stability provided by the radially arranged nanorutile rods which offered a relatively higher surface area. The Ru particles on the rutile rods were separated from each other due to the radial arrangement taken by the rutile nanorods.

The effect of different rutile morphologies as supports and different catalyst preparation methods on CO methanation in the absence and presence of excess CO<sub>2</sub> was studied using Ru as the active metal phase. The morphology of the rutile used as support affected the activity of the catalysts. Under CO methanation conditions, all the catalysts attained 100% CO conversion within the temperature range of the study but incomplete conversion was observed for the thermally produced rutile TiO<sub>2</sub> at  $T < 200$  °C. The same applied to methanation reactions that occurred in the presence of CO<sub>2</sub>. It was observed that the activity of the catalyst depended strongly on the experimental condition used (e.g. reaction temperature).

The rutile crystalline morphology in the form of dandelion-like structures with higher surface area than typically made by thermal conversion of anatase to rutile demonstrated similar activity to the TiO<sub>2</sub> P-25 support. The advantage of using the rutile rather than the anatase support is that the rutile is thermodynamically stable at high temperatures. This suggests that

methods to synthesize rutile with even higher surface areas than made in this study could be advantageous for reactions where metal/titania catalysts need to be used at temperatures greater than 500 °C.

#### 4.7 Acknowledgement

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#### 4.7 Supplementary data

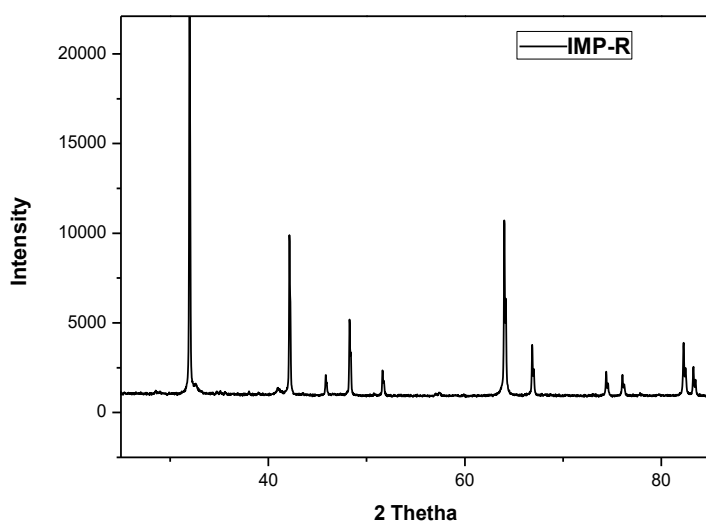


**Figure 4.S1.** PXRD pattern of the IMP-R catalyst.

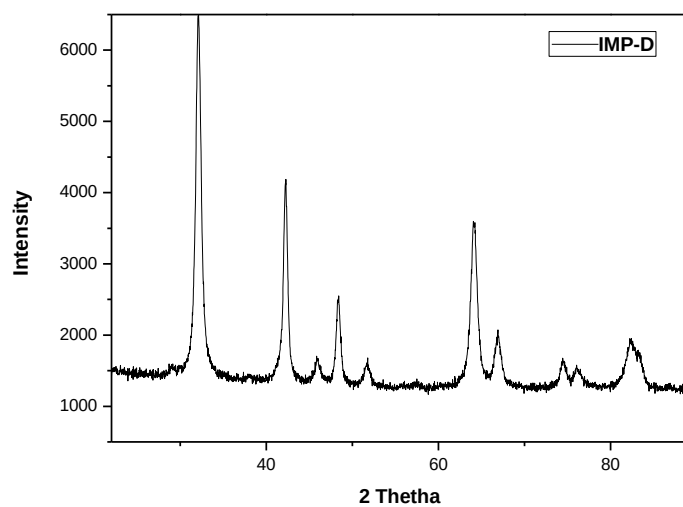


**Figure 4.S1.** PXRD pattern of the IMP-D catalyst.

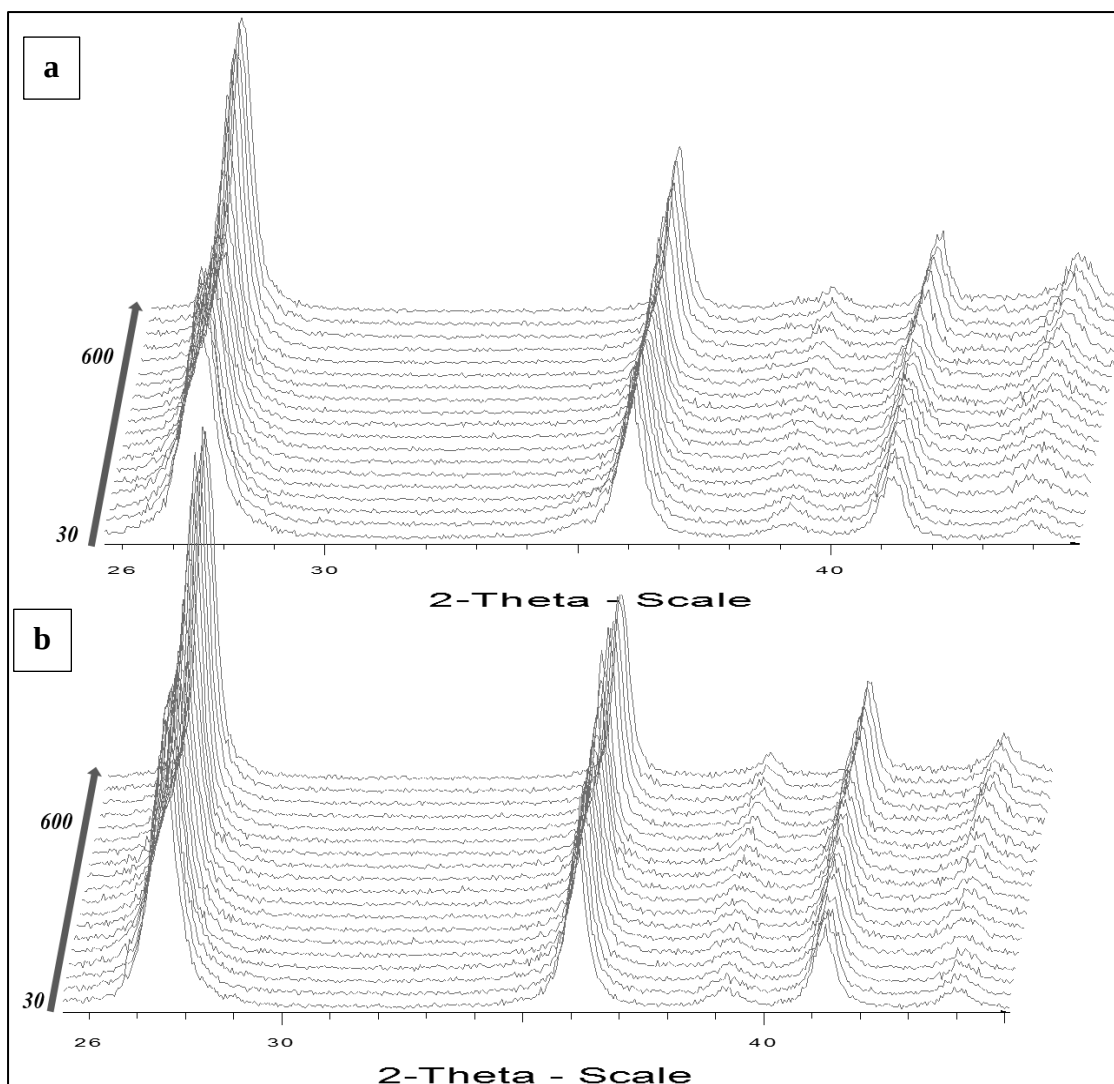
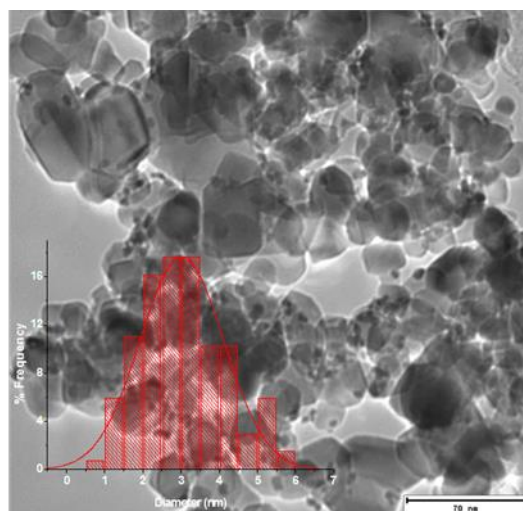


Figure 4.S3. In situ PXRD pattern of the DPU-D catalysts.



. Figure 4.S4. TEM image of  $\text{TiO}_2$  P25.

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# Chapter 5

## MICROWAVE INDUCED SYNTHESIS OF Ru PARTICLES SUPPORTED ON CNTS FOR SELECTIVE CO METHANATION

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### Abstract

Herein we report the purification of a H<sub>2</sub>-rich feed gas for a PEMFC using selective CO methanation over Ru nano catalysts supported on carbon nanotubes (CNTs). The Ru particles synthesised were manipulated by using a microwave polyol method and results have been compared with incipient wetness impregnation catalyst preparation methods. The CNTs were synthesized using a 5%Fe-Co/CaCO<sub>3</sub> catalyst. The chemical vapor deposition (CVD) technique was used in the synthesis and the as-synthesized CNTs were purified and functionalized in 55% HNO<sub>3</sub>. They were characterized using BET, XRD, Raman, TEM, chemisorption and TPR techniques. The RuO<sub>2</sub> particles on the CNT support prepared by the different techniques were observed in TEM images. Small and uniformly dispersed RuO<sub>2</sub> nanoparticles were formed in the microwave-assisted synthesized procedure. For the impregnated catalyst, the particles observed were larger. This was mainly due to the short thermal induction period used in the microwave process, resulting in smaller, Ru crystallites with a narrow size distribution and improved dispersion. A significantly higher catalytic activity was obtained for CO conversion recorded for the catalyst synthesized by the microwave-assisted method. The activity was attributed to the high Ru metallic surface area

containing more exposed surface atoms and the related high dispersion observed as revealed in the TEM and confirmed by chemisorption studies.

**Keywords:** Microwave, polyol, carbon nanotubes, selective CO methanation, ruthenium catalyst

## 5.1 Introduction

The catalytic methanation of CO is considered as a potential and effective way to reduce CO in a reformat gas mixture. The reformat gas is mostly produced by steam and dry reforming of organic compounds and the CO produced has found application in fuel cells [1]. This method employs  $H_2$  as a reducing agent without any additional agent. This is different to preferential oxidation (PROX) which relies on an oxidizing agent from an external source to remove CO. For practical applications in fuel cells, the content of CO should be at trace-levels as the Pt used anode can only tolerate  $<10$  ppm CO and  $<100$  ppm CO for Pt alloyed anodes used in a  $H_2$ -rich fuel feed [2, 3]. It is also imperative to design a catalyst that suppresses methanation of  $CO_2$  which coexists with CO and can consume large amounts of  $H_2$ .

Interest in the use of nano metal crystallite catalysts has surged recently. A decrease in crystallite size exposes a higher number of surface atoms per unit of the active component which is available for a reaction. Implying, the activity per mass increases with decreasing metal crystallite size [4]. The CO dissociation rate depends on the size of the active metal crystallites used and is thus a structure-sensitive reaction [5, 6]. Several studies in selective CO methanation have attributed the higher catalytic activity to a small and narrow range of Ru nano particles. Tada and co-authors [7] studied the effect of reduction treatment on Ru supported on  $TiO_2$  and  $Al_2O_3$  for selective CO methanation. They observed decreased CO methanation conversions, as Ru crystallite size growth occurred through increase in the thermal treatment temperature. Takenaka and co-workers studied the complete removal of CO in a hydrogen-rich gas stream and observed that, the smaller Ru particle sizes were the most active in this process [8].

Various synthetic approaches have been developed over time to make nanostructured catalysts. These methods include physical vapour deposition [9], electrochemical deposition [10, 11], colloidal routes [12], impregnation reduction routes [13], etc. The polyol method

has been shown to be one of the promising methods used to prepare Pt nano particles loaded on a carbon support [14] and Pt-based bimetallic supported nanoparticles on carbon support [15]. This procedure allows the synthesis of nanoparticles by metal precursor reduction in ethylene glycol [16]. This is achieved without the use of a surfactant, making the procedure less expensive. In the polyol synthesis method, the reaction mechanism involves the oxidation of the solvent ethylene glycol (E.G) into glycolic acid which is preceded by oxidation to an aldehyde intermediate. Reduction of metallic ions to their elemental state then proceeds following decomposition of the ethylene glycol (120-160 °C) [17, 18]. Usually the reduction reaction is activated by temperatures above 120 °C for several hours [14, 16, 19, 20]. Microwave heating of a polyol solution has also been used for the reduction of metal salt. Microwave irradiation is believed to favour dehydrogenation of the aldehyde intermediate which plays a critical role in the reduction of the metallic salt. This arises because of the high reduction ability as well as high dielectric losses of ethylene glycol. Generally, microwave irradiation offers significant advantages over conventional heating. This includes, homogeneous nucleation as a result of uniform heating, very short thermal induction periods and shorter crystallization times. Localized high temperatures generated at reaction sites also enhances the reduction rate of metallic salts and usually super heating above the solvent's boiling point occurs due to the microwave dissipation over the whole liquid volume. Due to the above mentioned advantages microwave dielectric loss heating is a good option for a synthesis process in view of its energy efficiency, time saving, lack of thermal convection (uniform heating across the whole solvent volume) and simplicity [21, 22].

Since their discovery [23], carbon nanotubes have been used in many research applications, including catalysis. Since the first report in 1994 of the use of CNTs as a catalyst support [24], interest in the use of CNTs as a support for metal catalyst has continued to be high. The carbon metal support-interaction influences activity. The CNT has a lack of microporosity, the active phase is accessible to reactant molecules, has good mechanical strength, it is easily functionalized and aids in the metal dispersion. The chemical composition of the CNT can be easily changed by doping with heteroatoms (e.g. nitrogen and boron) [25-29].

Several reports exist on the use of carbon nanomaterials as model catalyst support in Fischer-Tropsch synthesis (FTS). The CNTs permit study of the roles of different reaction parameters, such as pore size or confinement, the active metal particle size [30-33], promoters, nitrogen doping and pretreatment. In contrast, there have been very few reports on

the use of functionalized shaped carbon nanomaterials, especially CNT supported catalysts, in the selective CO methanation reaction. Herein, we report on the efficient synthesis of varying Ru particles sizes with a narrow size distribution supported on HNO<sub>3</sub> functionalized CNTs without increasing, decreasing metal loading or heat treatment by conventional heating to vary the particle sizes as existing in literature. This was achieved through a microwave induced polyol method. The microwave oven (infra-red temperature) was varied between 190 to 220 °C, while, keeping the microwave power constant at 600 W. The variation of the microwave temperature influenced the synthesis time and this influenced the Ru crystallite sizes. The effect of particles size on the functionalized CNTs were studied for both CO methanation and selective CO methanation reactions in the presence of excess CO<sub>2</sub>

## 5.2 Experimental

### 5.2.1 Support and catalyst preparation

The CNTs were synthesized by a modified chemical vapour deposition (CVD) method. Typically, acetylene was decomposed over a 10% wt Fe-Co bimetallic catalyst supported on CaCO<sub>3</sub> at 700 °C [34]. A quartz tube boat containing the spread catalyst was placed in the middle of a quartz tube reactor which was placed in a furnace. Nitrogen was allowed into the reaction chamber at a flow rate of 40 ml/min while heating at 10 °C/min up to 700 °C. The acetylene was further allowed into the reactor (flow rate of 240 ml/min) and left to run for 1 h in flowing N<sub>2</sub>. The reactor was then cooled to room temperature under N<sub>2</sub>. The as-synthesized CNTs were added to 55% HNO<sub>3</sub>, stirred and refluxed at 110 °C for 8 h to remove any catalyst residue (Fe-Co/CaO) and to functionalize the surface of the CNTs. They were then dried in 100 °C overnight. The purified and functionalized CNTs were used as a support for the catalyst.

The impregnation and microwave assisted polyol techniques were used to synthesize the Ru/CNT supported catalysts. For the impregnation method, a desired RuCl<sub>3</sub> solution (5 wt.%) was directly impregnated onto the functionalized CNTs, and then dried at 110 °C for 12 h. The catalyst was calcined at 220 °C in air to remove impurities was denoted as Ru/CNTIMP. For the microwave assisted synthesis, 1 g of the functionalized CNTs were dispersed in 15 ml of ethylene glycol and stirred for 5 min. The mixture was then sonicated for 15 min. An appropriate amount of RuCl<sub>3</sub> solution (5% Ru loading) was mixed with 15 ml of ethylene

glycol and sonicated for 10 min. Both mixtures were added rapidly together and stirred for 5 min and later transferred into a microwave Teflon vessel placed in a microwave reactor (Anton-Paar Multiwave 3000). The following conditions were used on the microwave experiments; IR temperature of 190, 210 and 220 °C; pressure of 60 bar; stirrer 2 setting; rate 0.5 bar/s and power 500 W which was kept constant. The microwave was switched off when the desired temperature for the syntheses was achieved (190, 210 and 220 °C). The mixtures were then centrifuged at 4000 rpm and washed several times with ethanol and deionized water after the microwave experiment. The catalyst was dried for 12 h in an oven at 110 °C and calcined in air at 220 °C for 2.5 h. The microwave assisted synthesized catalysts were denoted by Ru/CNT190, Ru/CNT210 and Ru/CNT220 for the catalysts prepared at reaction temperatures of 190, 210 and 220 °C respectively.

### 5.2.2 Support and catalyst characterization

The structural morphologies of the samples were revealed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The images were taken using a SEM FEI Nova Nanolab 600 and TEM Tecnai T12. The samples for TEM analyses were dispersed in methanol and sonicated. The suspension formed was loaded on SPI-carbon coated copper grid. Several images were taken for both supports and catalyst. For all the size distribution plots, averages of 120 RuO<sub>2</sub> species were counted using the Image J software.

X-ray powder diffraction patterns for the support and the calcined catalyst were measured on a Bruker D2 diffractometer using Co with K $\alpha$  radiation. This was equipped with a Ni filter. A stepwise of fraction 0.02° with a scan range of 10-90° (2 $\theta$ ) was used in obtaining diffraction patterns. The primary crystallite size was calculated using the Rietveld refinement:

$$d_{Ru} = \frac{0.9\lambda}{\beta \cos\theta} \quad (5.1)$$

where  $d_{Ru}$  is the average Ru crystallite size,  $\lambda$  = X-ray wavelength of Co-K $\alpha$  radiation (0.1789 nm),  $\beta$  = broadening (in radians) of the RuO<sub>2</sub> and  $\theta$  = the diffraction angle associated with the peak broadening.

N<sub>2</sub> adsorption-desorption experiments were done on a Micromeritics ASAP 2000 apparatus at -196 °C to examine the surface area and surface porosity of the catalyst support. The samples

(0.2 g) were degassed *ex-situ* for all samples under N<sub>2</sub> for 4 h at 150 °C using a Micromeritics flow Prep 060 degas system prior to the experiment.

Raman spectroscopy was used to measure the D and G bands associated with the CNT support. This was done using a Jobin-Yvone T64000 micro Raman spectrometer. The sample was excited using an argon laser with a wavelength of 514.5 nm and the spectrometer made use of a charge coupled detection system.

TGA analysis of the as-synthesized and the functionalized CNTs were conducted in a TGA-4000 (Perkin Elmer) analyser equipped with Pyris software. The analyses were done in air to ascertain the degree of functionalization. Approximately 10 mg of the sample was placed in the sample holder and air (flow rate of 20 ml/min) was allowed to flow over the sample. The samples were heated to 900 °C at a heating rate of 10 °C/min from 35 °C.

The reducibility of the Ru was studied using H<sub>2</sub>-TPR and carried out using a Micromeritics Autochem 2910 instrument. Typically, 0.15 g of the catalyst was loaded into a U-shaped quartz tubular reactor. The reactor was heated to 150 °C under an argon atmosphere at a heating rate of 5 °C/min for 30 min and then cooled to 50 °C. The TPR analysis was performed by exposing the catalyst to 5% H<sub>2</sub>, (balance Ar) at a flow rate of 40 ml/min while heating at a rate of 5°C/min to 900 °C. Any change in the amount of H<sub>2</sub> flowing through the reactor and the reference was observed using a TCD.

A Micromeritics Autochem 2910 instrument was used to conduct chemisorption experiments. The samples were first degassed *in-situ* at 150 °C for 30 min. The samples were further reduced with H<sub>2</sub> (99.999% purity) at 250 °C for 2 h and cooled to an ambient temperature under helium gas. The pulsing experiments were carried out with a 423 µL sample loop filled with a mixture of helium and H<sub>2</sub> (99.999% purity). The sample was held at 70 °C in the reactor and then the gas was injected for adsorption to take place. The percentage metal dispersion and the mean Ru crystallite size were calculated based on the H<sub>2</sub> uptake assuming a H<sub>2</sub>:Ru stoichiometry of 1:2 [35]. The Ru crystallites were assumed to be spherical in all cases and calculated from the relation below:

$$d_M = \frac{6 \times 10^2 \times MW}{\rho_M \times \theta_M \times 6.022 \times 10^{23} \times D} \quad (5.2)$$

where  $d_M$  is the mean crystallite size, MW is the atomic mass for Ru (101.07g/mol),  $\rho_M$  is the Ru density (12.3 g/cm<sup>3</sup>),  $\vartheta_M$  is the exposed surface area per gram of Ru metal and D is the percentage dispersion of the Ru metal [35].

### 5.2.3. Catalytic evaluation

The methanation reactions were performed in a fixed-bed micro reactor near atmospheric pressure. The temperature of the reaction was measured using a K-type thermocouple fixed onto the catalyst bed. Gas cylinders containing H<sub>2</sub>/CO/N<sub>2</sub> (1% CO, 10% N<sub>2</sub> and H<sub>2</sub> balance 99.99% purity) and H<sub>2</sub>/CO/CO<sub>2</sub>/N<sub>2</sub> (1% CO, 20% CO<sub>2</sub>, 10% N<sub>2</sub> and H<sub>2</sub> balance 99.99% purity) mixtures were used in the experiments. The N<sub>2</sub> acted as internal standard to ensure an accurate mass balance. The catalyst (1 g) was loaded into the reactor and reduced in-situ under hydrogen gas (99.995%) for 3 h at 250 °C at 1 bar pressure. The reduction process was done with H<sub>2</sub> gas flowing at 60 ml/min. The methanation reactions were conducted within a temperature range of 100 - 360 °C with the above mentioned feed mixtures at a flow rate of 100 ml/min. The outlet gas feed was monitored using an online gas chromatograph (GC) equipped with Porapak Q and Carboxen-1000 columns coupled to a FID and a TCD. Traces from the GC were monitored by a computer running on Clarity software.

## 5.3 Results and discussion

### 5.3.1. Characterization of support

#### 5.3.1.1. TEM analysis

The tubular structures of the CNTs were revealed by the TEM analysis; the CNTs had thick walls comprising of graphite layers (Figure 5.1) [36]. The outer diameters were observed to range between 20 – 50 nm and inner diameter between 6 -17 nm. Fig. 1b shows an image of the functionalized CNTs confirming the removal of residue catalyst used in the synthesis. It has been reported that the acid treatment slightly reduces the diameters of the CNTs due to the interaction of the outer graphene walls with the acid [37].

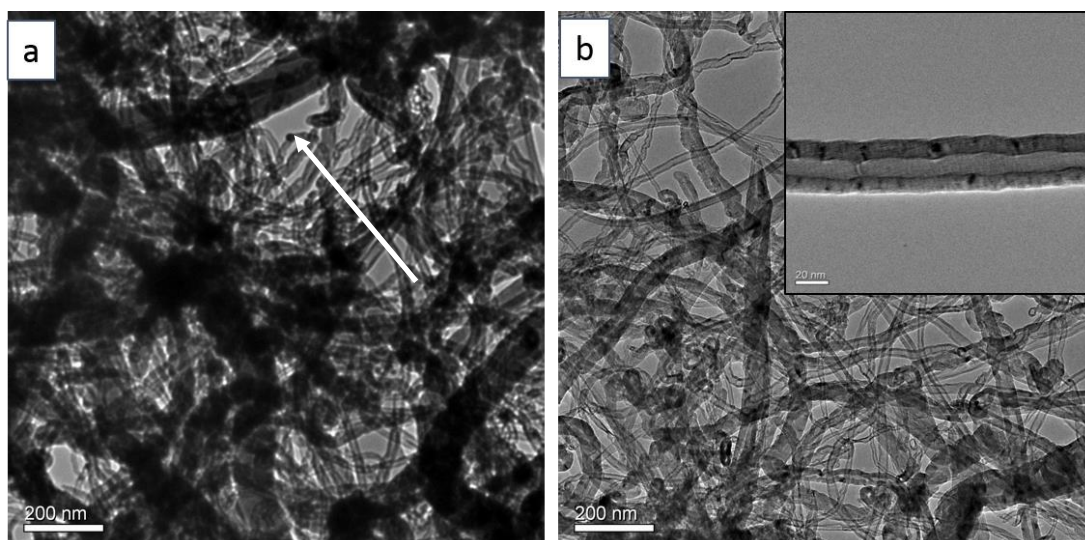


**Figure 5.1.** TEM images of CNTs; of (a) as-synthesised CNTs and (b) functionalized CNTs.

#### 5.3.1.2. TGA analysis

TGA analysis revealed the thermal stability and purity levels of the synthesized CNTs (Figure 5.S1). It was noted that the as-synthesized CNTs were stable up to ca. 672 °C, thereafter, ca. 87 % weight loss was observed when heated to 900 °C. The residual weight observed after decomposition was due the catalyst that remained from the CNTs synthesis. Two decomposition peaks were observed for the as-synthesized sample at 672 and 790 °C, as a result of carbon oxidation and decomposition of CaO respectively. A slight weight gain at ~ 500 °C was noted in the as-synthesized CNTs and this was due to the conversion of the metal catalyst to a metal oxide. For the functionalized CNTs, the thermal stability decreased to 536 °C due to the high defect content introduced into the matrix of CNTs. No decomposition was noted below 400 °C indicating the absence of amorphous carbon. Very little residual weight was seen after the acid treatment of the as-synthesized CNTs (ca. < 2%), indicating that the HNO<sub>3</sub> readily dissolved most of the catalyst while functionalizing the CNTs.

#### 5.3.1.3. BET analysis

Table 5.1 shows the BET surface area and pore volume data for the CNTs. The data indicate that the as-synthesized CNTs had a smaller surface area and pore volume (63 cm<sup>3</sup>/g and 0.17 respectively) than the functionalized CNTs. This increase could relate to removal of the

residue catalyst (Fe-Co/CaCO<sub>3</sub>) which had blocked the pores. Besides this, new voids were created through the functionalization process in the form of defects.

**Table 5.1.** N<sub>2</sub> adsorption-desorption data for the CNT supports and Ru CNT catalysts

| Sample              | BET surface area<br>(m <sup>2</sup> /g) | Total pore volume<br>(cm <sup>3</sup> /g) | Raman I <sub>D</sub> /I <sub>G</sub><br>Ratio |
|---------------------|-----------------------------------------|-------------------------------------------|-----------------------------------------------|
| As-synthesized CNTs | 63                                      | 0.17                                      | 0.703                                         |
| Functionalized CNTs | 77                                      | 0.26                                      | 0.969                                         |
| Ru/CNT190           | 64                                      | 0.14                                      | -                                             |
| Ru/CNT210           | 71                                      | 0.20                                      | -                                             |
| Ru/CNTIMP           | 60                                      | 0.31                                      | -                                             |
| Ru/CNT220           | 59                                      | 0.30                                      | -                                             |

#### 5.3.1.4. Raman spectroscopy

The structure of the CNTs were analysed with the aid of Raman spectroscopy. The laser Raman spectroscopy data revealed the characteristic disorder-induced band (D band) at ca. 1350 cm<sup>-1</sup> for both as-synthesised CNTs and functionalised CNTs, while the tangential mode (G-band) which describes the graphitic nature of the CNTs appeared at ca. 1390 cm<sup>-1</sup> (Figure 5.2). The intensity ratio of the D- and G-bands (I<sub>D</sub>/I<sub>G</sub>) allows for estimation of the level of defects in the CNT structure. The data indicated that the defects increased after functionalization I<sub>D</sub>/I<sub>G</sub> (from 0.703 to 0.969) of the as-synthesized CNTs with HNO<sub>3</sub> (Figure 5.2). This is in agreement with the TGA data where the high defect content resulted in easier oxidation of the CNTs. These defects may serve as docking points for the active metal species if applied in catalysis [37].

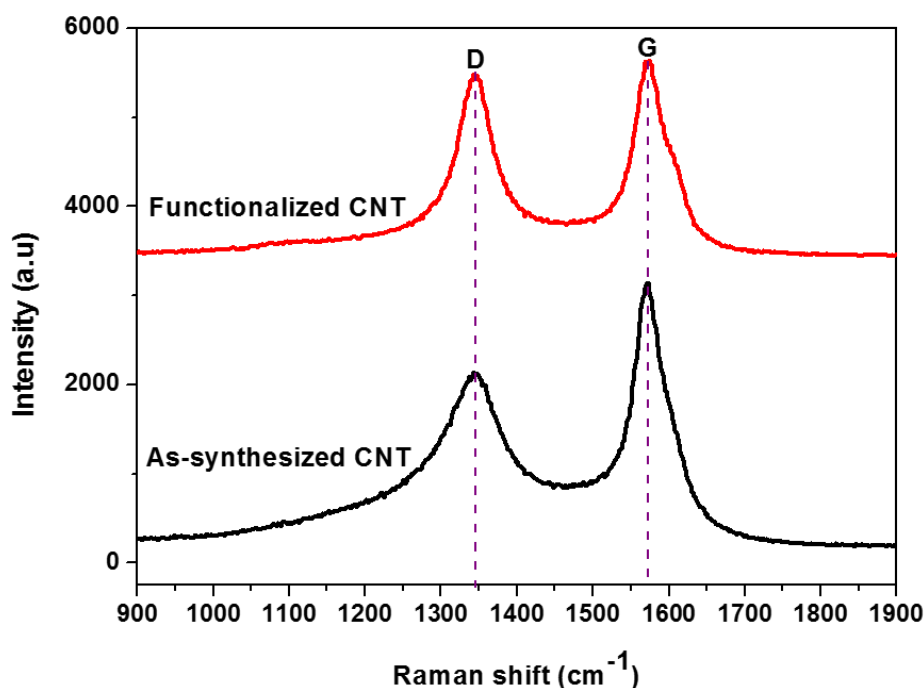


**Figure 5.2.** Raman spectra of functionalized and as-synthesized CNTs.

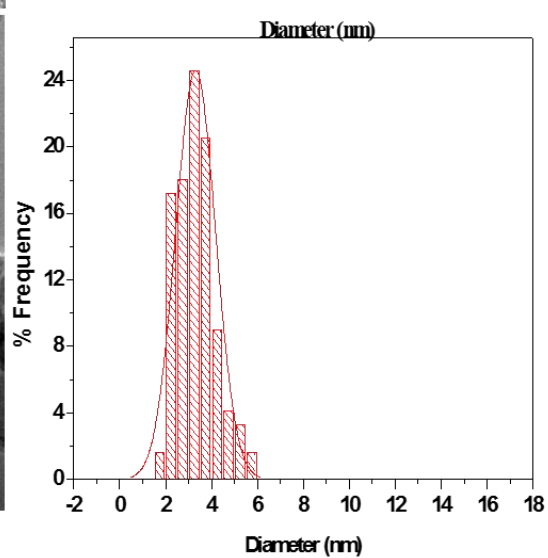
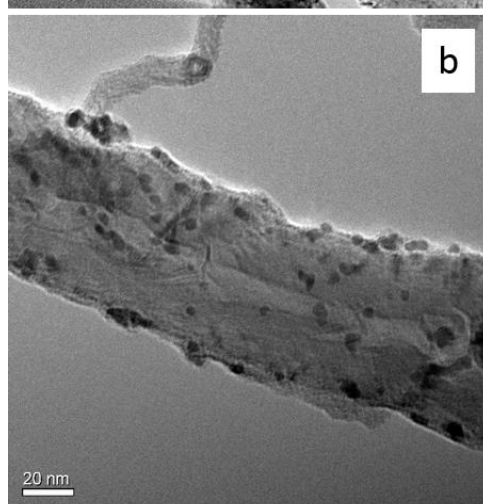
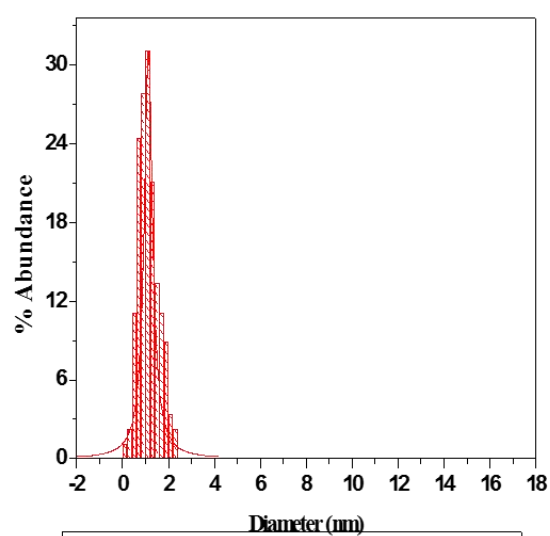
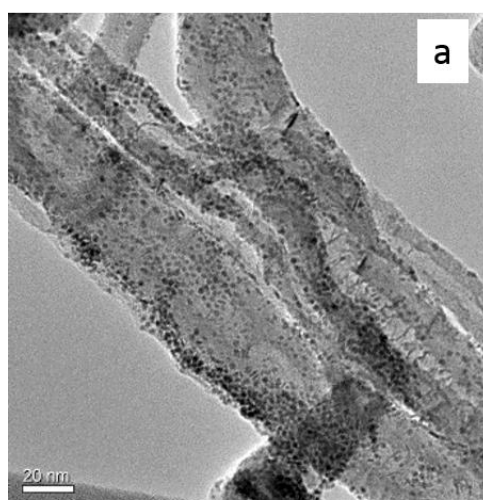
### 5.3.2 Catalyst characterization

#### 5.3.2.1. TEM analysis

Figure 5.3 shows the TEM images for the CNT supported Ru catalysts. The catalyst Ru/CNT190 had Ru oxide particles with an average diameter of 1.7 nm (Figure 5.3a) and they were very well dispersed on the CNT support. The microwave conditions employed gave a narrow Ru size distribution ( $1.7 \pm 0.5$ ) as seen in the particle size distribution graph. The TEM image for Ru/CNT210 (Figure 5.3b) revealed that the Ru particles were again well dispersed but were larger ( $3.1 \pm 0.8$ ) when the IR temperature was raised to 210 °C. The Ru oxide particles seen on Ru/CNT220 catalyst had agglomerated and had average size of about 10.3 nm. Despite the relatively larger Ru particles, the size distribution was narrow ( $10.3 \pm 1.4$ ). The Ru/CNTIMP TEM image revealed that the Ru particles had a larger average size ( $6.7 \pm 3.7$  nm). Thus, calcination at 230 °C gave a broader particle size distribution (varying particle sizes, between 0.2 to 20 nm). The particles were relatively poorly dispersed compared to the microwave synthesized catalyst. Thus the microwave polyol synthesis yielded good Ru dispersion and smaller particle sizes, based on the IR temperature used. This suggested, the control over Ru particles sizes in the impregnation method is more difficult to

achieve than by use of the microwave polyol process. The narrow range and well dispersed Ru particles resulting from the MW assisted synthesis were attributed to the effects of the rapid and uniform heating, usually referred to as thermal effects. The homogenous MW heating provides uniform nucleation and growth of nano Ru particles on the support. Again, the formation of uniform hot-spots and hot surfaces accelerates the reduction of the metal salt and it also enhances nucleation of the metal clusters which then manifest as small sized Ru nanostructures. The hot-spots are due to non-thermal (effects inherent to microwave heating) induced by microwave dielectric heating [21, 22].

The calculated particle sizes from PXRD ( $\text{RuO}_2$ ),  $\text{H}_2$  chemisorption (Ru) and TEM ( $\text{RuO}_2$ ) are recorded in Table 5.2. The data suggested large oxide particles of Ru ( $\text{RuO}_2$ ) before  $\text{H}_2$  reduction in the chemisorption process. The Ru particles became significantly smaller in size after reduction (chemisorption analysis). There were not significant decreases from  $\text{RuO}_2$  particles to Ru for the catalysts synthesized at 190 and 210°C after reduction as seen in the other catalysts. This was probably due to sintering occurring under the reduction conditions because the Ru particles were smaller and close to each other as seen in the TEM images in Figure 5.3a and 5.3b [38]. The Ru/CNT190 catalyst has the highest number of catalyst sites while Ru/CNT220 had the least active sites based on the particle sizes and the chemisorption data collected (Table 5.2). The  $\text{RuO}_2$  particle sizes calculated using Rietveld refinement showed that the residual weight function



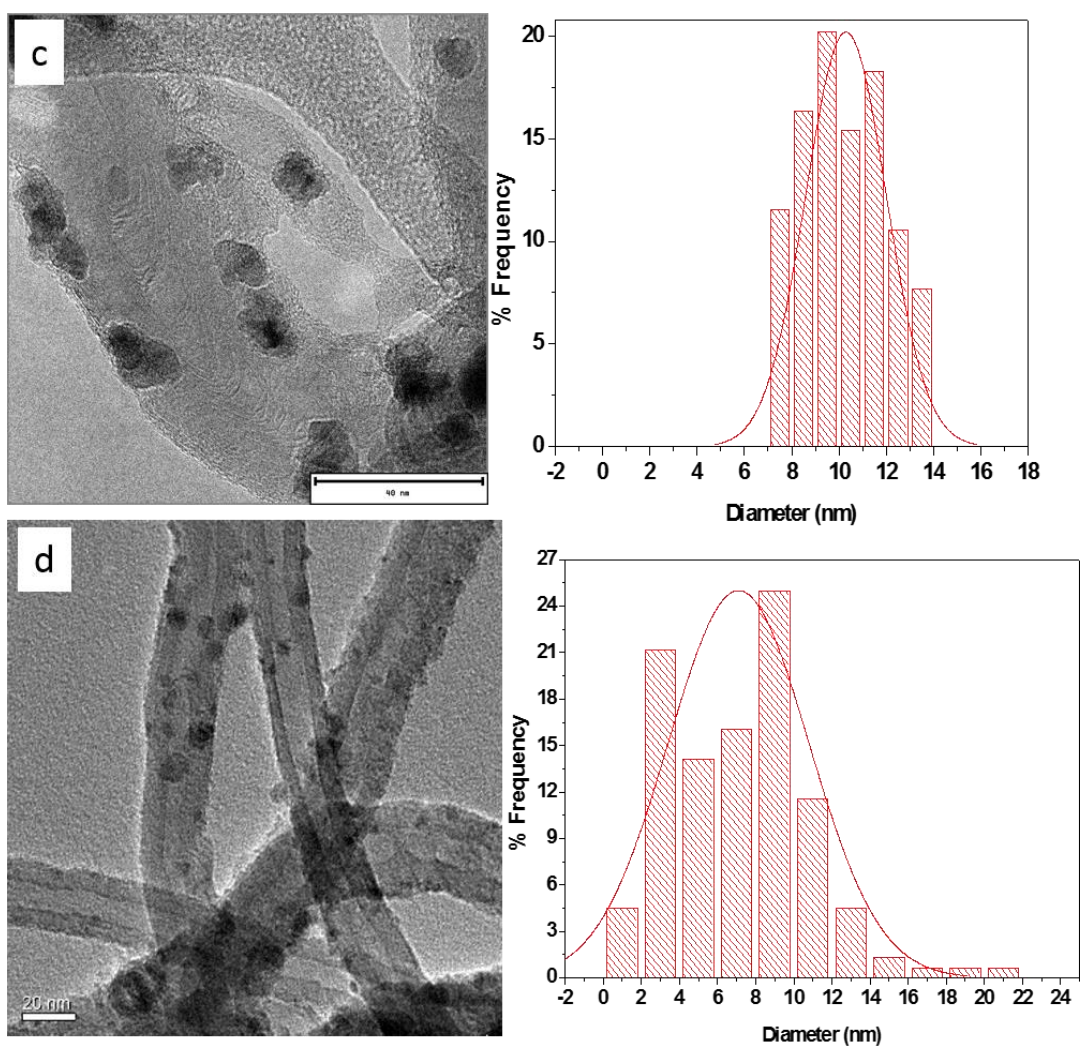


**Figure 5.3.** TEM images of Ru loaded on CNTs at different conditions (a) Ru/CNT190 (b) Ru/CNT210 (c) Ru/CNT220 IR temperature of 220 °C and (d) Ru/CNTIMP.

**Table 5.2.** Catalyst properties.

| Catalyst  | Ru             | $d_{H_2}$ (nm) <sup>a</sup> | $d_{TEM}$ (nm) <sup>b</sup> | $d_{XRD}$ (nm) <sup>c</sup> | RWP <sup>d</sup> |
|-----------|----------------|-----------------------------|-----------------------------|-----------------------------|------------------|
|           | Dispersion (%) | $d_{Ru}$                    | $d_{RuO_2}$                 | $d_{RuO_2}$                 |                  |
| Ru/CNT190 | 62.4           | 1.4                         | $1.7 \pm 0.5$               | -                           | -                |
| Ru/CNT210 | 54.2           | 1.9                         | $3.1 \pm 0.8$               | 3.8                         | 4.93             |
| Ru/CNTIMP | 23.1           | 4.7                         | $6.7 \pm 3.7$               | 7.2                         | 5.98             |
| Ru/CNT220 | 17.7           | 6.1                         | $10.3 \pm 1.4$              | 15.9                        | 5.65             |

<sup>a</sup>  $RuO_2$  sizes estimated by using  $H_2$  chemisorption.

<sup>b</sup>  $RuO_2$  sizes estimated by using TEM images.

<sup>c</sup>  $RuO_2$  sizes estimated by using Rietveld refinement.

<sup>d</sup> Rwp is the weighted residual function.

### 5.3.2.2. PXRD analysis

Figure 5.4 shows the diffraction patterns revealed from the XRD analysis of the different Ru/CNT samples. The relatively broad and intense peaks between ca. 25° and 32° are due to the characteristic diffraction peak of carbon. The peak at 30° was seen in all catalysts. The presence of  $RuO_2$  is also shown in Figure 5.4 No peaks for  $RuO_2$  were observed in the diffraction pattern of Ru/CNT190 due to their small size and high dispersion [37, 39, 40]. As also seen from the TEM analysis, an increase in IR temperature during the catalyst synthesis resulted in the formation of larger Ru particles which implies that the  $RuO_2$  had become more crystalline hence showed better defined  $RuO_2$  peaks in the XRD. The Ru/CNTIMP catalyst had a shoulder peak appearing at ca. 32° and a broader peak at 39.6° (indexed to 110 and 101 planes of  $RuO_2$ ) and smaller and weak  $RuO_2$  peak was observed at ca. 39.6° for Ru/CNT210. The results from the XRD analysis are in good agreement with TEM and  $H_2$  chemisorption data in terms of particle sizes and dispersion.

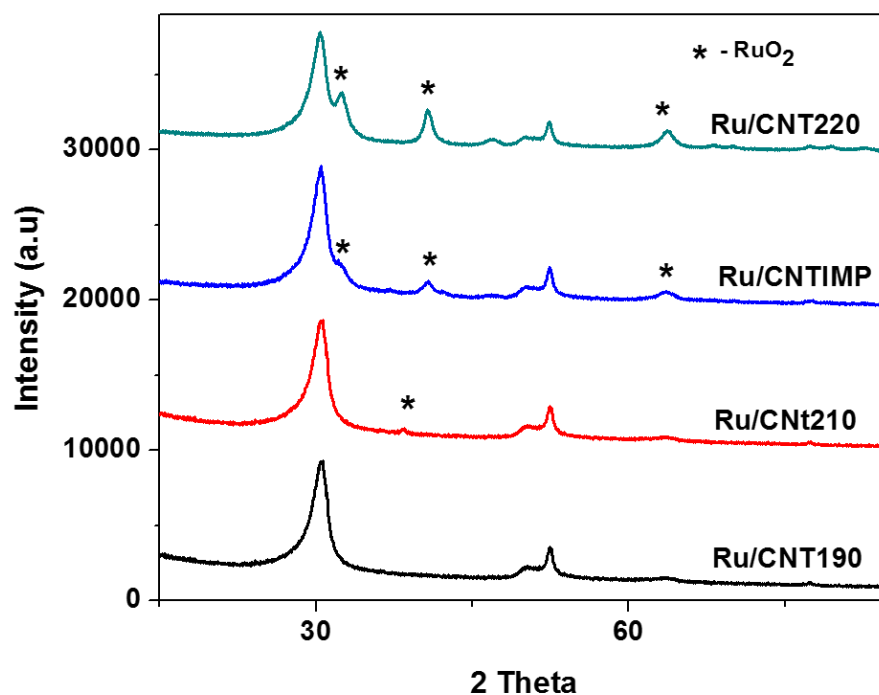


**Figure 5.4.** XRD pattern of Ru/CNT catalysts prepared at different microwave IR temperatures and the impregnation technique.

### 5.3.2.3. TPR studies

The reduction of the different Ru supported catalysts was monitored *via* TPR studies (Figure 5.5). The reduction of  $\text{RuO}_2$  to Ru (both supported and unsupported) is limited to a temperature lower than  $400^\circ\text{C}$  [41-43]. The catalysts revealed a single large peak located at  $\sim 100^\circ\text{C}$  for each catalyst. This reduction temperature increased as the particle size increased. Broadening of the peak was also observed with reaction temperature. Metal oxide supports give metal species that are reducible at very high temperature [44-47]. Carbon supports do not show such a metal-support interaction. Relatively higher temperatures were needed to fully reduce the larger Ru oxide particles to metal Ru. The broadening of the peaks were attributed to reduction of the intermediate oxidation states which could be detected e.g. Ru (IV) Ru (III)  $\text{RuO}_2 + \text{H}_2 \rightarrow \text{Ru}_2\text{O}_3$  [48]. The peaks appearing at higher temperatures (in the range  $450\text{--}500^\circ\text{C}$ ) could be due to  $\text{CH}_4$  from carbon oxidation or the reduction of Fe and Co residue that was not removed during the functionalization process as it was indicated in the TGA plot in Figure 5.S1.

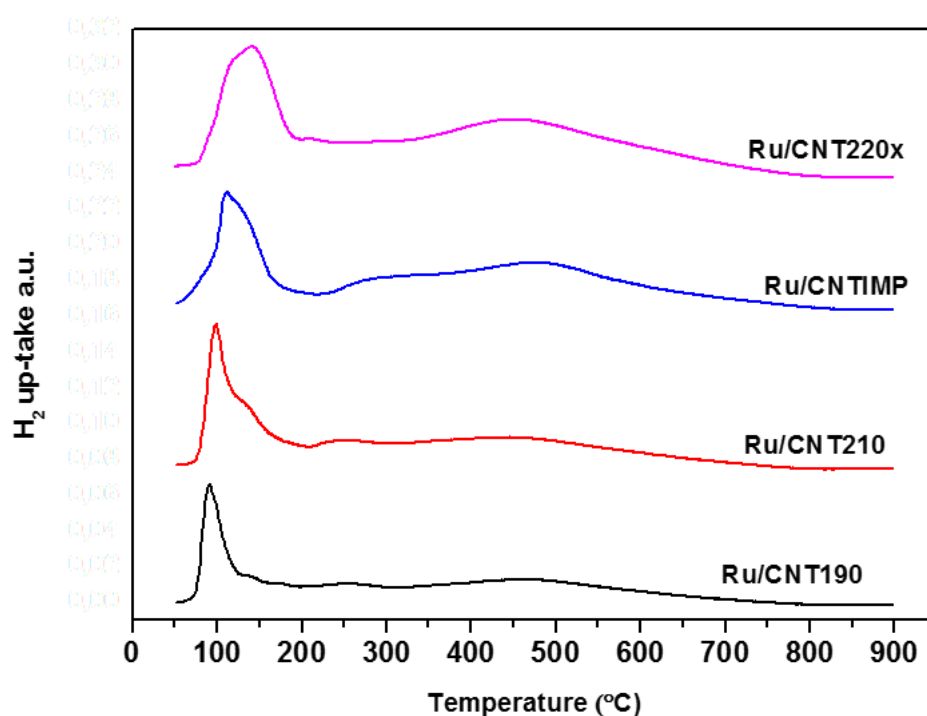


**Figure 5.5.** Temperature programmed reduction profile of the catalysts.

### 5.3.3 CO hydrogenation

Figure 5.6 summarizes of the catalytic performances of the different catalyst (5 wt.% Ru for all catalyst). The results show the percentage conversion of CO ( $X_{CO}$ ) plotted as a function of reaction temperature for the CO hydrogenation reaction. For all the catalysts studied the percentage CO conversion increased with increasing reaction temperature until a 100% conversion. The maximum CO conversions were attained at temperatures of about 280 and 320 °C for Ru/CNT190 and Ru/CNT220 respectively. Higher temperatures were equal for the other two samples. The activity was observed to decrease with increasing crystallite size.

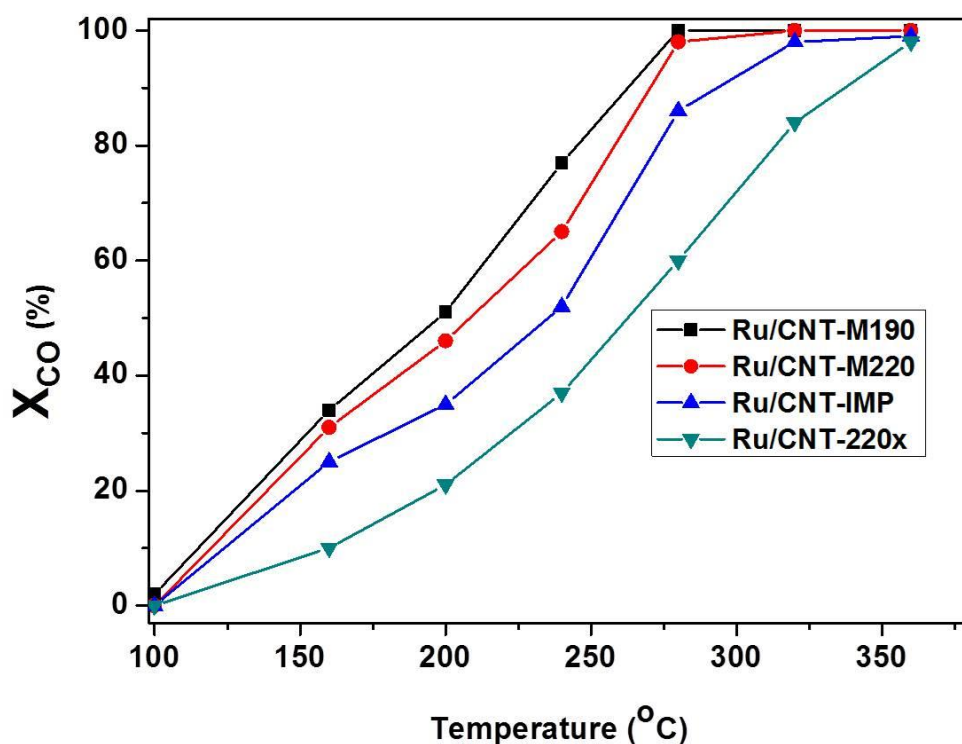


**Figure 5.6.** The effect of Ru particle sizes and catalyst preparation method of 5% Ru/CNT on the CO conversion ( $X_{CO}$ ) as a function of reaction temperature. Experimental conditions: mass of catalyst: 1 g; reactant composition: 1% CO, 89% H<sub>2</sub> (balance N<sub>2</sub>); total flow rate: 100 cm<sup>3</sup>/min.

The percentage CO conversion was plotted against the different average particle sizes (see Figure 5.S2). It is seen that at all reaction temperatures, that for CO methanation reaction decreased as the Ru particles size increased.

It should be noted that, besides methane, other higher hydrocarbons were also obtained under the experimental conditions employed for the CO hydrogenation reaction (Figure 5.7). The selectivity towards methane increased with an increase in reaction temperature, implying the formation of higher hydrocarbons were suppressed leaving methane as the only product at temperatures where CO had attained maximum conversions. This trend has been observed by other authors [49-51]. Although, there were only small differences in methane selectivity for all the catalyst, the smaller Ru particles were more selective towards CH<sub>4</sub>. Other analyses

have suggested that larger crystallite have an increased number of coordination sites on the larger Ru crystallite which support higher chain growth [52].

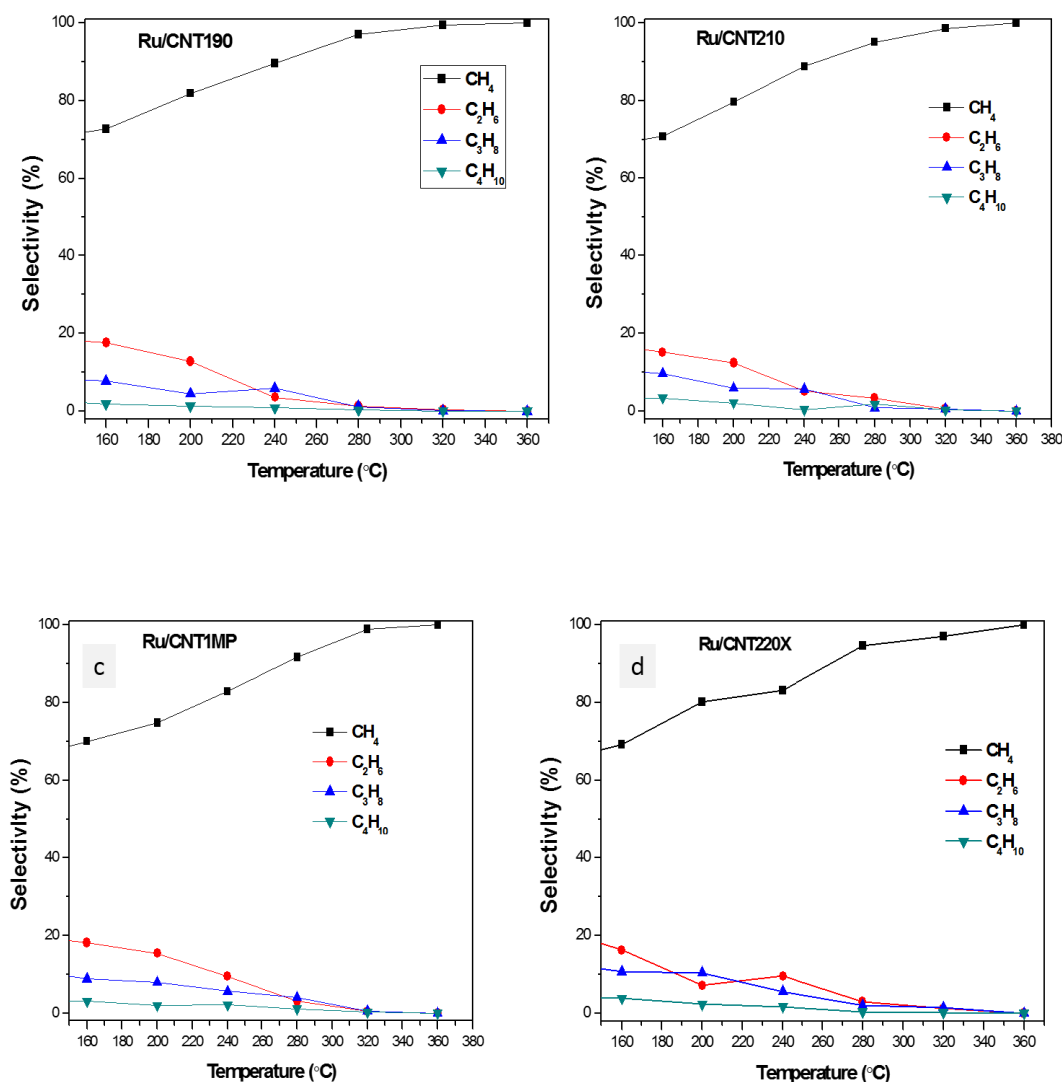


**Figure 5.7.** The effect of reaction temperature on the selectivity of (a) Ru/CNT190 (b) Ru/CNT210 (c) Ru/CNTIMP and (d) Ru/CNT220 catalysts.

### 5.3.4. Selective CO methanation

The catalytic performances of the different catalysts were investigated under conditions of selective methanation of CO in CO/CO<sub>2</sub> (Figure 5.8). It was observed that at 160 °C where significant CO conversion was noted, Ru/CNT190 and Ru/CNT210 converted nearly 25 and 17% CO respectively while the other catalysts showed conversions below 15%. It should be

noted that, all the catalyst attained maximum CO conversion at 280 °C, with Ru/CNT220 having the lowest conversion (at ca. 38%) while the highest was achieved with Ru/CNT190 (at ca. 69%). These results can be attributed to the Ru particle size and the well dispersed Ru particles. A further increase in the temperature gave a rapid decrease in CO conversion. This was more pronounced for the Ru/CNT190 catalyst, where the CO percentage conversion assumed negative conversions at temperatures ca. 340 °C and above. This implies that under the conditions, the reverse water gas shift reaction (RWGS,  $\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$   $\Delta H^\circ_{298} = 41 \text{ kJ/mol}$ , Eq. 5.2) runs parallel to the CO hydrogenation reaction and the RWGS reactions dominates at temperature from 320 °C and above. Here the rate of CO production *via* RWGS reaction exceeds the rate of CO conversion to methane. Thus a higher outlet CO concentration was observed from the reactor. It was also observed that CO<sub>2</sub> methanation was practically inactive for all catalysts  $T < 240 \text{ °C}$  except for Ru/CNT190 which showed a small CO<sub>2</sub> conversion of (ca. 5%). Significant CO<sub>2</sub> conversions initiated after all the catalyst had attained maximum CO conversion (Figure 5.8). This showed that the CO interacted strongly with the surface of the catalyst [3, 53]. The Ru/CNT190 showed higher activity than the other catalyst and this was attributed to the Ru crystallite sizes. Again, it was observed that a very low activity was recorded for Ru/CNT220. Dagle and co-authors reported that, larger crystallite Ru sizes had gave a lower percentage CO conversion than smaller Ru sizes but H<sub>2</sub> consumption indicated CO<sub>2</sub> methanation was between 3-6% for larger Ru, while smaller Ru crystallites gave ~ 4-18% conversions. They explained it that, though the large sizes Ru particles which were poorly dispersed could initiate CO methanation but suppressed CO<sub>2</sub> methanation. This implied smaller Ru crystallites were less selective towards CO. Our results agree with Dagle's and co-authors since the smaller Ru particles showed much higher activity for CO<sub>2</sub> methanation compared to the larger Ru crystallites.

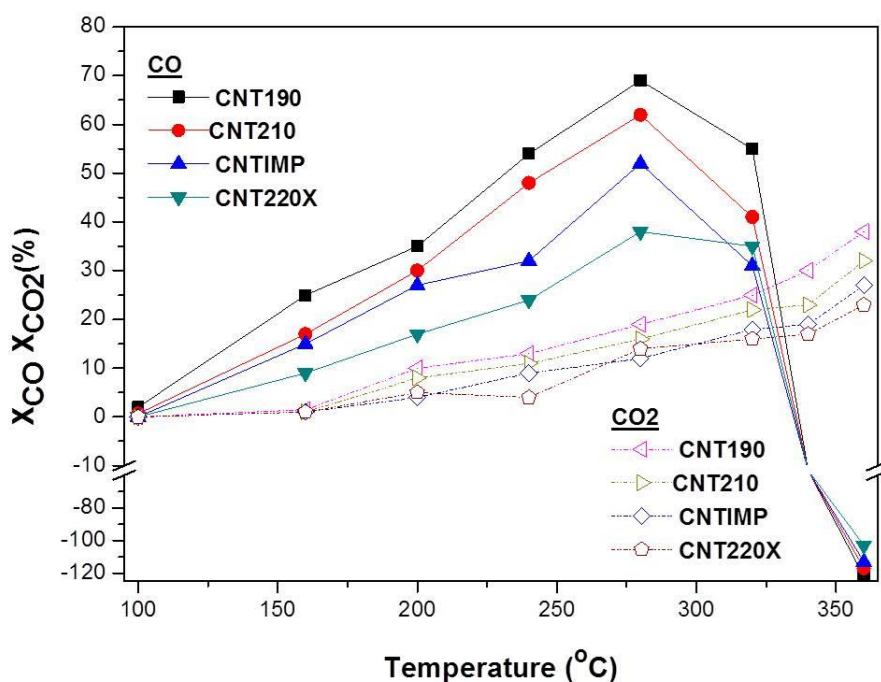


**Figure 5.8.** The effect of Ru particle sizes and catalyst preparation method of Ru/CNT on the selective CO conversions ( $X_{CO}/X_{CO_2}$ ) as function of reaction temperature using 5 wt.% Ru. Experimental conditions: mass of catalyst: 1 g; reactant composition: 1% CO, 89% H<sub>2</sub> (balance N<sub>2</sub>); total flow rate: 100 cm<sup>3</sup>/min.

## 5.4 Conclusions

CNTs were successfully synthesized using chemical vapour deposition and it was applied as catalyst support for Ru catalyst. The CNT-supported Ru nanocrystallite with average sizes ranging from 1.7 to 10.3 nm were prepared by employing microwave polyol synthesis by varying the microwave IR temperature and keeping the power constant. This was efficient way to manipulate particle sizes without heat treating (calcination) at elevated temperature or increasing metal loading to achieve larger crystallite sizes. The Ru synthesized showed a very narrow range with high dispersion as observed in TEM analyses. The catalyst prepared by impregnation showed limited control over the size distribution.

Our studies revealed that both CO and selective CO methanation were structure sensitive reactions. Also smaller Ru crystallite had higher methane selectivity at lower temperatures than the larger Ru crystallites. All the catalysts studied did not attain total CO conversion

when CO<sub>2</sub> was introduced in the gas mixture. Again, the catalysts showed significant promotion of reverse water gas shift reaction.

## 5.6 Supplementary data

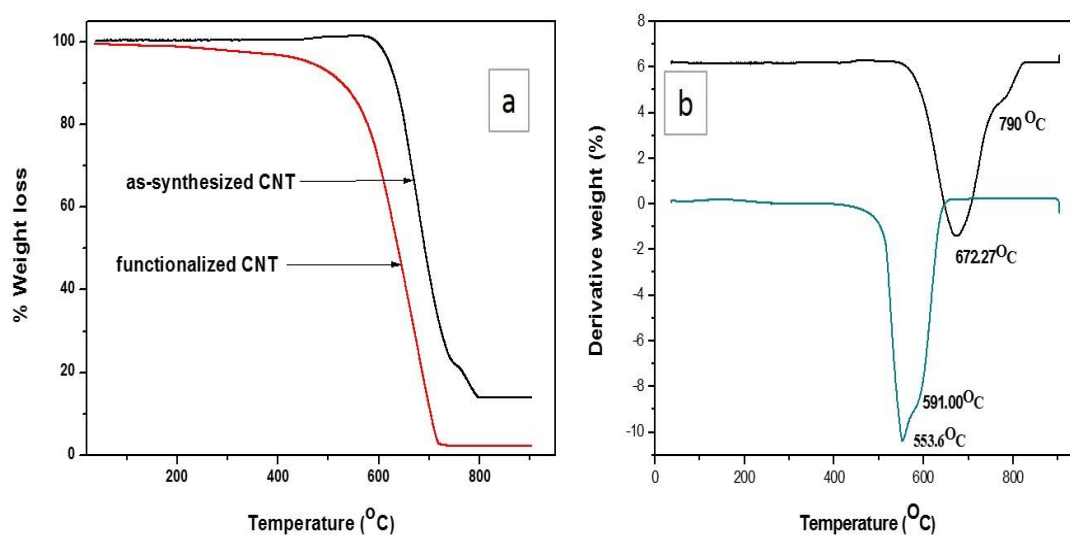


**Figure 5.S1.** TGA and DTG profiles for as-synthesised CNT and purified (functionalised) in 55% HNO<sub>3</sub> CNT.

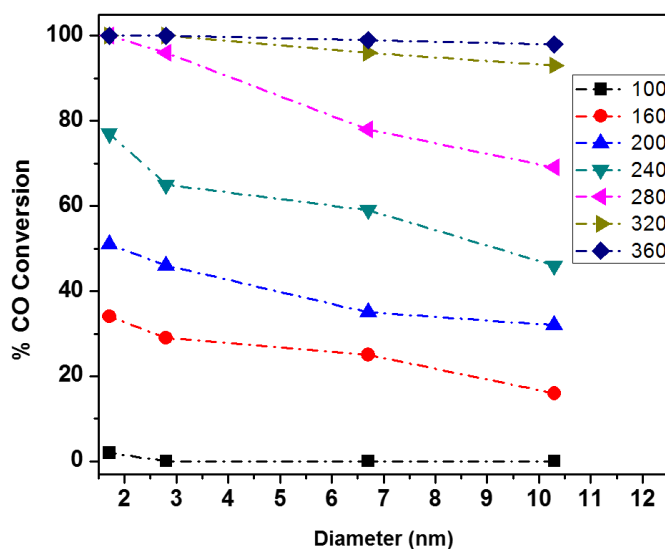


**Figure 5.S2.** The effect of particle size on conversion of CO to methane at different reaction temperatures.

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# Chapter 6

## EFFECT OF A TITANIA COVERING ON CNTS AS SUPPORT FOR THE Ru CATALYSED SELECTIVE CO METHANATION

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### Abstract

One of the major set-backs in the selective CO methanation process, as the final clean-up step in removing residual CO from reformat gas feed, is the reverse water gas shift (RWGS) reactions. This reaction is an undesired reaction because, it runs parallel with the selective CO methanation reaction. This increases the CO outlet concentration. The catalytic performance of ruthenium supported on carbon nanotubes (CNTs), nitrogen doped carbon nanotubes (NCNTs), titania coated carbon nanotubes (NCNT-TiO<sub>2</sub> and CNTs-TiO<sub>2</sub>) and TiO<sub>2</sub> anatase (TiO<sub>2</sub>-A) for selective CO methanation was investigated. The feed composition relevant to reformat gas was used but in the absence of steam. The experiments were conducted within a temperature range of 100 °C and 360 °C. It was observed that carbon dioxide methanation was suppressed until CO methanation attained a maximum conversion for all the catalysts studied. The Ru/NCNT showed higher activity than Ru/CNT at all temperatures examined due to the nitrogen incorporation in the carbon domains. Both Ru/CNT and Ru/NCNT however promoted the RWGS reaction at temperatures above 250 °C. The Ru/CNT-TiO<sub>2</sub> catalyst recorded the highest activity for the both CO and selective CO methanation followed by Ru/TiO<sub>2</sub>-A. The presence of titania on the carbon nanotubes significantly retarded the RWGS reaction from about -120 percentage CO conversion to about 80% CO conversion, while selectivity towards methane increased in all catalysts with increasing temperature.

**Keywords:** Carbon nanotubes; nitrogen dope; TiO<sub>2</sub> coating; CO methanation

## 6.1 Introduction

Numerous efforts to fine tune the proton exchange membrane fuel cell (PEMFC) technology have been reasonably successful, especially as relates to the transportation industry which uses electrical power sources. This would apply to both stationary fuel cell applications and portable fuel cells. One of the major setbacks hindering possible commercialisation of a low temperature PEMFC is the generation of a “nearly-CO-free” gas feed but the current processes use may leave residual quantities of CO in the H<sub>2</sub> rich feed [1]. Hydrogen rich fuels for PEMFCs are obtained by reforming hydrocarbons, e.g. liquefied petroleum and natural gas [1-3]. Trace amounts of CO impurities can deactivate the anode electrode of a PEMFC. For example, the anode electrocatalyst composed of Pt-Ru only tolerates a < 50 ppm CO concentration [4-6], while a Pt anode electrocatalyst can only tolerate concentrations of < 10 ppm [7-9].

Usually, the water gas shift (WGS) reaction is employed in initial process for clean-up when the CO concentration is in the range of 1 - 8%. Thus secondary processes are needed to reduce the CO level to ppm levels after the initial process.

There are several techniques that have been used to reduce CO in a reformat gas feed to lower concentrations, for use in a PEMFC [10]. These include using pressure swing adsorption (PSA), a method that makes use of special adsorptive materials (e.g. zeolites), which are employed as molecular sieves. The preferential CO oxidation (PROX) reaction Equation 6.3 has also been widely studied over the years but today much focus has shifted from PROX to selective CO methanation called SMET (Equation 6.1) as a technique for removal of the final traces of CO in reformat gas feed. This is because SMET can avoid the limitations experienced by PROX such as addition of air from an external source. The CO and CO<sub>2</sub> methanation reactions (as indicated in Equations 6.1 and 6.2) are less exothermic than the CO and H<sub>2</sub> oxidation reactions (Equation 6.3 and 6.4), which makes it inherently easier to control SMET than PROX.





The SMET process is considered as a most promising process to remove CO in a reformat gas stream for PEMFC applications. The key to development in SMET is the design of an efficient catalyst, capable of removing CO, retarding CO<sub>2</sub> and inhibiting the RWGS reaction (Equation 6.5) at a sufficiently low temperature. Otherwise the methanation of carbon dioxide would occur which would then be a major hydrogen-consuming reaction.

A number of catalysts have been tested for this methanation of CO. They include Rh [11-14], Ni [12, 15, 16] and Ru [14, 17, 18]. In the selective CO methanation reaction Ru and Rh are still considered to yield high activities and unlike Pt and Pd do not promote the undesired reverse water gas shift reaction [19]. The nature of the support plays a role in the overall performance of a catalyst and this suggests a strategy to modify the behaviour of SMET catalysts [13, 20, 21].

Recently the use of carbon nanotubes (CNTs) as model catalyst supports for hydrogenation reactions such as the Fischer-Tropsch (FT) reaction has increased. CNTs have become attractive due a number of advantages they possess such as facile modification of their surface properties, good hydrothermal stability and above all, their moderate interaction with the active metal [22]. The impressive mechanical nature of carbon supports and the absence of micro-porosity, which reduces intraparticle mass transfer in reaction media, as well as the easy accessibility of the active metal phases makes the CNT an excellent catalyst support.

Carbon supports do however have a very low density which is a problem in terms of using the CNTs in commercial reactors. Other types of supports, for example the metal oxides such as TiO<sub>2</sub>, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> can be used but they suffer from strong metal support interactions and even the formation of mixed metal compounds in some cases or spinel. Carbon does not experience spinel or possibly no strong metal support interactions.

Combining carbon and titania, could improve or merge the properties of both the carbon and oxide supports. The photocatalytic abilities of TiO<sub>2</sub> are known to be enhanced by doping or coating titania with carbon. The position that carbon occupies in a TiO<sub>2</sub> matrix will determine its effect on the carbon [23]. Since the density of carbon materials is enhanced by coating carbon with TiO<sub>2</sub> (or vice versa) [24] these methodologies suggests a process for increasing the catalyst /support density when C is used in the support.

In this paper we report on the enhanced catalytic activity and suppression of the RWGS reaction using Ru as the active metal phase supported on TiO<sub>2</sub> coated CNTs. A simple hydrothermal route was employed to coat the CNTs with TiO<sub>2</sub>.

## 6.2 Experimental

### 6.2.1. The synthesis of CNTs

CNTs and nitrogen doped CNTs (N-CNTs) were synthesized by using the chemical vapour deposition (CVD) technique [25]. The CNTs and N-CNTs were grown using a 5%Fe-5%Co/CaCO<sub>3</sub> catalyst [25, 26]. About 1 g catalyst was placed in a quartz boat and placed in the middle of a quartz tube in a furnace. The furnace was heated to 700 °C at a rate of 10 °C per minute under a nitrogen flow rate of 240 ml/min. Once the reaction temperature was attained, acetylene gas was introduced into the reaction chamber at a flow rate of 90 ml/min. The reaction was then allowed to continue for 1 h. After the reaction, the acetylene gas flow was stopped and the reactor was allowed to cool to room temperature under a flow of nitrogen gas. For the N-CNT synthesis, acetylene was bubbled through acetonitrile (acetonitrile the source of nitrogen) [26], and the CH<sub>3</sub>CN/C<sub>2</sub>H<sub>2</sub> introduced into the CVD reactor.

The CNTs were washed with 55% HNO<sub>3</sub> to remove both residues of the catalyst and to functionalise the CNTs at the same time. To do this, a concentrated solution of 55% HNO<sub>3</sub> was added to the as-synthesised CNTs or the N-CNTs in a round bottom flask. The mixture was then refluxed at 110 °C for a period of 12 h. The residue was washed with a large amount of deionised water till the solution had a neutral pH. The CNTs were collected by filtration and then dried overnight in an oven at 100 °C.

### 6.2.2. Synthesis of CNT-TiO<sub>2</sub> composites and TiO<sub>2</sub> anatase

CNT-TiO<sub>2</sub> was synthesized by modifying the procedure used by Yan *et al.* [27]. In a typical synthesis, 1.0 g of CNTs were dispersed in 30 ml of butanol and sonicated for 30 min. Titanium butoxide was dissolved separately in 10 mL butanol, sonicated for 20 min and then added drop-wise to the functionalised CNTs while stirring at a temperature of 30 °C. Diethylamine (0.6 ml) was added dropwise to the above mixture which was stirred for 10

min at room temperature to catalyse Ti-O-Ti formation reactions. The mixture was then transferred into a Teflon lined autoclave and the reaction was carried out at 150 °C for 14 h. The product was centrifuged, washed several times with ethanol followed by water and then calcined at 250 °C for 4 h under nitrogen. The same procedure was repeated without any CNTs to synthesise titania with an anatase polymorph. This support was denoted as TiO<sub>2</sub>-A.

#### 6.2.3. Preparation of the catalyst by wet impregnation

The catalysts were prepared by using RuCl<sub>3</sub> as metal precursor. Approximately 1.74 mL of RuCl<sub>3</sub> solution was dissolved in 10 mL of deionised water and then sonicated for 15 minutes. The RuCl<sub>3</sub> solution was then added drop-wise into a beaker containing 1 g of the support (CNT, N-CNT, TiO<sub>2</sub> or CNT-TiO<sub>2</sub>). The thick paste formed was dried in an oven overnight and then calcined at 250 °C for 3 h to remove unwanted residues.

#### 6.2.4. Catalyst activity studies

Catalyst performance was tested in a fixed-bed tubular reactor (FBTR) of height 250 mm and an internal diameter of 16 mm. The reaction was carried out at atmospheric pressure. The temperature of the reaction was measured in the catalyst bed using a K-type thermocouple. For each run, 1 g of the catalyst was weighed and placed in a reactor. Prior to the reactions, the catalyst was reduced at 250 °C for 4 hours at 1 bar pressure under 99.995% H<sub>2</sub> gas. The various reactions (CO methanation, CO<sub>2</sub> methanation and selective CO methanation in the presence of CO<sub>2</sub>) were investigated in the temperature range 160 – 360 °C using a gas feed with composition of 1% CO, 20% CO<sub>2</sub>, 10% N<sub>2</sub> and H<sub>2</sub> balance. A flow rate of 90 ml/min was used to feed the gas feed to the reactor. Online GCs were connected to the FBTR to monitor the reaction. Both a flame ionization detector (FID) and a thermal conductivity detector (TCD) were used.

#### 6.2.5. Characterization

The surface areas of all the catalysts and supports were analysed by BET using N<sub>2</sub> physisorption (Micromeritics ASAP-2000 Tri-star analyser). Before the surface area analysis, 0.2 g of the sample was degassed for 6 h at 150 °C under a N<sub>2</sub> flow using a

Micromeritics flow Prep 060. The weight losses of the carbon samples were monitored on a Perkin-Elmer STA6000 TG/DTA Thermogravimetric analyser. The analyses were performed in air at a heating rate of 10 °C/min. Powder X-ray diffraction (XRD) studies were done on a Siemens D2 diffractometer using Co K $\alpha$  radiation equipped with a Ni filter. Steps of 0.02° with a scan range of 10-90° were used. The morphologies of the samples were identified using SEM (FEI Nova Nanolab 600) and TEM (Tecnai T12) images. TEM samples were prepared by dissolving the catalyst in ethanol followed by sonication for 2 min. A drop of the ethanol suspension was transferred to a copper grid and dried. The disorder in the carbon based supports was measured with a micro-Raman attachment of a Jobin-Yvon T64000 Raman spectrometer. The excitation wavelength used was 514.5 nm from an Ar ion laser and the spot size on the sample was ca. 1.5  $\mu$  in diameter.

## 6.3 Results and discussion

### 6.3.1. Support characterization

#### 6.3.1.1. TEM and SEM analysis

TEM analysis was used to elucidate the structural and morphological features of the different supports. From the images (both SEM and TEM) shown in Figure 6.1, the expected tubular structure for the CNTs and N-CNTs was observed. Incorporation of nitrogen in the CNT's is usually characterized by the presence of bamboo like structures, which are typically seen as a series of compartments inside the tube. The TEM insert of Figure 6.1a shows this structure. Both CNTs and N-CNTs were identified to be multi-walled. Their diameters were found to be in the range of 40 – 70 nm and 30 - 80 nm for CNTs and N-CNTs respectively. Analysis carried out to quantify the nitrogen content present in the N-CNTs was found to be 3.7% by mass using CHNS analysis. This was confirmed with the presence of the bamboo structure seen in the TEM image. Figure 6.1c shows the SEM and TEM images of the CNTs coated with TiO<sub>2</sub>. A closer view of the TEM image (insert in Figure 6.1c; higher resolution image) showed that the coverage of the TiO<sub>2</sub> was not complete on the CNTs. There were some regions with little coating and other regions where the titania nanoparticles formed aggregates along the length of a carbon nanotube. The anatase coating on N-CNT (NCNT-TiO<sub>2</sub>) produced smaller TiO<sub>2</sub> particles and these covered the NCNTs (Figure 6.S1) more than observed for the CNT-TiO<sub>2</sub> sample. This could be due to the presence of surface nitrogen.

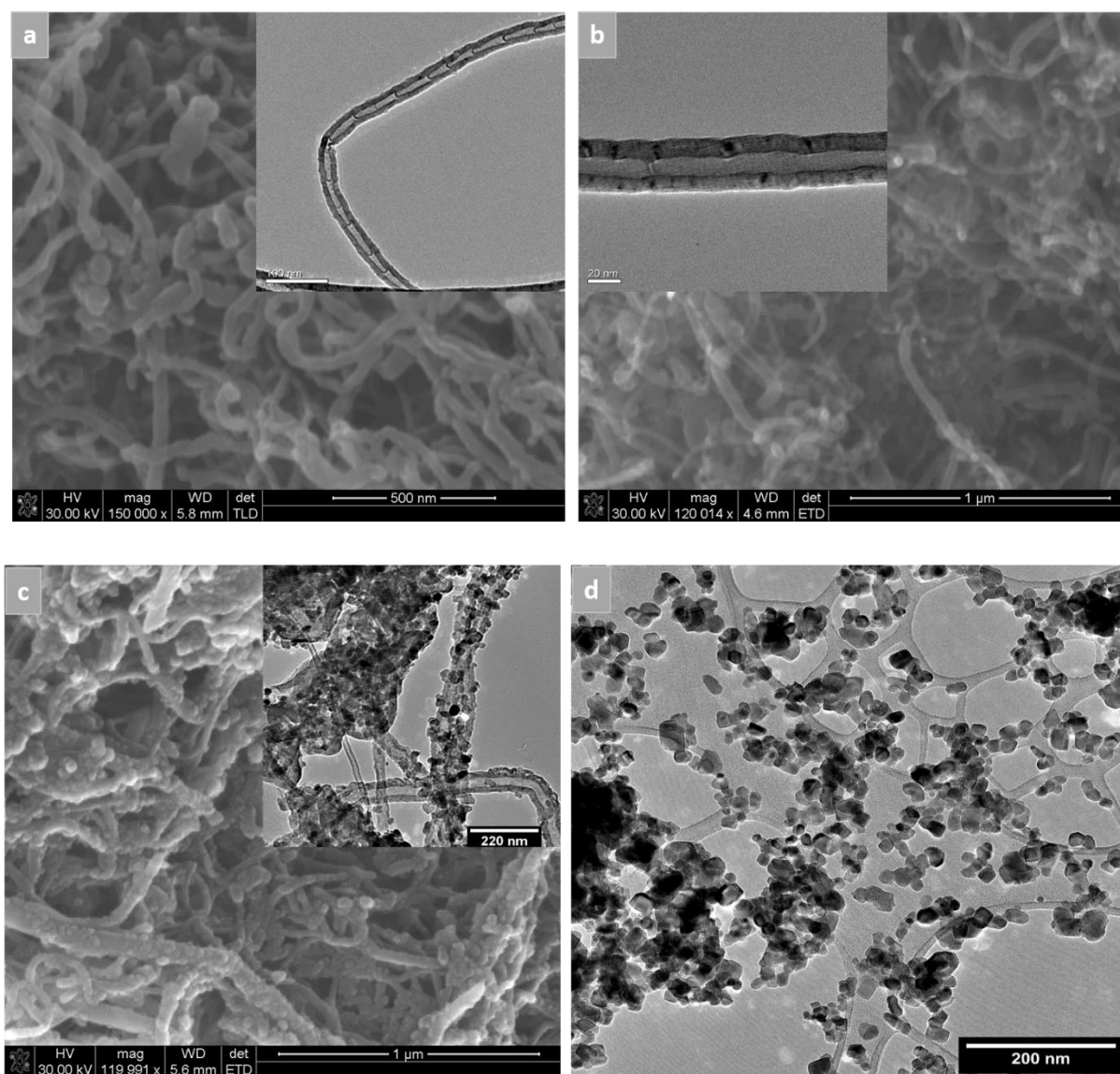


**Figure 6.1.** Images of the different supports synthesised: (a) SEM and TEM image of N-CNTs, (b) SEM and TEM image of CNTs, (c) SEM and TEM image of CNT-TiO<sub>2</sub> and (d) TEM image of TiO<sub>2</sub>.

Table 6.1. Physiochemical properties of the supports and Ru catalysts.

|                                       | Sample |      |                      |                        |                  |
|---------------------------------------|--------|------|----------------------|------------------------|------------------|
|                                       | CNT    | NCNT | CNT-TiO <sub>2</sub> | N-CNT-TiO <sub>2</sub> | TiO <sub>2</sub> |
| <b>Support</b>                        |        |      |                      |                        |                  |
| BET surface area (m <sup>2</sup> /g)  | 75     | 91   | 119                  | 121                    | 52               |
| Pore volume area (cm <sup>3</sup> /g) | 0.22   | 0.31 | 0.38                 | 0.29                   | 0.21             |
| D-band (cm <sup>-1</sup> )            | 1344   | 1357 | -                    | -                      | -                |
| G-band (cm <sup>-1</sup> )            | 1571   | 1583 | -                    | -                      | -                |
| I <sub>D</sub> /I <sub>G</sub> ratio  | 0.70   | 0.85 | -                    | -                      | -                |
| Decomposition Temperature (°C)        | 591    | 433  | 615                  | 514                    | -                |
| <b>Catalyst</b>                       |        |      |                      |                        |                  |
| BET surface area (m <sup>2</sup> /g)  | 66     | 71   | 108                  | 116                    | 41               |
| Pore volume area (cm <sup>3</sup> /g) | 0.25   | 0.41 | 0.35                 | 0.31                   | 0.23             |
| d <sub>RuO<sub>2</sub>TEM</sub>       | 6.4    | 3.8  | 2.3                  | -                      | 3.6              |
| d <sub>RuO<sub>2</sub>XRD</sub>       | 7.9    | 4.6  | -                    | -                      | 4.2              |
| Ru dispersion (%)                     | 23     | 38   | 52                   | 50                     | 38               |

### 6.3.1.2. Raman spectral analysis

Raman spectroscopy was used to determine the crystallinity and information on the defects in the synthesised CNTs and N-CNTs. Two main characteristic peaks are associated with carbonaceous materials. These peaks are the D-band (approximately 1350-1360 cm<sup>-1</sup>) which identifies with the defects, while the G-band (1590-1600 cm<sup>-1</sup>) corresponds to the C-C bond

stretching mode in the graphite plane. The area ratio of the G- to D-bands ( $I_D/I_G$ ) gives an idea of the extent of defects in the carbon material. A high ratio suggests high levels of defects [28]. The Raman spectrum (Figure 6.2) showed that nitrogen incorporation into the CNTs increased the defect concentration as seen by the increased  $I_D/I_G$  ratio (Table 6.1). The broadening of the D and G-bands coupled with a slight shift to higher wave numbers again confirmed an increased defect concentration in the N-CNTs [29]. Usually, defects result in the creation of anchorage sites for nano metal particles which serve as the active species in catalysis.

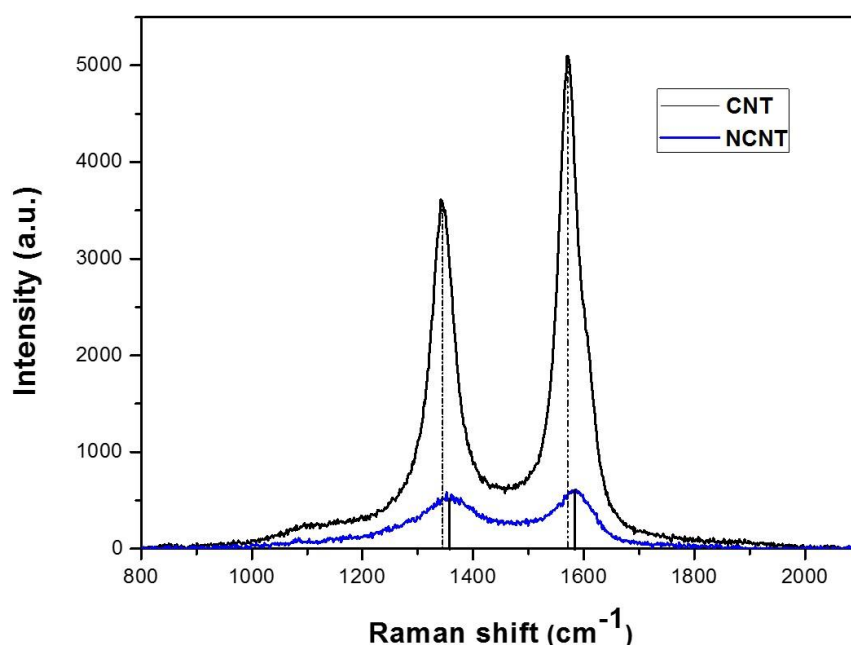


**Figure 6.2.** Raman spectra of the in CNTs and N-CNTs.

### 6.3.1.3 PXRD analysis

The crystalline phases in the support materials were identified by PXRD. As shown in Figure 6.3, graphite carbon peaks at  $2\theta$  angles of ca.  $31^\circ$  were present in all the carbon containing supports (N-CNTs not shown). The diffraction patterns for the hydrothermally produced  $\text{TiO}_2$  and the  $\text{TiO}_2$  coated CNTs (NCNT- $\text{TiO}_2$  similar to the CNT- $\text{TiO}_2$ ) corresponded to the anatase polymorph of  $\text{TiO}_2$ . The peaks obtained were similarly sharper as the pure anatase which indicates that the titania and carbon nanotubes were crystalline.

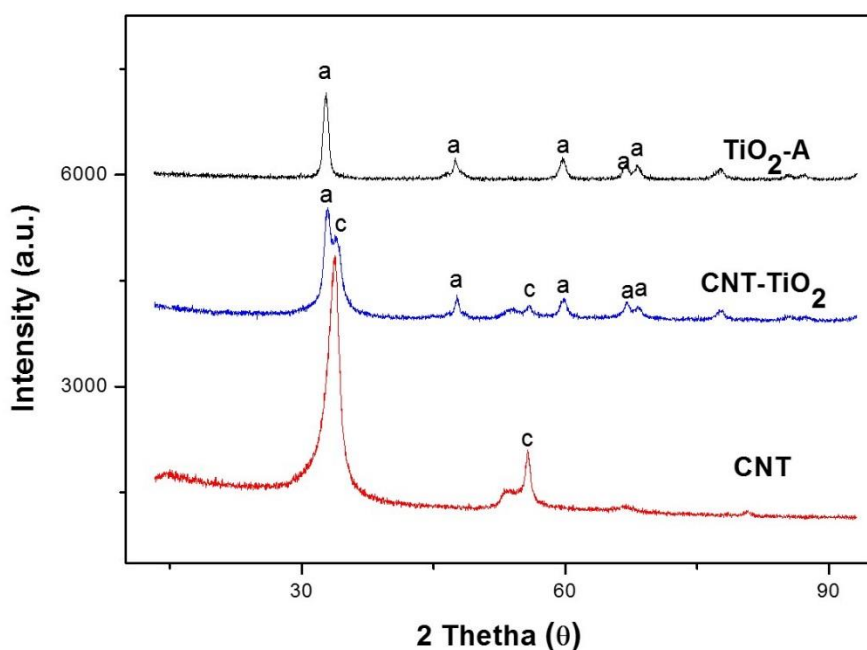


**Figure 6.3.** PXRD pattern of supports: CNT, CNT-TiO<sub>2</sub> and TiO<sub>2</sub>-A.

#### 6.3.1.4. Thermogravimetric analysis (TGA)

The TGA plots in Figure 6.4 allows for the determination of the percentage purity and the thermal stability of the CNTs, N-CNTs and the coated CNTs. The TGA plots of the unpurified samples (as-synthesised CNTs and N-CNTs) are shown in Figure 6.S2. It is noted that the HNO<sub>3</sub> acid treatment was effective in removing the bulk of the residue of the Fe and Co catalyst. The functionalization process significantly removed impurities (residue from catalyst) from about 30% < 1.5% and from 45% to < 2% for CNTs and N-CNTs respectively (Figure 6.S2). There were no weight loss registered below 400 °C which suggested that there was no amorphous carbon present [30, 31]. The N-CNTs decomposed below 500 °C i.e. about 100 °C less than the CNTs. This is also an indication that presence of defects present in the carbon framework reducing the thermal stability of the carbon.

The TGA results also showed a small weight loss in the low temperature region of Figure 6.4; this is due to the decomposition of butanol, diethylamine or other residual organic materials that were adsorbed onto/into the CNTs. The maximum decomposition temperature for the CNT-TiO<sub>2</sub> was around 631°C, relatively higher than that for the CNTs. The TGA data indicated that about 25 % of the CNT-TiO<sub>2</sub> was composed of TiO<sub>2</sub> (Figure 6.S2). The

improvement in the thermal stability was as a result of the  $\text{TiO}_2$  covering which shielded the carbon from oxidation.

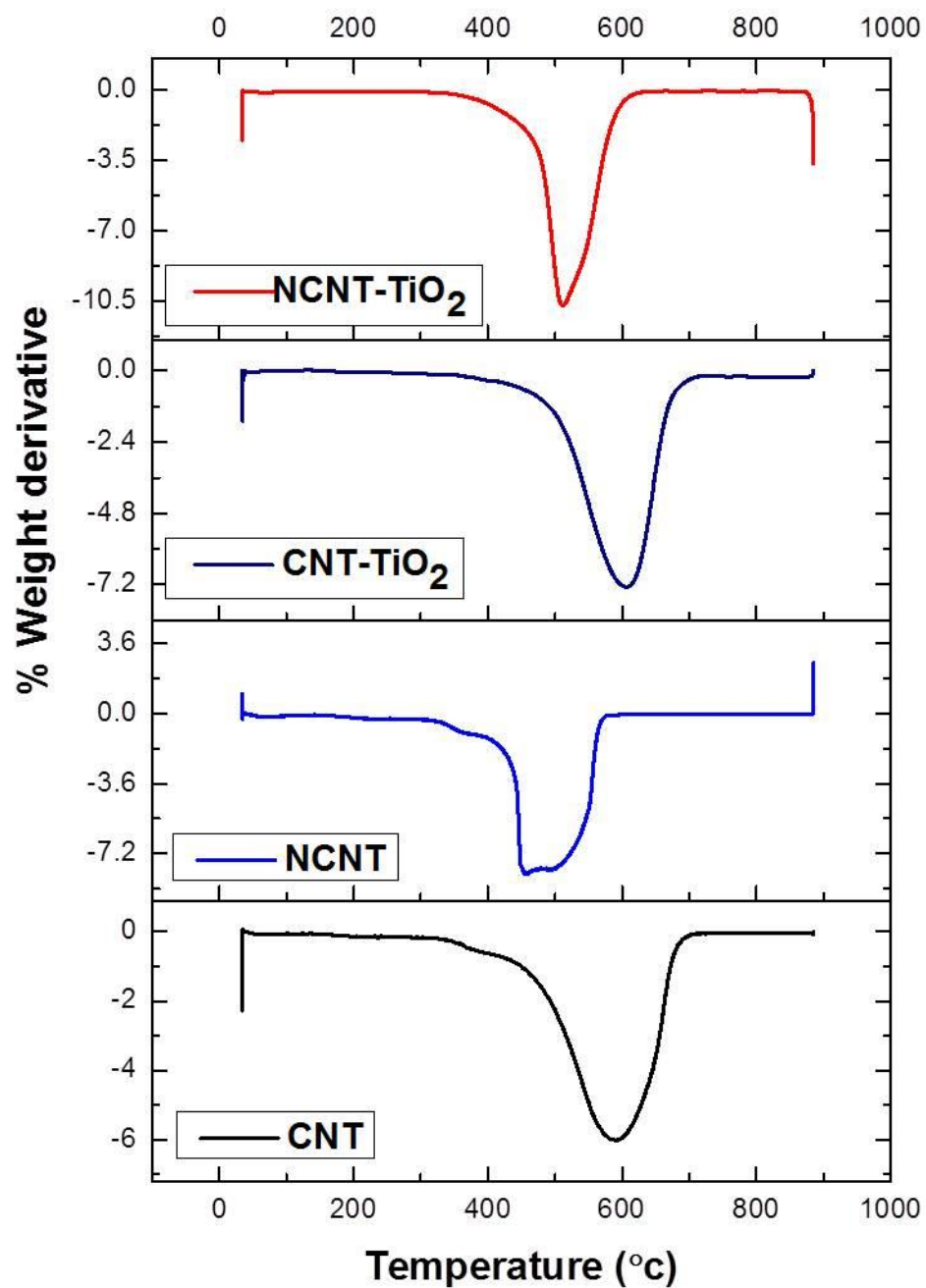


**Figure 6.4.** TGA derivative profile showing CNT, NCNT, NCNT-TiO<sub>2</sub> and CNT-TiO<sub>2</sub>.

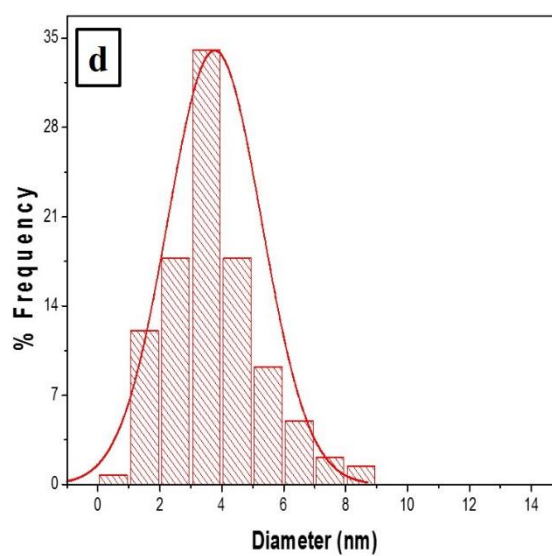
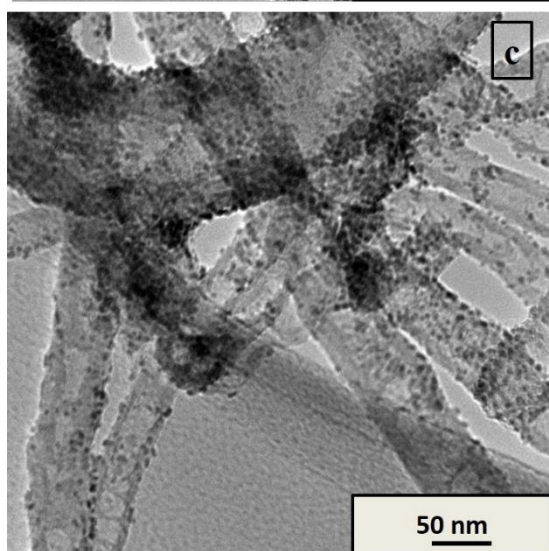
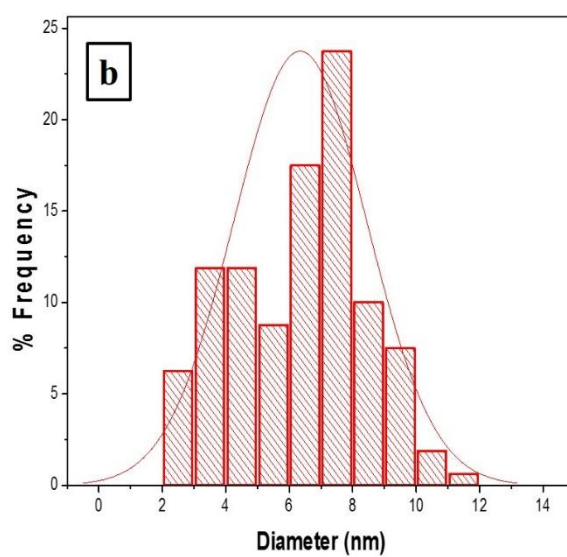
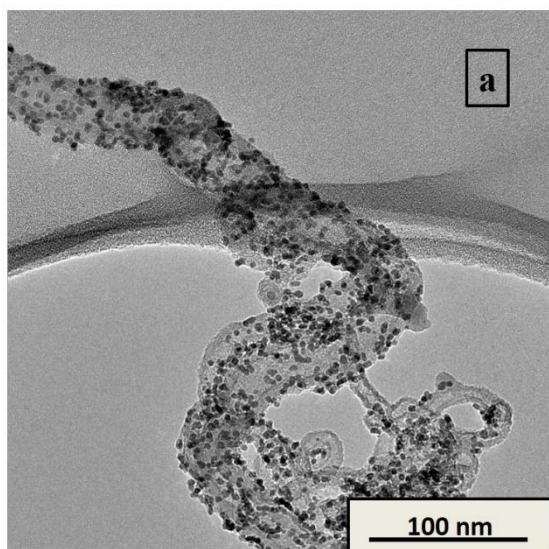
#### 6.3.1.5 $N_2$ adsorption studies

The surface area and porous structure of materials were determined using the nitrogen adsorption technique [32]. Introduction of nitrogen into the carbon matrix increased the surface area and increased the pore volume of the CNTs. This was attributed to both the functionalization process and the doping [25, 29]. The hydrothermally produced anatase  $TiO_2$  had the lowest surface area ( $52\text{ m}^2/\text{g}$ ) which correlated with literature data. Combining CNT with  $TiO_2$  to form a CNT- $TiO_2$  composite significantly improved the surface area (from 75 and 52 to  $119\text{ m}^2/\text{g}$ ).

### 6.3.2 Catalyst characterization

#### 6.3.2.1 TEM analysis on the catalyst

TEM images of the various catalysts prepared and studied are presented in Figure 6.5. The darker spots observed in all the TEM images are due to  $RuO_2$  nano particles. The average  $RuO_2$  particle size distribution calculated from the TEM images are shown in the size distribution plots. The  $RuO_2$  particles on the CNT were observed to have an average size of 6.4 nm and to have a wider size distribution range compared to the other catalysts (Figure 6.5b). The  $RuO_2$  particle sizes on the N-CNTs were smaller with an average size of 3.8 nm (Table 6.1) with a relatively narrower size distribution (Figure 6.5d). The presence of the nitrogen enhanced anchoring of the  $RuO_2$  particles [33]. The Ru supported CNT- $TiO_2$  particles were smaller (2.3 nm) than those found on the pure anatase  $TiO_2$  support which also had fairly small  $RuO_2$  particles (3.6 nm). This was probably due to the synergetic effect offered by the CNT- $TiO_2$  composite and the larger surface area. The Ru particles were distributed on both  $TiO_2$  and the CNT surfaces as show in the TEM images.



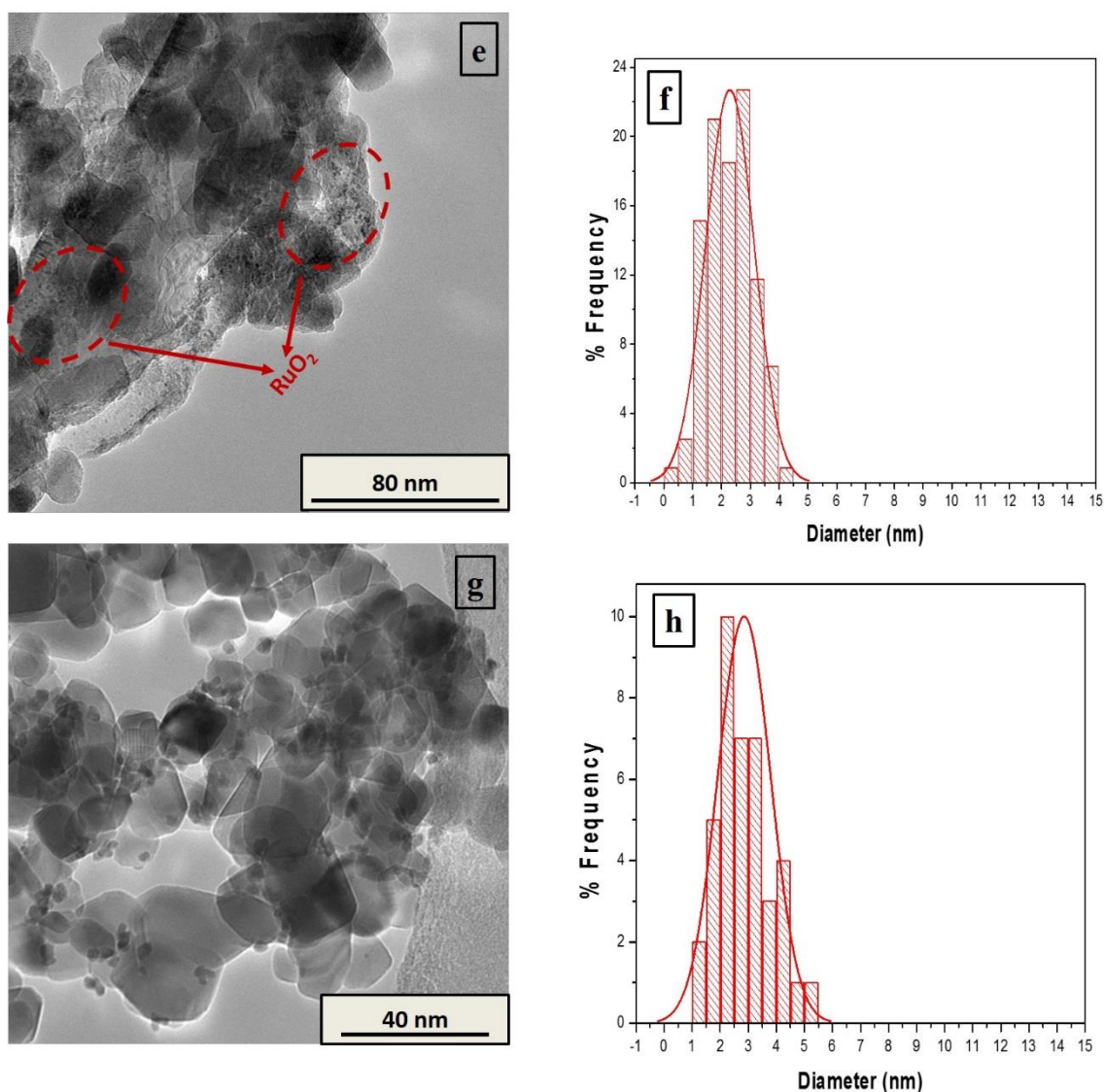


**Figure 6.5.** Representative images showing RuO<sub>2</sub> particles (and their size distribution) dispersed on the different supports: (a) TEM image of 5%Ru/CNT, (b) particle size distribution diagram for 5%Ru/CNT (c) TEM image of 5%Ru/N-CNT, (d) particle size distribution diagram for 5%Ru/N-CNT (e) TEM image of 5%Ru/CNT-TiO<sub>2</sub> and (f) particle size distribution diagram for 5%Ru/CNT-TiO<sub>2</sub> (g) TEM image of 5%Ru/TiO<sub>2</sub> (h) particle size distribution diagram for 5%Ru/TiO<sub>2</sub>.

#### 6.3.2.2. BET analysis on the catalyst

The surface areas of the catalysts decreased compared to the supports (Table 6.1). This was due to the occupation of the pores of the supports by Ru, particles. The pore volume

increased slightly due to occupation of smaller pores after loading of the Ru except for the 5%Ru/CNT-TiO<sub>2</sub> sample [34].

### 6.3.2.3. PXRD analysis on the catalyst

The phases present in the Ru catalysts on the support were investigated by XRD and are presented in Figure 6.6. The peaks observed at 32.5° and 40.8° 2 $\theta$  were indexed to RuO<sub>2</sub> (110) and (101) planes respectively. No peaks for Ru were observed on 5%Ru/CNT-TiO<sub>2</sub> and 5%Ru/NCNT-TiO<sub>2</sub> (Figure 6.S2). This was due to the small undetected RuO<sub>2</sub> particles which were well dispersed as observed on the TEM analysis and also the difficulty of observing Ru on TiO<sub>2</sub>. The RuO<sub>2</sub> peaks observed on the CNT sample indicated larger particle sizes (7.9 nm from XRD, Table 6.1). The RuO<sub>2</sub> peaks for 5%Ru/N-CNTs and 5%Ru/TiO<sub>2</sub>-A were almost similar (broad and less intense) which confirmed the relatively smaller particles observed by TEM analysis.

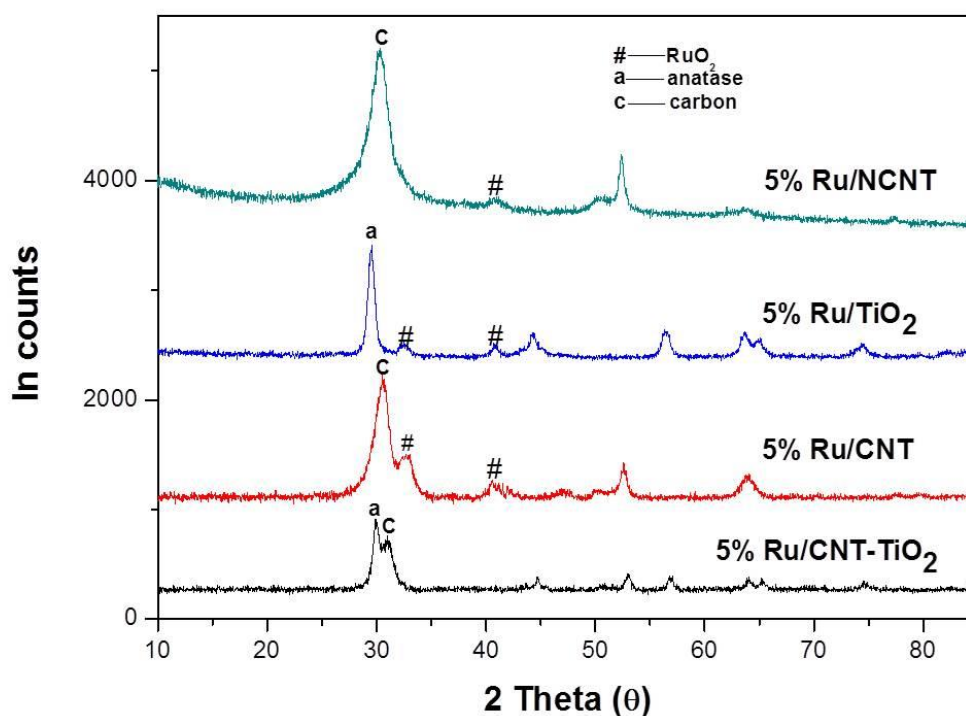


**Figure 6.6.** PXRD patterns of the catalysts showing the RuO<sub>2</sub> crystalline phases.

#### 6.3.2.4. TPR studies

The reduction profiles of the different catalysts are shown in the H<sub>2</sub>-TPR plots in Figure 6.7. Reduction of RuO<sub>2</sub> to Ru for all the catalyst occurred below 200 °C. The reduction profile for the carbon and titania composite revealed maximum broad reduction peaks at elevated temperatures 163 °C and 174 °C Ru/CNT-TiO<sub>2</sub> and Ru/N-CNT-TiO<sub>2</sub> respectively. This suggested Ru particles were dispersed on both the CNTs and TiO<sub>2</sub> components of the composites as observed in the TEM images. The broadness was attributed to RuO<sub>2</sub> reduction on the different support (carbon and titania supports). The RuO<sub>2</sub> particles were believed to have interacted slightly more strongly with the functional groups present on the carbon supports. This was revealed by the reduction RuO<sub>2</sub> to Ru occurring at relatively higher temperature compared to TiO<sub>2</sub>-A supported catalyst. Reduction on the N-CNTs (RuO<sub>2</sub> to Ru) occurred at slightly higher temperature than the RuO<sub>2</sub> on CNTs. This could be due to the extra lone pair of electron made available by the surface nitrogen (pyridinic nitrogen) which formed a stronger bond with the RuO<sub>2</sub> i.e. the nitrogen on the surface provided strong anchorage to Ru particles. Surprisingly, the RuO<sub>2</sub> supported on the TiO<sub>2</sub>-A reduced at unexpectedly lower temperature (113 °C) than both CNT and N-CNTs supports. To confirm this reduction observed on the anatase TiO<sub>2</sub>, a series of anatase supports were synthesised using a sol gel method and a resin gel method and used as a Ru catalyst support. Their reduction profiles were compared to Degussa P25 TiO<sub>2</sub> Ru supported catalyst as shown in the Figure 6.S3. This may suggest that the CNTs and N-CNTs binds the Ru particles firmly through the functional groups or alternatively, the density (catalyst bed height) of the Ru/CNT and Ru/N-CNT contributed in a longer interaction of the hydrogen (reducing gas) which resulted in the shift in RuO<sub>2</sub> reduction peaks. This possibly affected the composite graphs. Further studies should be conducted (as stated in the recommendations) on TPR to clarify this.

The methanation or gasification of the carbon support was the reason assigned to the peaks occurring at higher temperatures. This peak was absent on the Ru/TiO<sub>2</sub>-A profile.

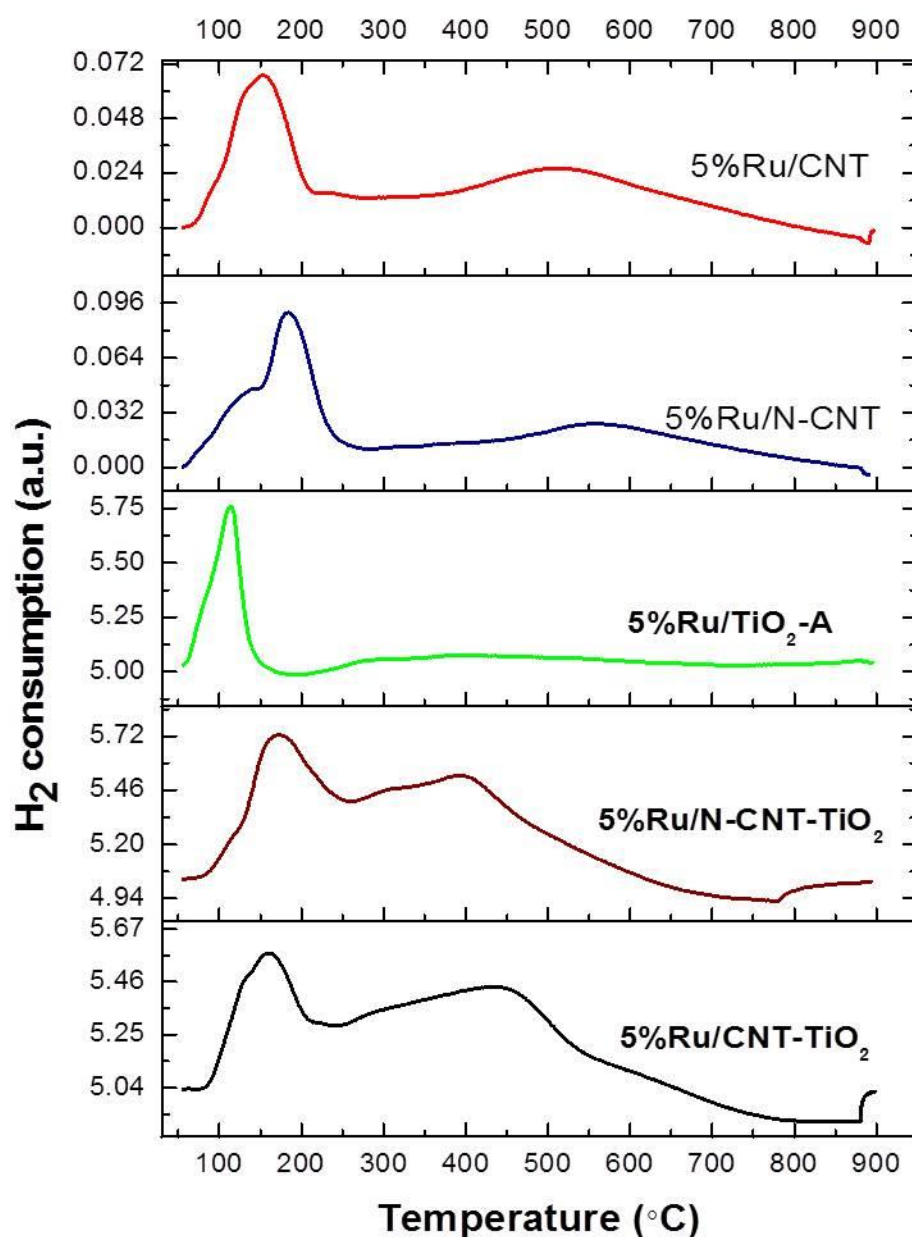


**Figure 6.7.** H<sub>2</sub>-TPR for the different catalyst.

#### 6.4 CO hydrogenation

The activity and selectivity performance of the different supports (CNTs, NCNT, CNT-TiO<sub>2</sub> and TiO<sub>2</sub>-A) for CO hydrogenation over Ru catalyst with performed with the same Ru loading (5 wt.%). The reactions were performed using CO or CO/CO<sub>2</sub> to study methanation and selective CO methanation conversion in the presence of CO<sub>2</sub>. Figure 6.8 summarizes the conversion data when only CO was used. Above ca.140°C, all the catalysts investigated

showed a steady increase in CO conversion (Figure 6.8) and all attained 100% conversion at temperatures beyond 280 °C. The N-CNT Ru supported catalyst showed a higher activity than observed when CNT was used as a support. This was attributed to the presence of pyridinic nitrogen with an extra lone pair of electron which contributed extra electrons making the surface of the tubes more electronegative. This resulted in increased nucleation sites which served as anchorage sites thereby enhancing dispersion of the active phase while restricting the Ru particle sizes [33]. Again, the extra electrons due to the incorporation of nitrogen atom increased the electron density around the Ru and the electrons were then back donated from Ru d-orbitals to a  $\pi^*$  antibonding molecular orbital of CO. This strengthened the Ru-C bonds (back bonding) weakening the C-O bonding, promoting the dissociation of CO and increasing the methanation of CO with Ru/N-CNT over Ru/CNT [35]. It should be noted that, titania coating on the carbon nanotube as support exhibited the highest activity, performing better than Ru/TiO<sub>2</sub>-A. This was due to the higher specific surface area of the coated support and the smaller particle sizes of the Ru.

Anatase on its own has a high surface energy which tends to facilitate agglomeration of metal particles supported on it [36-38]. Defects on titania surfaces (Ti<sup>3+</sup> are related to anionic oxygen) which are known to be stabilize of metallic species from agglomerating [37], These Ti<sup>3+</sup> surface defects are mostly associated with anatase-rutile transformation but Kongkiat et al. [39] reported they could modify the surface structure (Ti<sup>3+</sup> defects) of anatase by using varying oxygen content in their calcination process under temperatures below the anatase-rutile transformation [39]. These defects could have been introduced on the surface of our coated CNTs due to the presence of oxygen (made available through functionalizing the CNTs) present during the synthesis or calcination process. Alternatively, the small Ru particles found on the coated support may have resulted from synergetic effects between the CNT-TiO<sub>2</sub> which is believed to have improved the specific surface area. The NCNT-TiO<sub>2</sub> performed slightly better than the CNT-TiO<sub>2</sub> composite. It can be concluded that the activity of CO hydrogenation is dependent on the type of support used in our experiments.

In spite of the small surface area recorded for the TiO<sub>2</sub>-A support, the Ru catalyst showed much higher activity than the Ru/NCNT and Ru/CNT catalysts. Besides the presence of anionic vacancies that are present at the edges of the oxide-metal boundaries on the TiO<sub>2</sub>, a complex is formed between the oxygen groups on the TiO<sub>2</sub> and the adsorbed CO [40]. Sachler and Ichikawa and co-authors suggested that the Lewis acid/base bonding interaction that occurs between the adsorbed CO and oxygen end and a promoter influence at the

oxide/active metal interface [41, 42]. These effects are said to enhance the cleavage of the C-O bond which results in higher activity for TiO<sub>2</sub>.

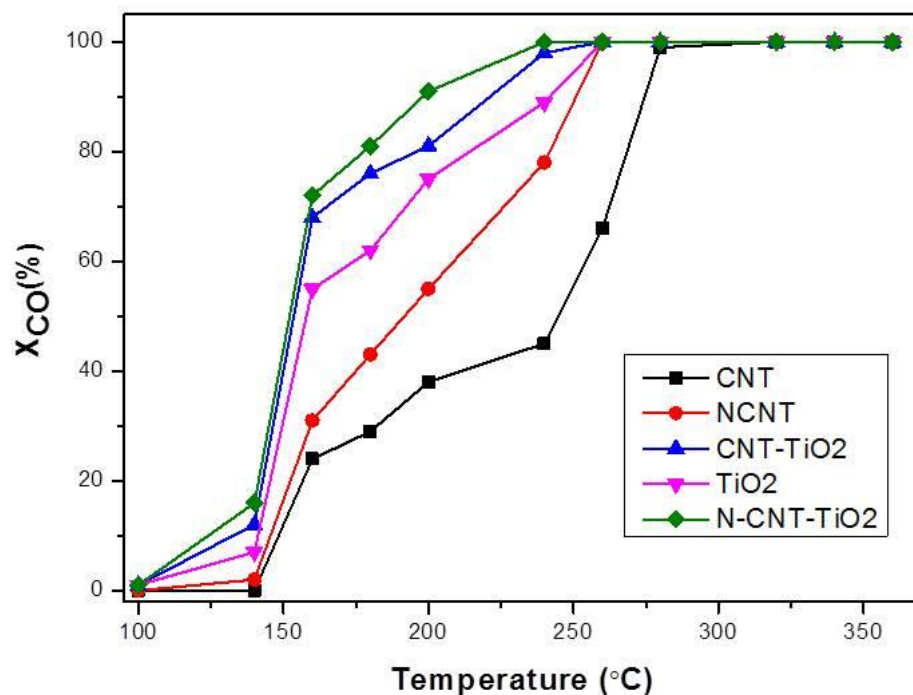


**Figure 6.8.** The effect of the support on the catalytic performance of the CO conversions ( $X_{CO}$ ) as function of reaction temperature using 5% wt.% Ru supported catalyst. Experimental conditions: mass of catalyst: 1 g; reactant composition: (a) 1% CO, 10% N<sub>2</sub> (balance H<sub>2</sub>); total flow rate: 90 cm<sup>3</sup>/min.

## 6.5 CO<sub>2</sub> hydrogenation

The hydrogenation of CO<sub>2</sub> was initiated above ca 150 °C as shown in Figure 6.9. Conversion remained below 20% until 325 °C for all catalyst except Ru/CNT. It should be noted that no significant conversion occurred within the temperature window in which our catalysts were tested. This means significant methanation of CO<sub>2</sub> (above 50% conversion) may only occur at higher temperatures. The supports 5%Ru/CNT and 5%Ru/N-CNT had higher activity than the other catalysts, and suggested the supports had effects on the CO<sub>2</sub> conversion. Several studies acknowledge that CO<sub>2</sub> mostly adsorbs on the supports while hydrogen is adsorbed on the metal to produce methane. The presence of OH groups could have contributed to the

higher activity of the functionalized carbon supports [43]. The 5%Ru/CNT was slightly more active than 5%Ru/N-CNT, which could mean particle size played a role in the reaction.

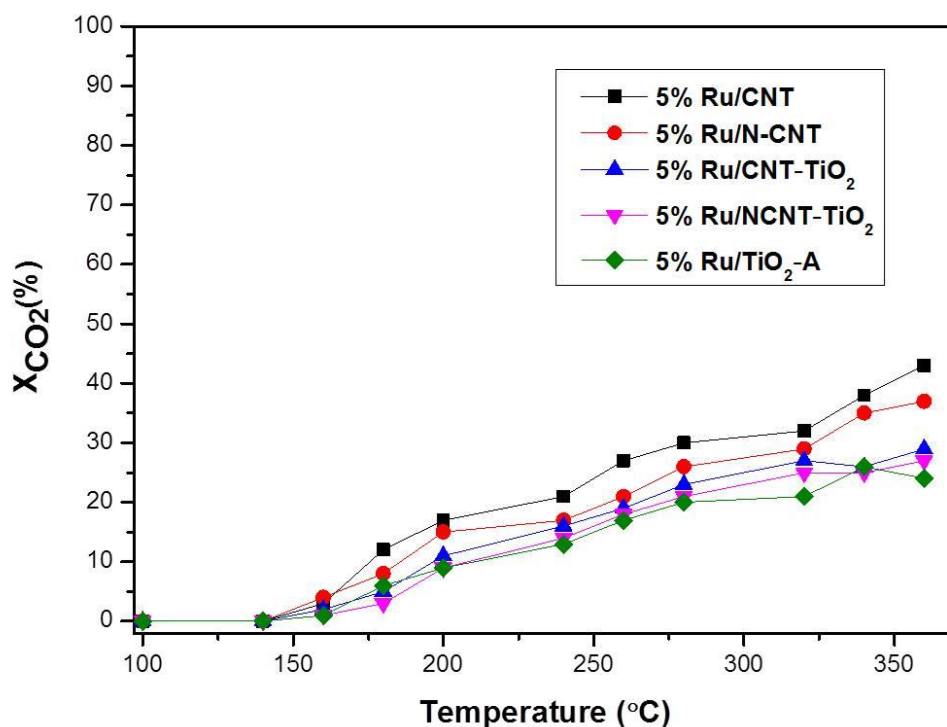


**Figure 6. 9.** The effect of the support on the catalytic performance of CO<sub>2</sub> conversions ( $X_{CO_2}$ ) as a function of reaction temperature using 5% wt.% Ru supported catalyst. Experimental conditions: mass of catalyst: 1 g; reactant composition: 20% CO<sub>2</sub>, 10% N<sub>2</sub> (balance H<sub>2</sub>); total flow rate: 90 cm<sub>3</sub>/min.

## 6.6 Selective CO methanation

Figure 6.10 summarises the performances of all the catalyst investigated for the selective methanation of CO in the presence of CO<sub>2</sub>. The Figure showed a similar activity sequence for all the catalysts performance as seen when only CO was hydrogenated. The same explanations can be given to the activity trend noted for the selective CO methanation reaction. CO conversion was initiated at about ca. 140 °C for all catalysts. The conversion of CO increased with increasing temperature for all the catalyst; at 280 °C, both Ru/CNT and Ru/N-CNT attained maximum conversions of 64% and 78% respectively. Increasing the temperature further above (> 280 °C) indicated a drop in CO conversion revealing “negative”

percentage values for CNT and N-CNT at about 320 °C. This is due to the CO hydrogenation reaction (Eq. (6.1)) running parallel to the RWGS reaction (Eq. (6.5)) under the experimental conditions. The “negative” CO conversion showed that the effluent CO concentration drastically increased due a slower rate of CO hydrogenation compared to the rate at which CO was produced via the RWGS reaction. This behaviour implies that both CNT and N-CNT promoted the RWGS reaction. Although, a drop in CO conversion was observed for NCNT-TiO<sub>2</sub> and CNT-TiO<sub>2</sub> at ca. the same temperature, the effect is small. Clearly, the presence of anatase TiO<sub>2</sub> suppressed the RWGS reaction relative to the Ru/N-CNTs and Ru/CNTs. This result is in agreement with the study by Jiménez et al. [44] who used different carbon nanofibers; they observed that the carbon material promoted a high RWGS [44].

Hydrogenation of CO<sub>2</sub> in the presences CO was minimal at temperatures before CO attained maximum conversion for all the catalysts investigated. This confirms that CO interacted more strongly on the surface of the catalyst than CO<sub>2</sub>, in agreement with reports by several authors [45-47]. It is widely accepted that CO<sub>2</sub> hydrogenation proceeds by the adsorption of CO<sub>2</sub> on the support with H<sub>2</sub> on the metal [48-51]. The work of Shohei et al. [43] suggested that the presences of hydroxyl groups on TiO<sub>2</sub> at elevated temperatures facilitated the hydrogenation of CO<sub>2</sub> [43]. The CNT and N-CNT supports are known to have hydroxyl groups on the surface from the acid treatment. This could possibly explain the relatively higher conversion of CO<sub>2</sub> on Ru/CNT.

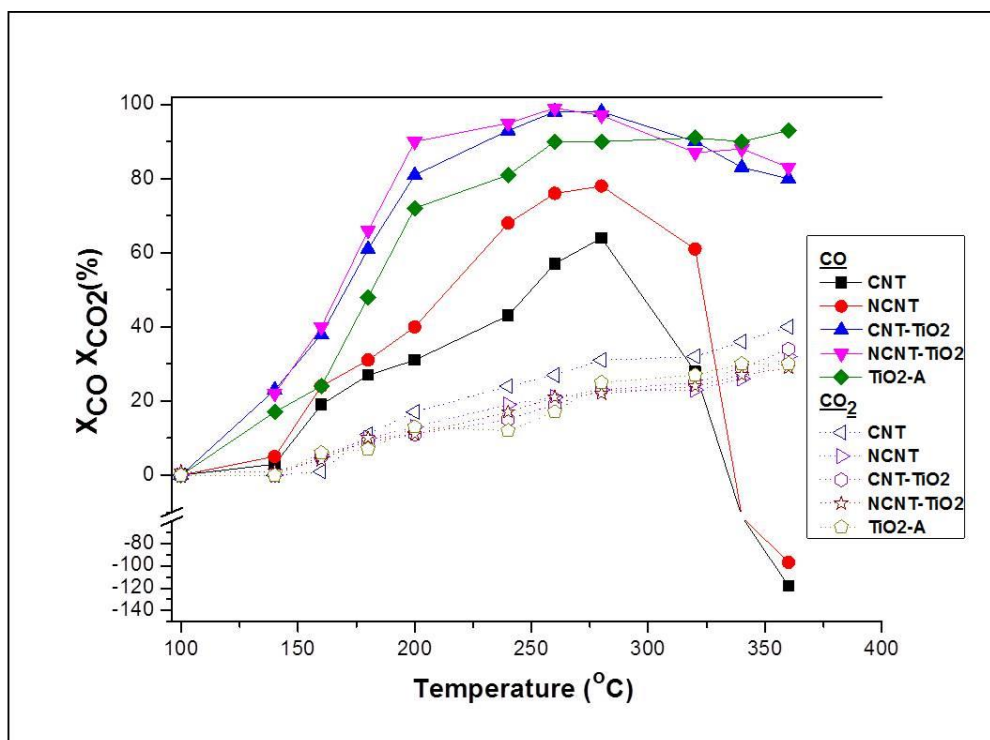


**Figure 6.10.** The effect of the support on the catalytic performance of Ru the on selective methanation of CO in the presence of CO<sub>2</sub> ( $X_{CO}X_{CO_2}$ ) as a function of reaction temperature using 5% wt.% Ru. Solid symbols: CO conversion: open symbols: CO<sub>2</sub> conversion. Experimental conditions: mass of catalyst: 1 g; reactant composition: 1% CO, 20% CO<sub>2</sub>, 10% N<sub>2</sub> (balance H<sub>2</sub>); total flow rate: 90 cm<sup>3</sup>/min.

## 6.6 Methane selectivity

Several studies that have focused on selective CO methanation have shown that besides methane other higher hydrocarbons are formed, especially at low temperatures when CO conversions are low. In our studies, plots revealed that besides methane, the hydrogenation of CO/CO<sub>2</sub> resulted not only in methane but other higher hydrocarbons (Figure 6.11). The catalyst supported on pure anatase (5%Ru/TiO<sub>2</sub>-A) showed the highest selectivity towards methane. Figure 6.10d shows that other than methane only C<sub>2</sub> and C<sub>3</sub> molecules were formed at low temperatures. Above 260 °C only methane was observed. The CNT-TiO<sub>2</sub> composite showed 100% methane selectivity at temperatures above 300 °C. Both 5%Ru/N-CNT and 5%Ru/CNT did not attain total methane selectivity in the temperature range of this study. The data show that larger Ru particle sizes support higher carbon growth. Similar results were observed for CNT-TiO<sub>2</sub> and NCNT-TiO<sub>2</sub> (not shown).

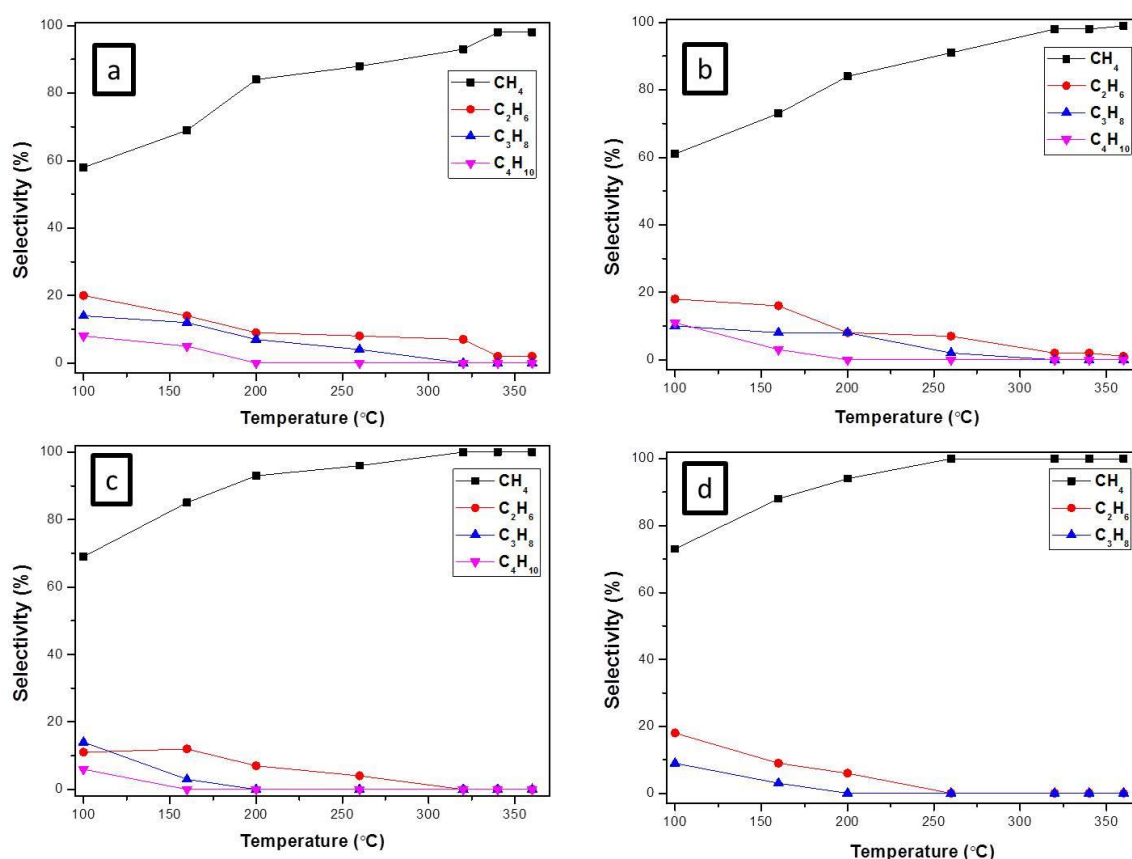


**Figure 6. 11.** The effect of reaction temperature on the selectivity of (a) 5%Ru/CNT (b) 5%Ru/N-CNT (c) 5%Ru/CNT-TiO<sub>2</sub> and (d) 5%Ru/TiO<sub>2</sub> catalysts during the selective CO hydrogenation.

## 6.7 Conclusions

The coating of CNTs and N-CNTs using titania was successfully done. However, the coating did results in total coverage. The coating of CNTs and N-CNTs with titania produced a catalyst support with better thermal stability and a larger surface area compared to the functionalised CNTs. The catalytic activity as well as selectivity in this study depended on the support used and experimental conditions used (e.g. only CO methanation, the mixture of CO and CO<sub>2</sub>, reaction temperature etc.). Total CO conversion was attained for all catalyst at a temperature ca. 280 °C when only CO was methanated. In the presence of CO<sub>2</sub>, a slight variation of conversions was recorded for all catalysts. The titania coated CNT showed significantly higher activity compared to the uncoated CNTs and N-CNTs. The presence of

TiO<sub>2</sub> on the CNTs suppressed the RWGS reaction and the CO methanation rate. Higher temperatures increased methane selectivity at the expense of higher hydrocarbon.

### 6.8 Supplementary data

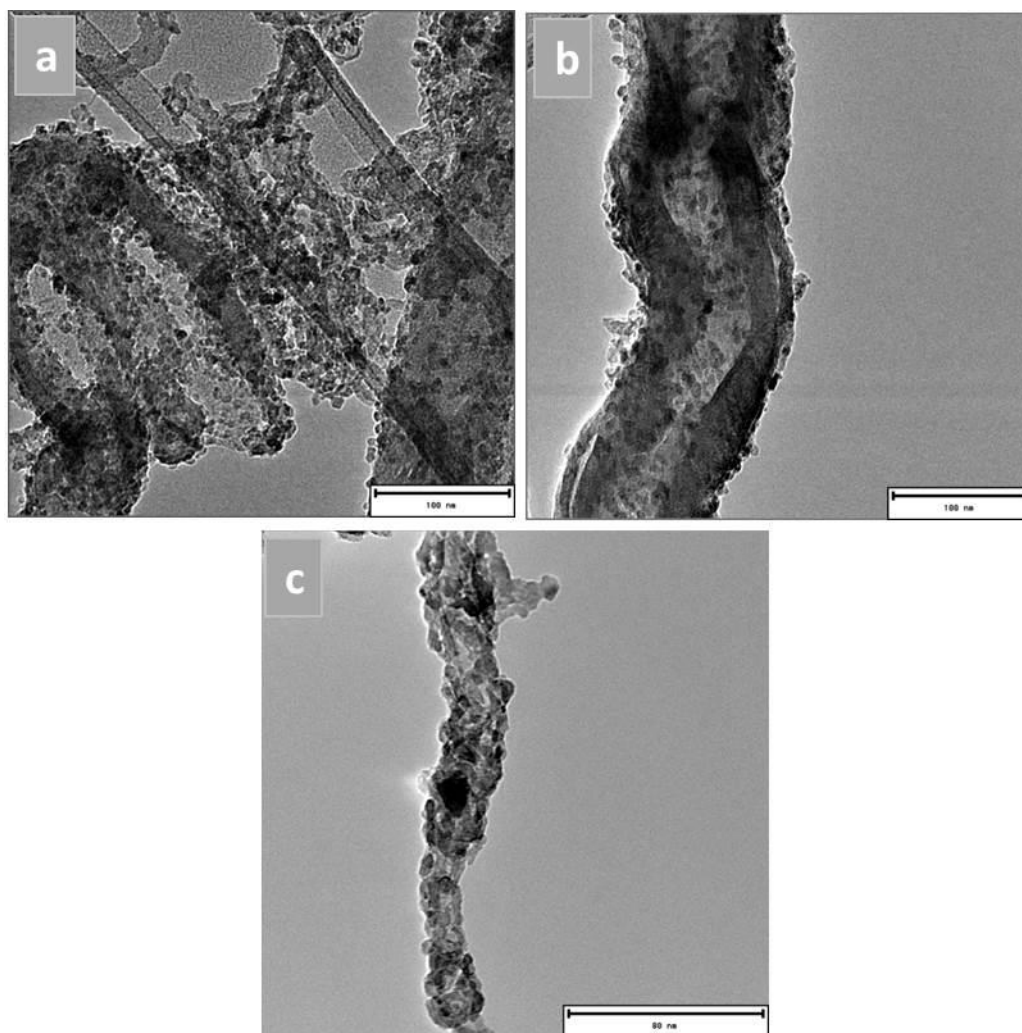


**Figure 6.S1.** TEM images of NCNT-TiO<sub>2</sub>.

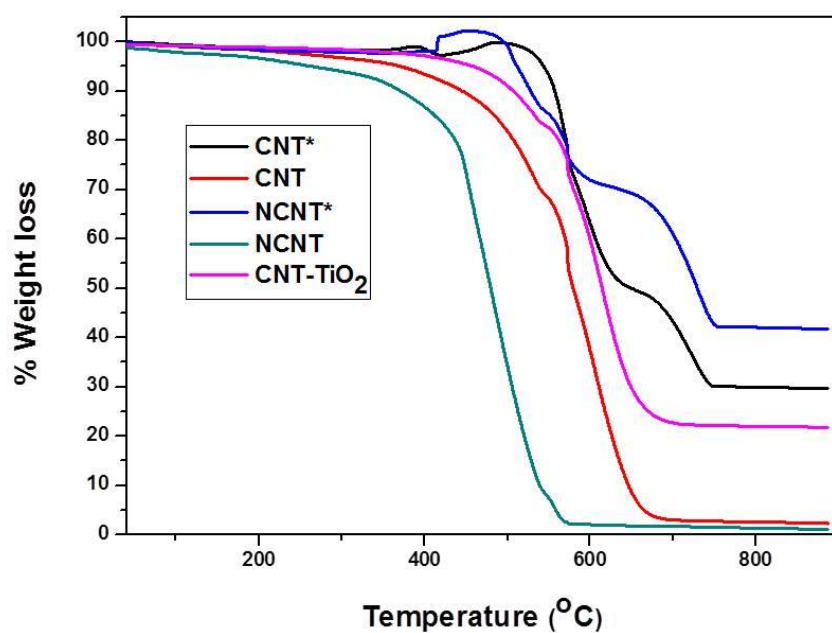


**Figure 6.S2.** TGA profile functionalized and un-functionalized CNTs and N-CNTs and CNT-TiO<sub>2</sub>.

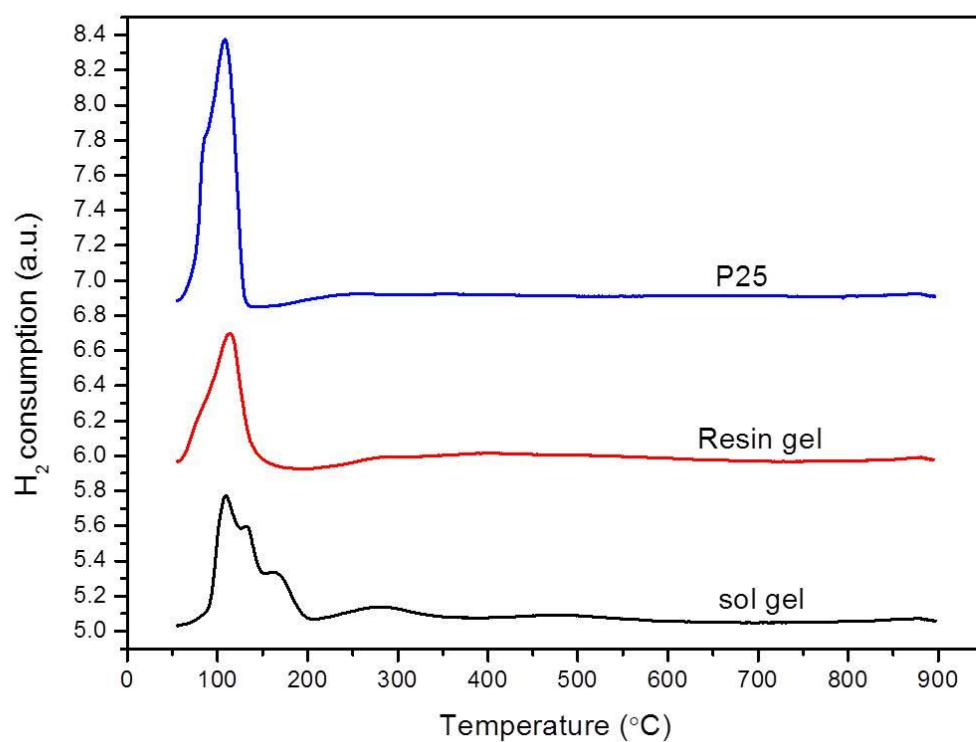


**Figure 6.S3.** Ru catalyst supported on anatase synthesised using different methods.

## 6.9 References

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# Chapter 7

## THE USE OF MESOPOROUS CARBON SPHERES AS SUPPORT FOR Ru NANOPARTICLES FOR SELECTIVE CO METHANATION

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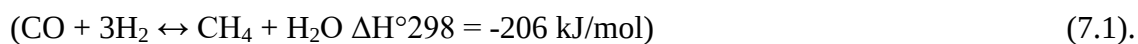
### Abstract

Mesoporous carbon spheres (CSs-H) were hydrothermally synthesised using sugar as carbon source. The closed pores of the as-synthesized CSs-H (microporous with smaller surface area) were observed to be mesoporous (surface area of  $463 \text{ m}^2\text{g}^{-1}$ ) after thermal treatment at  $900^\circ\text{C}$  for 4 hours. Further treating the annealed CSs-H with  $\text{HNO}_3$  acid to fictionalize the CSs-H also introduced high defect content in the carbon matrix which resulted in an increase in surface area ( $509 \text{ m}^2\text{g}^{-1}$ ). The functionalized and un-functionalized CSs-H were used to support nano Ru particles for CO,  $\text{CO}_2$  and selective CO methanation reactions. The Ru supported catalysts were prepared using both impregnation and microwave polyol synthesis. It was evident from the reduction studies that the functional groups on the surface of the CSs-H influenced the reduction of the  $\text{RuO}_2$  to Ru. The catalyst with smaller  $\text{RuO}_2$  particles (microwave polyol technique) seen in the TEM analysis generated high activity for both CO and selective CO methanation studies. This was due to the smaller, uniform and well dispersed sizes Ru particles. The larger Ru particles observed on the un-functionalized CSs-H had poor activity for CO and selective CO methanation reaction but did not promote the reverse water gas shift reaction (RWGS).

**Keywords:** CSs-H, mesoporous, functional groups, selective CO methanation

## 7.0 Introduction

Hydrogen presents an alternative to fossil fuel since it can be fed into fuel cells to generate electric power cleanly. Hydrogen is among the most abundant elements on earth and it is generally produced from catalytic reforming of hydrocarbons followed by the water gas shift reaction (WGS). The secondary hydrogen production process (WGS) leaves the H<sub>2</sub> rich feed with ~1% carbon monoxide. The CO in this H<sub>2</sub> rich feed is regarded as a major setback because this concentration of the CO is high enough to poison the anode catalyst of a polymer electrolyte fuel cell (PEMFC) usually made of Pt or a Pt-alloy (max. CO conc permissible 10 ppm for Pt electrodes and 50 ppm for Pt-alloy) [1-3]. One plausible way of removing the trace CO is through methanation of the CO (Equation (7.1)) [4-6]. The methane produced in removing CO is harmless to the fuel cell electrode and can be used in the afterburner. The methanation of CO<sub>2</sub> and reverse water gas shift reactions (RWGS) which are undesired reactions can occur if the reaction conditions and the catalyst are not carefully chosen. These results in the consumption of large quantities of H<sub>2</sub>. This implies that efforts need to be made in designing a catalyst with high activities at sufficiently low temperatures to overcome the CO<sub>2</sub> methanation and RWGS reaction.



Recent studies have focused on exploring mesoporous materials as catalyst supports to stabilize metal/metal oxide species within the mesopores. This is to address the sintering of the active metal species [7]. To a large extent, catalytic performance can be connected to the effective loading of the metal species into the pore network of the mesopores. Mesoporous supports tend to provide easy accessibility to the dispersed active metal species [8]. High dispersion has been reported when nickel or noble metal nanoparticles were loaded into an aluminum oxide framework *via* in-situ metal ion incorporation [1, 9-13]. The active centers were found to be isolated from each other which enhanced the catalyst sinter resistance [9].

Numerous previous studies have revealed that the nature of a support can alter the dispersion and the surface area of catalytically active species. This affirms the crucial role played by a catalyst support material in immobilizing the active phase species against the loss of surface area via sintering. This influences the overall activity of the catalyst [14-16].

Selective CO methanation studies on carbon based supported catalyst has focused on the use of carbon nanotubes (CNTs) and carbon nanofibers (CNFs) [17-24] with fewer studies

reported on carbon spheres (CSs). Similar properties might be expected when CNFs, CNTs and CSs are used as catalyst support materials. However, studies have revealed that typical synthesis methodologies to produce CNFs and CNTs do not remove all the catalyst used to make the carbon even after acid treatment [25]. The exact effect of the residual catalyst on a catalysis reaction is difficult to quantify. CSs on the other hand are made without the use of a catalyst and so metal purification issues are not a problem. Further the advantages known to be associated when using CNTs and CNFs as catalyst supports should apply to CSs as well.

Different routes have been established to synthesize CSs, and these include the chemical vapor deposition technique [26] and the hydrothermal technique [27]. Herein, we have employed hydrothermally synthesized CSs which are known to have high surface areas and well-structured pores [27]. We have used CSs as a catalyst support for the selective CO methanation reaction. The CSs were also prepared by modifying the surface by acid treatment ( $\text{HNO}_3$ ) which has been confirmed in previous studies [28, 29] to introduce functional groups such as COOH and hydroxyl group species onto the surface and to study the effect of the surface groups on the methanation reaction. Catalysts were also prepared without acid functionalizing the surface of CSs and to study the effect of these functional groups on the reverse water gas shift reaction (RWGS).

## **7.2 Experimental**

### *7.2.1 Hydrothermal synthesis of carbon spheres (CSs-H)*

The hydrothermal approach was employed to synthesize the carbon spheres (CSs-H) [27, 30]. The carbon source used was sucrose. The experiment was conducted using a 0.3 M aqueous sucrose solution was added into a Teflon vessel (90% filling ratio) with a total volume of 90 mL. The vessel and its contents were placed in a stainless steel autoclave and heated to 190 °C ramping at a rate of 1 °C/min. The reaction temperature was sustained 190 °C for 4 h. The autoclave was left to cool to ambient temperature. The suspension was gathered and then washed several times with ethanol and water respectively. The product was left overnight in an oven at 90 °C. To further purify the product, a Soxhlet extraction method was used to remove polyaromatic hydrocarbons (PAHs) from the CSs-H with toluene as the solvent. After the extraction the CSs-H were dried again overnight at 90 °C.

### *7.2.2. Annealing of the CSs-H*

The CSs-H prepared were subjected to a further heat treatment under inert ( $N_2$ ) condition. To carry out the annealing experiment, about 3 g of the as-prepared CSs-H was placed in a quartz boat in the quartz tube. The boat and its content were placed in the middle of the quartz tube reactor and the reactor was inserted into a furnace. Nitrogen (flow rate of 20 mL/min) was passed through the reactor while the temperature was ramped at 10 °C/min to 900 °C for one and half hours. The annealing was left to proceed for 4 h while keeping the temperature at (900°C). This material was labeled as CSs-H.

### *7.2.3. Functionalization of CSs*

The annealed CSs-H (1.5 g) were added to 100 mL of 55 %  $HNO_3$ . The suspension was then stirred and refluxed at 110 °C for 2.5 h. The product was washed with a large amount of distilled water until the pH attained a neutral value (pH 7). It was then left in the oven overnight at 100 °C to give F-SCs-H.

### *7.2.4. Catalyst preparation*

Two catalyst preparation methods were employed in this study. A set of Ru catalysts were made by adding Ru to the un-functionalized and functionalized supports (SCs-H and F-SC-Hs respectively) using the impregnation method. This was achieved by addition of the desired amount of  $RuCl_3$  in water and adding this solution to the support drop-wise to achieve a 5%wt Ru loading. The materials were labelled as CSs-HIMP and F-CSs-HIMP

Another set of catalysts were prepared by the microwave irradiation polyol method as described in Chapter 5. The  $RuCl_3$  solution and the CSs-H materials were dispersed in ethylene glycol and sonicated for 15 min. The Ru solution was added drop wise, the reaction content transferred into Teflon vessels and then placed in the microwave oven. All the catalysts were prepared to make up 5% wt Ru on the support. They were labeled as F-CSs-HMIC. All the catalysts were calcined at 220 °C for 2.5 h and later characterized using TEM, BET, TPR and chemisorption techniques.

### 7.2.5. Catalyst testing

The methanation reactions were carried out in a tubular fixed bed reactor (FBTR). The dimensions of the reactor have been mentioned in the previous chapters. The K-type thermocouple was employed to monitor the temperature in the reactor on the catalyst fixed bed. The methanation gasses were fed into the reactor chamber from gas cylinders (for CO methanation, 1% CO, 10% N<sub>2</sub> and H<sub>2</sub> balance 99.99% purity, for selective CO methanation, 1% CO, 20% CO<sub>2</sub>, 10% N<sub>2</sub> and H<sub>2</sub> balance 99.99% purity and for CO<sub>2</sub> methanation 20% CO<sub>2</sub>, 10% N<sub>2</sub> and H<sub>2</sub> 99.99% purity). A gram of the catalyst was typically reduced *in-situ* at using hydrogen gas (99.995% purity) at 250 °C for 3 h at 1 bar. For all the methanation reactions, the temperatures ranged between 100 – 360 °C. The gas flow rate was kept at 150 ml/min for all the reactions. An online gas chromatograph (GC) equipped with Porapak Q and Carboxen-1000 columns coupled to a FID and a TCD were used to monitor outlet gas feed.

## 7.3 Results and discussion

### 7.3.1. Support characterization

Insight into the morphology of the hydrothermally synthesized CSs was gained through TEM analysis. Figure 7.1 shows the TEM images and size distribution graph for the synthesized CSs. It was observed that the carbon materials were spherical in shape and consisted of sizes ranging from 300 nm to 1000 nm as show in the size distribution graph in Figure 7.1c. They appeared to be monodispersed (Figure 7.1a and 7.1b) but showed a necklace like accreted conformation. Dlamini et al. reported that when the spheres were annealed their surface roughened due to removal of PAHs and this led to the opening of the pores [27].

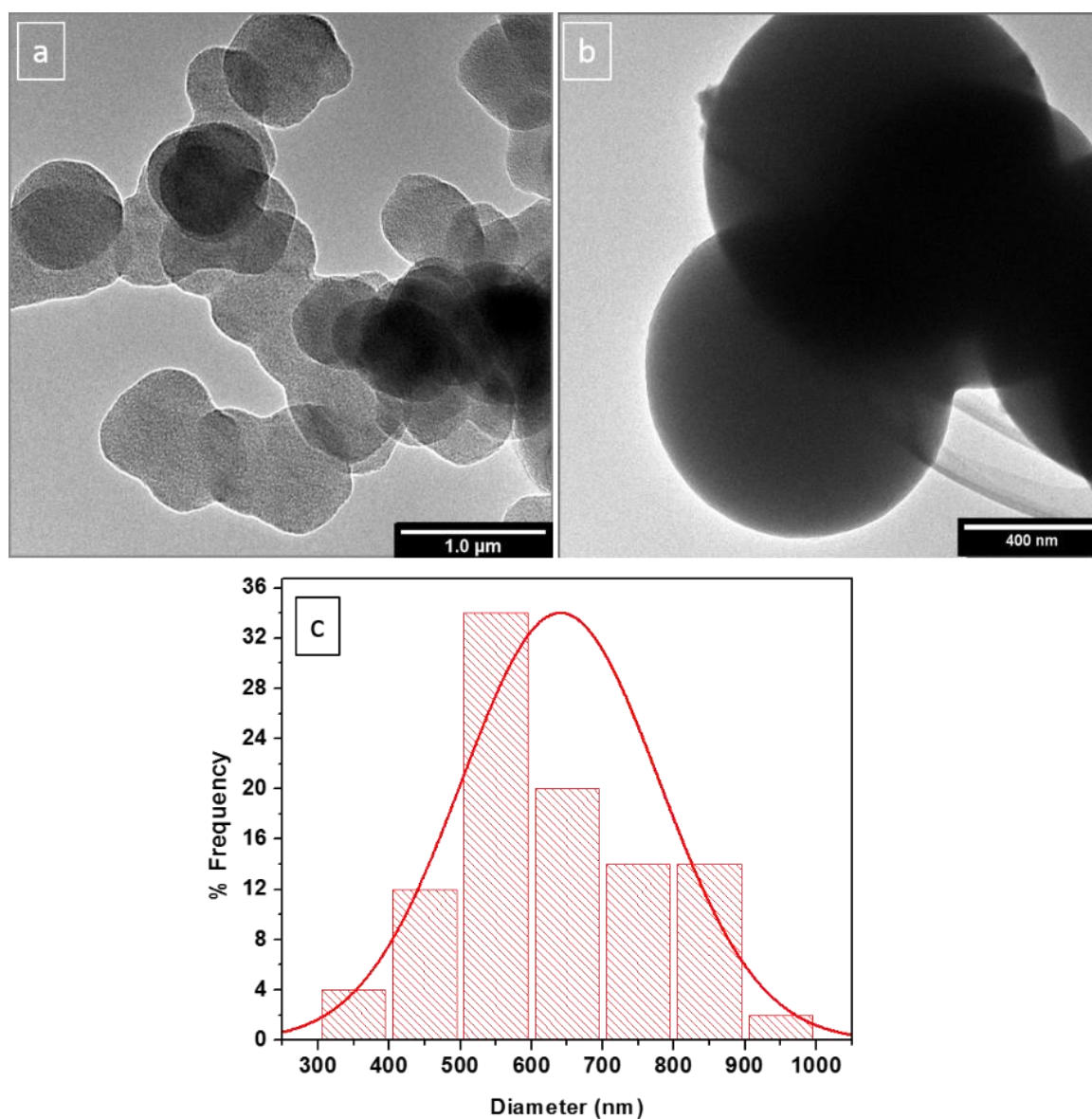


**Figure 7.1.** TEM images and size distribution graph of the hydrothermally synthesized carbon spheres.

### 7.3.2. Nitrogen adsorption-desorption

Nitrogen physisorption studies were performed on the annealed CSs-H sample (functionalized and un-functionalized). A comparison of the two adsorption-desorption isotherms and pore size distributions are presented in Figure 7.2 and Table 7.1. Both samples exhibited micro and mesopores (type 4 according to the IUPAC classification, also indicating a sharp capillary condensation occurring between 0.4 – 0.6 relative pressure). Interestingly, the functionalized sample displayed a relatively higher N<sub>2</sub> adsorption at lower relative pressure ( $p/p_0$ ) and a larger hysteresis loop (at  $p/p_0 = 0.4-0.9$ ) than the un-functionalized CSs-H. The hysteresis curve loops confirm the presence of well-defined mesopores. Coupled with a larger hysteresis loop on the functionalized sample was a high pore volume ( $30 \text{ cm}^3 \text{ g}^{-1}$ ) and the sample also had an average pore diameter between 4.5-6.5 nm (Figure 7.2 c and d respectively). This hysteresis loop was relatively smaller than that found for the un-functionalized CSs-H and the sample also had a smaller pore volume ( $19 \text{ cm}^3 \text{ g}^{-1}$ ) with an average pore diameter between 3 - 4 nm (Figure 7.2a and 7.2c respectively). This implied that functionalizing the CSs-H created more and larger pores. This gave the higher surface area ( $509 \text{ m}^2/\text{g}$ ) when compared to the un-functionalized CSs-H ( $428 \text{ m}^2/\text{g}$ ) (Table 7.1).

**Table 7.1.** Properties of the CSs-H.

| Analysis                                               | F-CSs-H | CSs-H |
|--------------------------------------------------------|---------|-------|
| BET ( $\text{m}^2/\text{g}$ )                          | 509     | 463   |
| Pore volume ( $\text{cm}^3/\text{g}$ )                 | 0.31    | 0.21  |
| Pore diameter (nm)                                     | 4.9     | 3.5   |
| D-band ( $\text{cm}^{-1}$ )                            | 1351    | 1595  |
| G-band ( $\text{cm}^{-1}$ )                            | 1344    | 1590  |
| $I_D/I_G$                                              | 0.96    | 0.69  |
| Decomposition Temp ( $^{\circ}\text{C}$ ) <sup>a</sup> | 578     | 661   |

<sup>a</sup> in air from TGA analysis

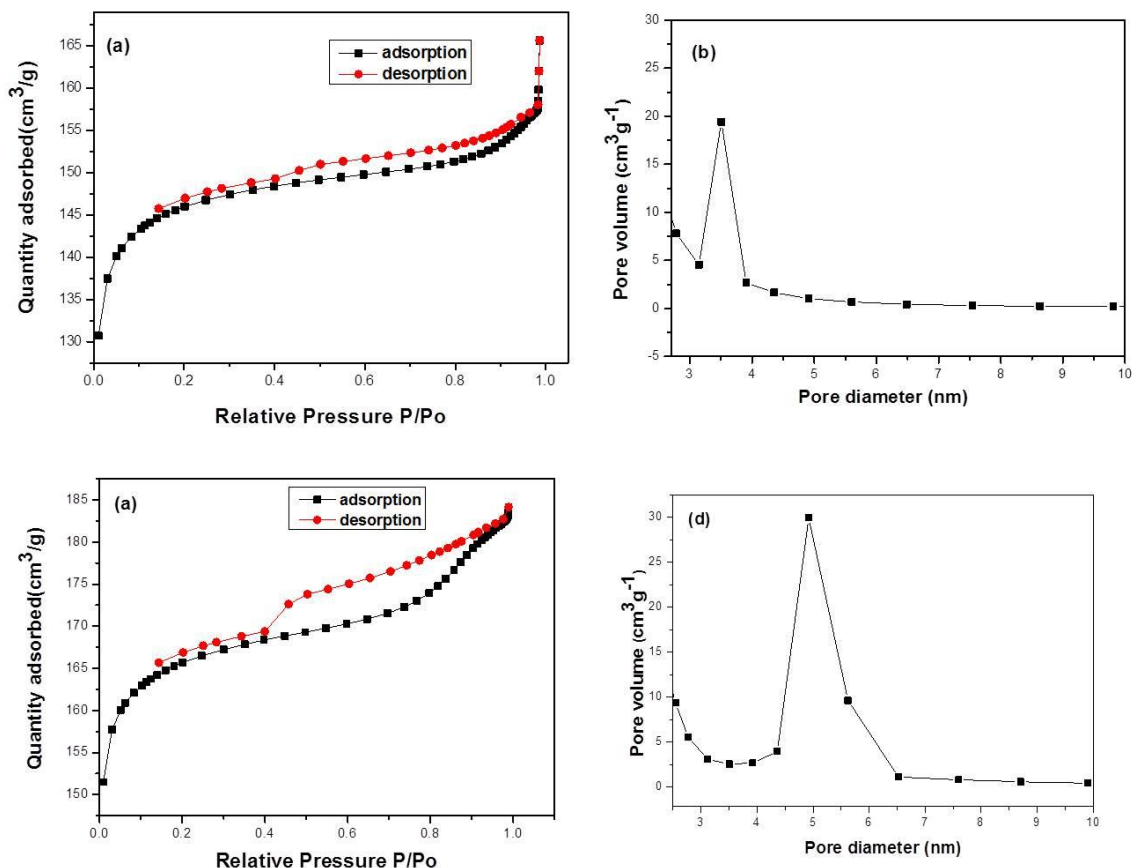


**Figure 7.2.** N<sub>2</sub> adsorption-desorption isotherms and pore size distribution plots for functionalized and un-functionalized CSs-H.

### 7.3.3. Raman spectral analysis

The graphitic order in the carbon framework was measured using Raman spectroscopy. In Figure 7.3, the Raman spectra for functionalized and un-functionalized CSs-H were compared. The in-plane vibration of the sp<sup>2</sup> carbon atom indicated a G-band (at approximately 1590 cm<sup>-1</sup>) whereas the D-band characterized a defect-induced Raman feature, representing the degree of non-perfect crystalline structures (at approximately 1350 cm<sup>-1</sup>). The analysis on the intensities of bands (D versus G,  $I_D/I_G$ ) gives information about bond features in the carbon framework. An increase in the  $I_D/I_G$  ratio was observed when the annealed sample was functionalized and this is consistent with higher defect content as result of the acid treatment [25, 31]. This result agrees with the BET data (Table 7.1).

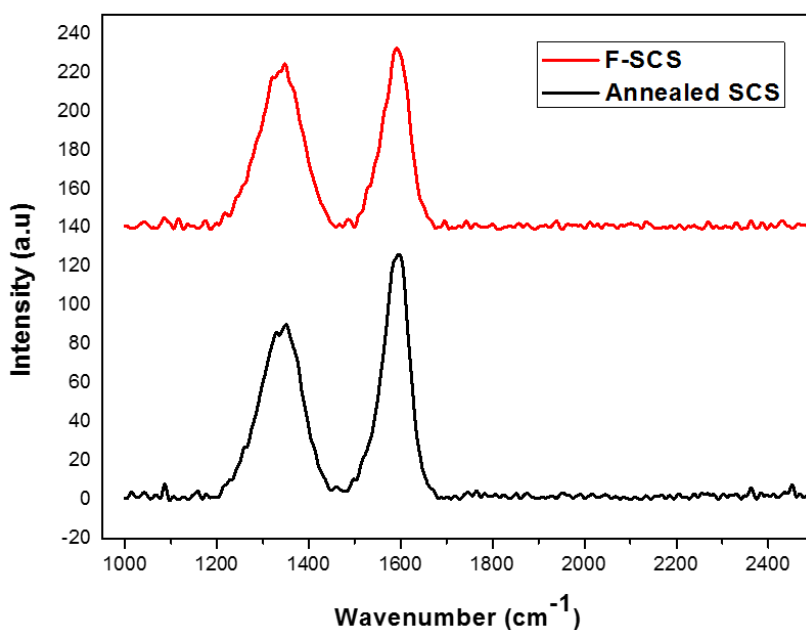


**Figure 7.3.** Raman spectra of the functionalized and un-functionalized CSs-H.

#### 7.3.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis profiles of the CSs-H are shown in Figure 7.4. The measurements were carried out under an oxidizing atmosphere. Notably, the un-functionalized sample which demonstrated high graphitic nature, from Raman studies, also showed good thermal stability with decomposition above 600 °C. This implied that acid treatment which introduced oxygen containing functional groups compromised the CSs-H thermal stability (< 600°C). The oxidation onset at lower temperature for the functionalized spheres was due to the removal of the functional groups on the surface of the carbon spheres. The derivative weight loss plot showing the actual weight losses for the functionalized and un-functionalized carbon spheres are presented in Figure 7.S1.

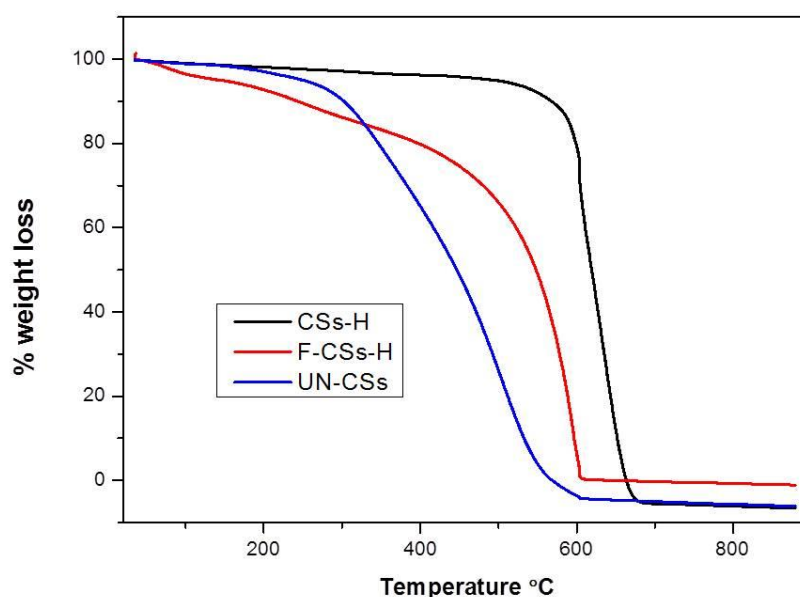
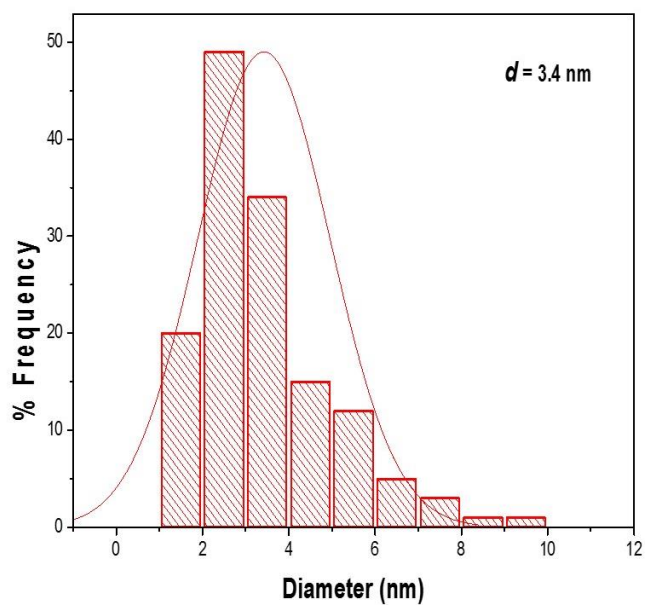
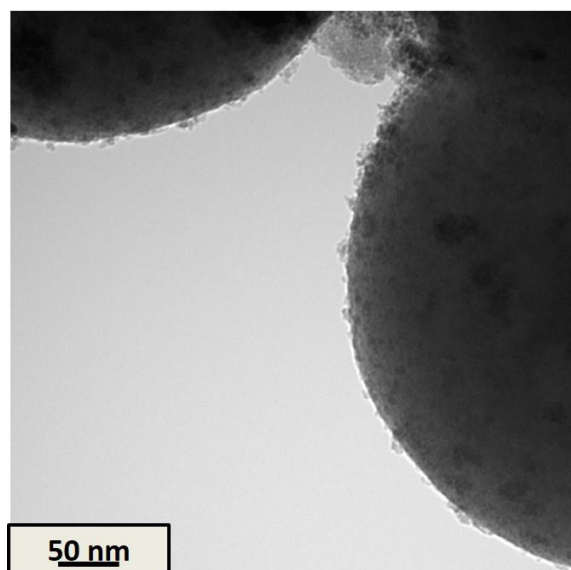
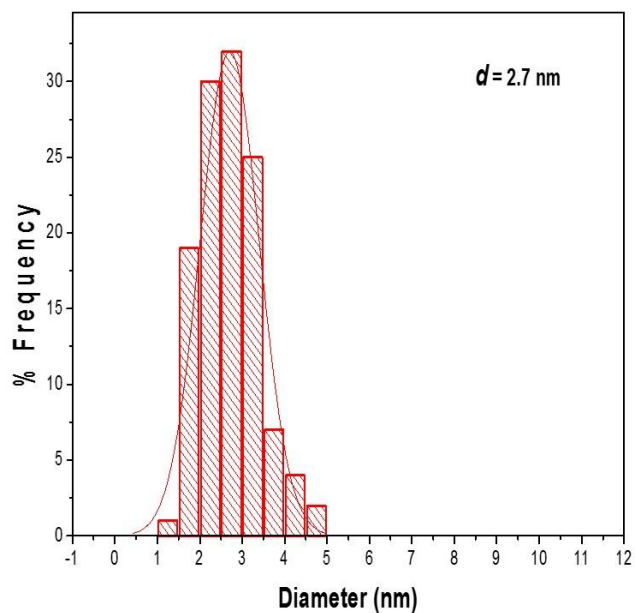
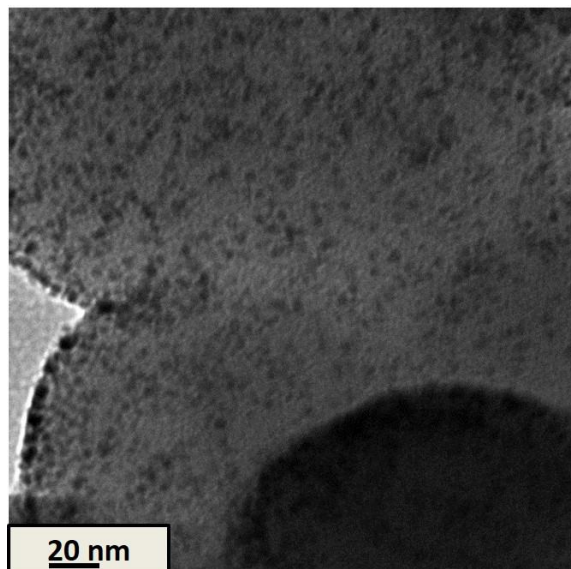


**Figure 7.4.** TGA plots showing functionalized, un-functionalized and un-annealed SCs-H. (UN-CSs: un-annealed carbon solid spheres).

### 7.3.5. Catalyst Characterization

Figure 7.5 shows TEM images of the three different Ru nanoparticle supported catalysts on CSs-H and the Ru size distributions. In the TEM images the RuO<sub>2</sub> particles are noted as dark spots on the carbon supports. The catalyst prepared by the microwave polyol technique demonstrated fairly small Ru particles and which were relatively well dispersed on the support (Figure 7.5a). The size distribution graph indicated the particles had a narrow size distribution. This was attributed to the fact that the microwave technology offered good control over Ru particles using the selected conditions for the preparation of the catalyst as discussed in the previous Chapter (3). Again, functionalizing the solid spheres created enough pores, arising from the defects in the carbon framework, for the RuO<sub>2</sub> and also the oxygenated functional groups provided docking sites to bind the RuO<sub>2</sub> nanoparticles. The Ru impregnated on the acid treated support gave RuO<sub>2</sub> particles with average particle size of 3.4 nm. The Ru had slightly wider size distribution compared to the microwave prepared catalyst as indicated in the particle size distribution graph in Figure 7.5d. The absence of functional groups and a high defect content resulted in the synthesis of relatively larger RuO<sub>2</sub> particles with a significantly wider size distribution range on the CSs-H (Figure 7.5e and 7.5f). The

particles might have sintered further during the calcination process due to limited restriction for growth of the Ru particles.



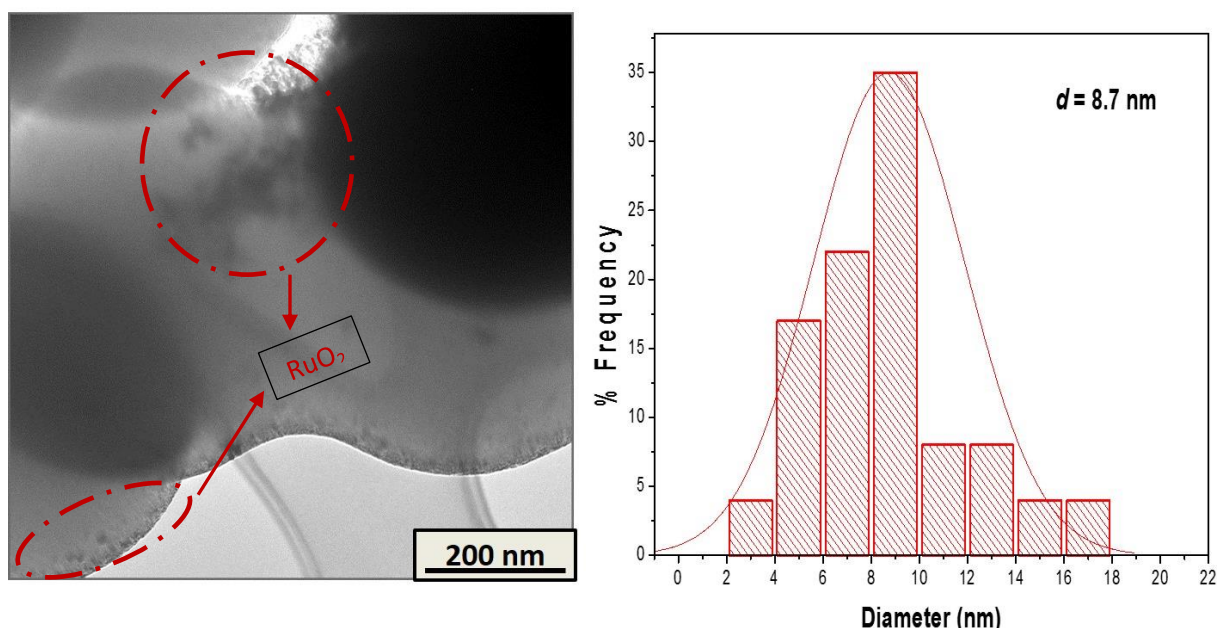


**Figure 7.5.** Ru catalyst supported SCs-H (a) F-SCs-HMIC (b) F-SCs-HIMP and (c) SCs-HIMP.

Table 7.2 summarizes both physio and chemical properties of the Ru supported on CSs-H. The surface areas for all the catalyst reduced after loading Ru. These were largely due to blocking of the mesopores by the Ru metal particles. Marginal reductions were experienced in the pore volumes of this catalyst. The catalyst prepared using the microwave polyol method generated smaller Ru particles hence resulting in higher dispersion (64%). The larger Ru particles observed on the un-functionalized were poorly dispersed and this was confirmed by the chemisorption technique. The impregnated catalyst supported on functionalized CSs-H had a relatively higher dispersion for the Ru particles. The Ru particles measured on the TEM images in the oxide form were relatively larger than the Ru particle sizes recorded from the chemisorption data.

**Table 7.2.** Physio and chemical properties of the catalysts.

| Sample     | BET (m <sup>2</sup> /g) <sup>a</sup> | Pore Volume<br>(cm <sup>3</sup> /g) | $d_{\text{Ru}}$ (nm) <sup>b</sup> | $d_{\text{Ru}}$ (nm) <sup>c</sup> | Dispersion<br>(%) |
|------------|--------------------------------------|-------------------------------------|-----------------------------------|-----------------------------------|-------------------|
| SCs-HIMP   | 443                                  | 0.21                                | 8.7                               | 5.9                               | 17                |
| F-SCs-HIMP | 468                                  | 0.28                                | 3.4                               | 2.2                               | 56                |
| F-SCs-HMIC | 471                                  | 0.29                                | 2.7                               | 1.8                               | 64                |

*a: surface area BET.*

*b: RuO<sub>2</sub> from TEM.*

*c: Ru from chemisorption.*

### 7.3.6. TPR studies

The different catalysts were subjected to reduction studies (Figure 7.6). Reduction from RuO<sub>2</sub> to Ru occurred at different maximum temperatures for the different CSs-H supported catalysts, indicating that both support and the catalyst preparation method slightly influenced the reduction of the active metal. From the graphs, the reduction of RuO<sub>2</sub> to Ru occurred at a slightly higher temperature on functionalized supports compared to an un-functionalized supported catalyst. This was attributed to the loosely bound RuO<sub>2</sub> on the un-functionalized support due to the absence of functional groups. The F-CSs-HIMP with larger RuO<sub>2</sub> particles reduced at relatively higher wider temperature compared to the smaller and uniform RuO<sub>2</sub> particles generated by the microwave irradiation technique. All the reduction occurred between a temperature range of 10 to 119 °C. No significant strong metal support interaction (SMSI) was observed implying functional groups did not form strong chemical bonds which required higher energy or temperature to reduce the RuO<sub>2</sub> particles. The reduction was revealed to be dependent of the surface of the support and size. The broad peaks observed between 300 °C and 600 °C as a result of carbon oxidation to form methane.

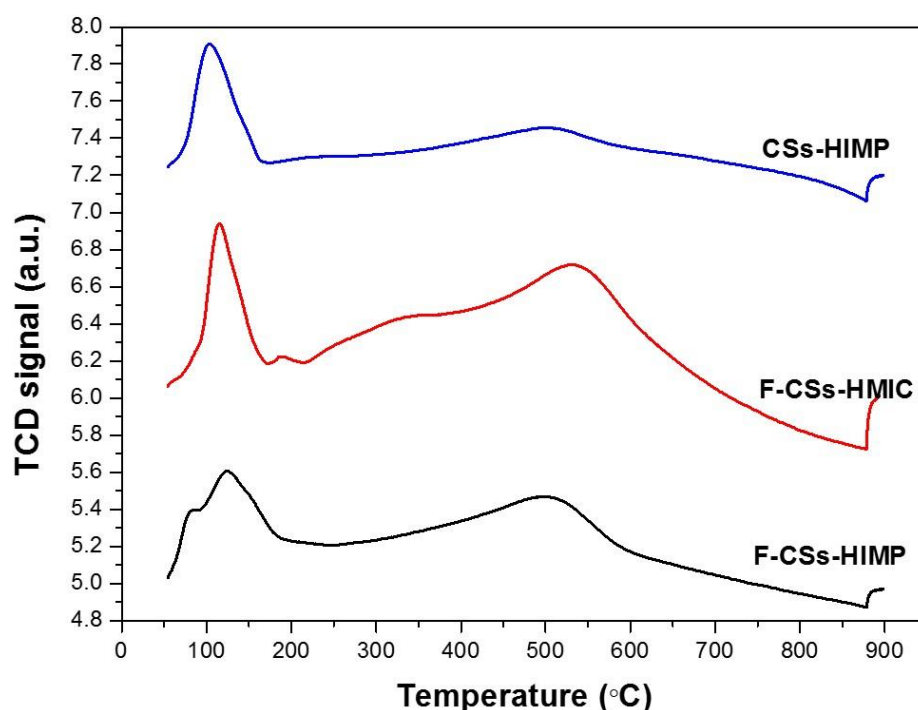


**Figure 7.6.** Temperature programmed reduction plots for the different catalysts.

#### 7.4 CO methanation

Figure 7.7 shows the behavior of the individual Ru catalysts on CSs-H as support for CO hydrogenation. Increasing temperature resulted in an increased CO conversion. All the catalysts completely converted CO within a temperature range of 240 -300°C, typically, modifying the surface of the CSs-H support by acid functionalization which introduced oxygenated groups that correlated with the CO methanation activity. It can be observed from the conversion plots (Figure 7.7) that, both CSs-HIMP and CSs-HMIC displayed significantly higher activity when compared to the un-functionalized (CSs-H). From the Raman studies, it was confirmed that acid treatment increased the defects in the support material. The BET data also revealed a higher surface area as well as mesopore volume after acid treatment of the support. The defects are believed to increase anchorage sites for the Ru particles. Also, the oxygenated functional groups help dock Ru specie and stabilize them to sintering under mild heat treatment conditions [32, 33]. This improved dispersion of Ru species on the support is seen in the chemisorption data (Table 7.2). This explained the higher activity recorded.

From the plots in Figure 7.7, there is an indication that catalyst preparation also affected the catalyst activity. The microwave irradiation polyol technique generated relatively smaller narrowly uniformly dispersed Ru particles. Our study using the microwave catalyst preparation indicated good control over the size and size distribution by altering the infra-red temperature (Chapter 5). This clearly shows that the microwave polyol technique is appropriate for preparing laboratory scale catalysts.

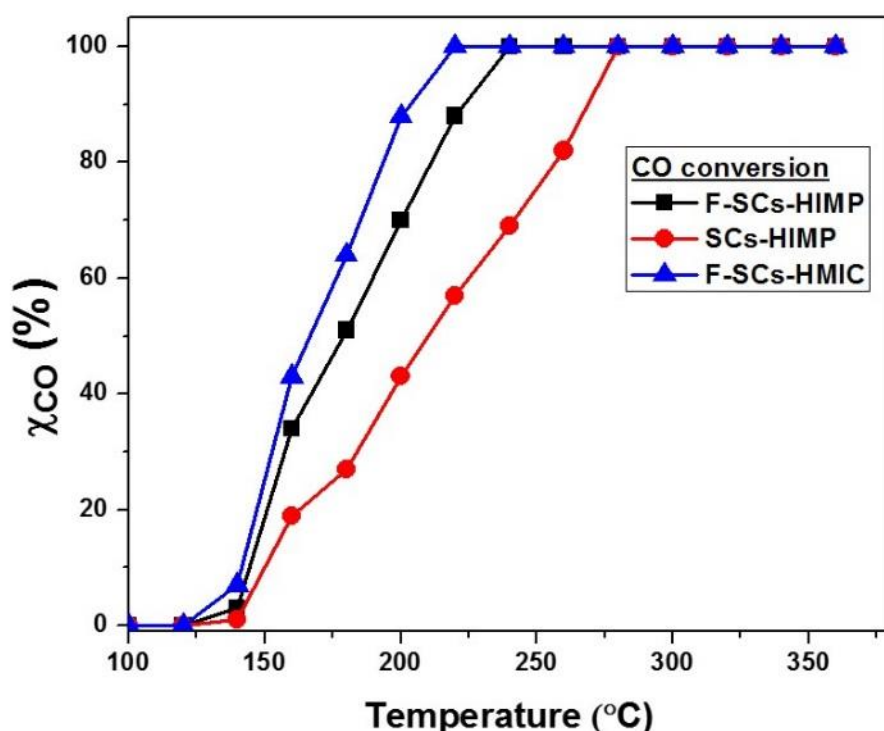


**Figure 7.7.** The effect of temperature on the CO conversion ( $X_{CO}$ ) as a function of reaction temperature using 5 wt.% Ru. Experimental conditions: mass of catalyst: 1 g; reactant composition: 1% CO, 89% H<sub>2</sub> (balance N<sub>2</sub>); total flow rate: 150 cm<sup>3</sup>/min.

## 7.5 CO<sub>2</sub> methanation

CO<sub>2</sub> methanation was also studied with the different catalysts using similar experimental condition to those used in the CO methanation reaction. The results are presented in Figure 7.8 and show that the CO<sub>2</sub> conversion was less than 40% within the total range of temperature over which the reaction was conducted. The catalysts prepared from the functionalized

support had almost similar conversions. This indicated that the catalyst preparation had little effect on CO<sub>2</sub> activity. The CSs-HIMP catalyst was practically inactive below 250 °C. A conversion above 10% occurred at 320 °C which implied that the support affected on this reaction.

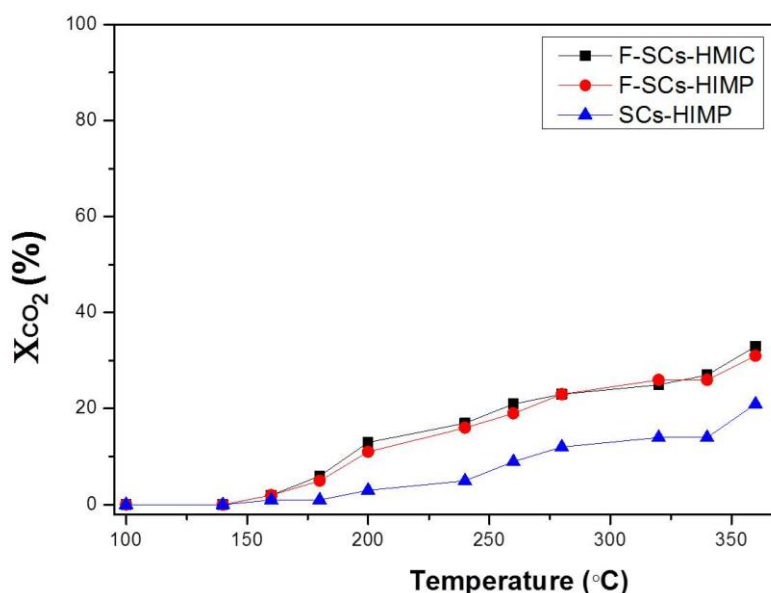


**Figure 7.8.** The effect of temperature SCs-H on the CO<sub>2</sub> conversion ( $X_{CO}$ ) as a function of reaction temperature using 5 wt.% Ru. Experimental conditions: mass of catalyst: 1 g; reactant composition: 1% CO, 89% H<sub>2</sub> (balance N<sub>2</sub>); total flow rate: 150 cm<sup>3</sup>/min.

## 7.6 Methane selectivity

Methane dominated as the major product for the CO hydrogenation process at temperatures above 240 °C as show the Figure 7.9. It was noted that some other higher hydrocarbons were produced at lower temperatures. The un-functionalized supported catalyst with larger Ru particles produced other hydrocarbons besides methane at lower temperature. The main products formed below 240 °C over F-SCs-HMIC besides CH<sub>4</sub> was C<sub>2</sub>H<sub>6</sub> (15 % at 160 °C), while CSs-HIMP gave about 0.4% C<sub>3</sub>H<sub>8</sub> at 160 °C in addition to C<sub>2</sub>H<sub>6</sub>. Similar results have been reported in previous studies by Jiménez et al. when they studied the nature of carbon fiber supported Ru as an active catalyst. [21].

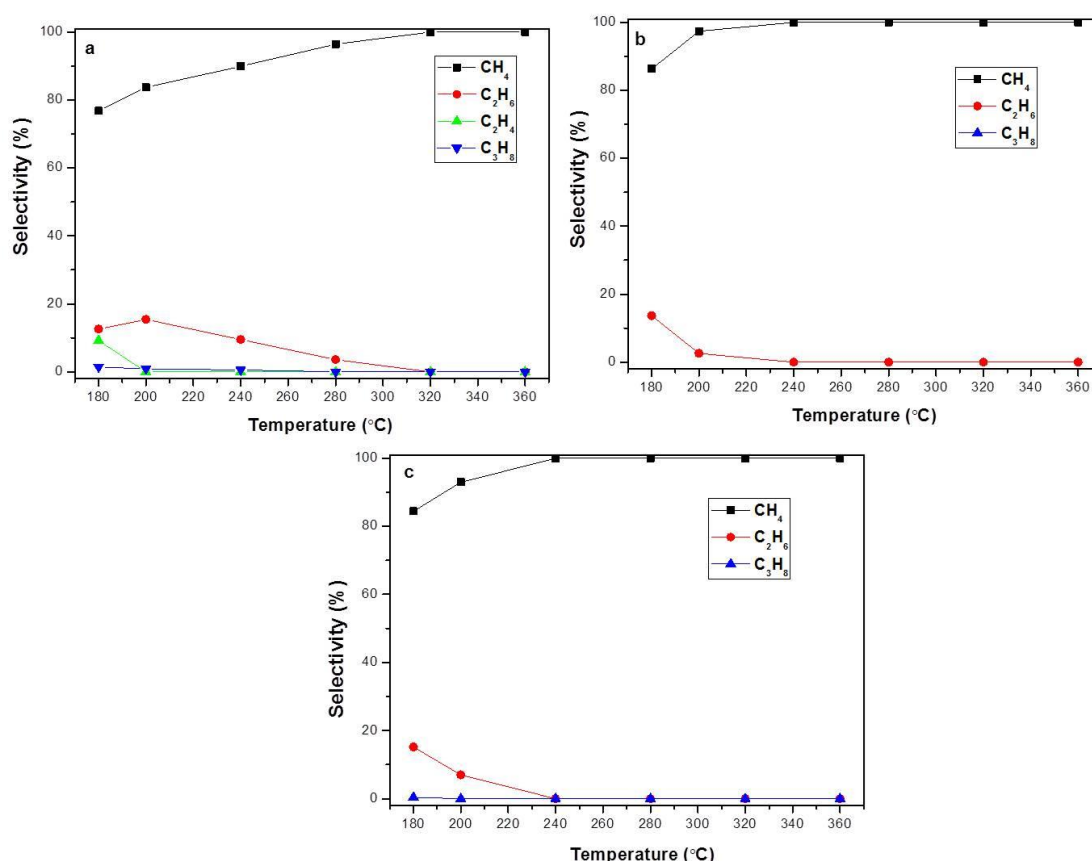


**Figure 7.9.** The effect of reaction temperature on the selectivity of (a) SCs-HIMP (b) F-SCs-HMIC and (c) F-SCs-HIMP catalysts.

## 7.7 Selective CO methanation

The different catalysts were studied under selective CO methanation conditions in the presence of excess CO<sub>2</sub> (Figure 7.10). Similarly, the functionalized supported catalysts displayed higher activity as seen for CO methanation in the absence of CO<sub>2</sub>. The same reasons can be used to explain both sets of results. None of the catalysts attained 100 % CO conversion under the selective methanation conditions employed.

The CO output for all the catalysts dropped after they attained their maximum conversion between 280 - 300 °C. This was due to formation of CO produced by CO<sub>2</sub>. This reaction, the reverse water gas shift (RWGS), runs parallel with the CO methanation process. The unfunctionalized supported Ru catalyst showed a lower CO conversion. However, the RWGS reaction was less significant when compared to the functionalized Ru supported catalyst. This

suggests that the presence of oxygenated functional groups, especially OH groups (which have been confirmed to be present on functionalized carbon materials[28, 29]) on the supports aided both CO<sub>2</sub> conversion [34, 35] and promoted the RWGS reaction under the experimental condition employed.

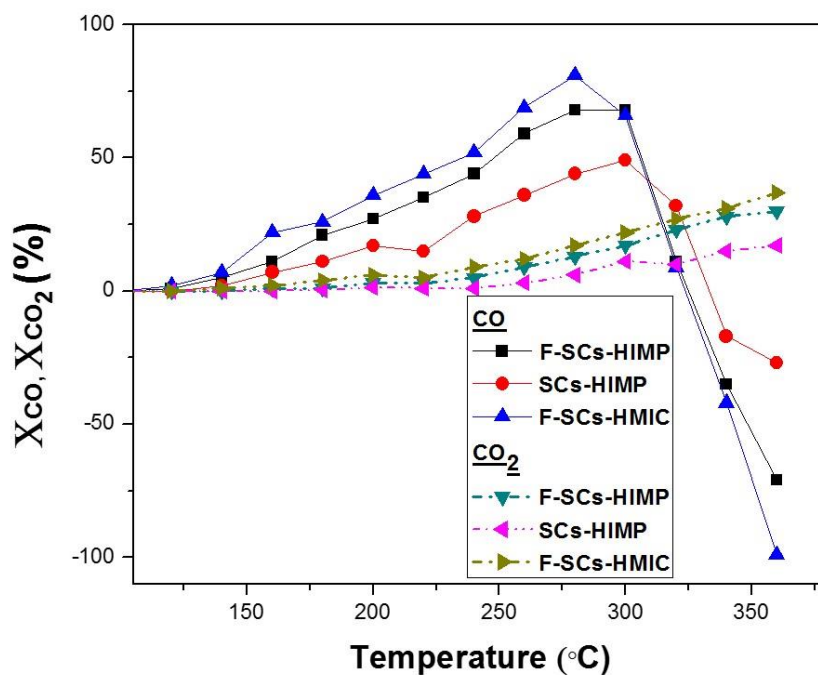


**Figure 7.10.** The effect of SCs-H support on catalytic performance (a) CO conversion ( $X_{CO}$ ) and (b) selective methanation of CO in the presence of CO<sub>2</sub> ( $X_{CO_2}$ ) as a function of reaction temperature using 5% wt.% Ru. (Solid symbols: CO conversion: open symbols: CO<sub>2</sub> conversion). Experimental conditions: mass of catalyst: 1 g; reactant composition: (a) 1% CO, 89% H<sub>2</sub> (balance N<sub>2</sub>) and (b) 1% CO, 20% CO<sub>2</sub>, 69% H<sub>2</sub> (balance N<sub>2</sub>); total flow rate: 150 cm<sup>3</sup>/min.

## 7.8 Conclusions

The hydrothermally synthesized solid carbon spheres after functionalizing with  $\text{HNO}_3$  recorded a significant increase in the specific surface areas resulting from the high defect content. This remarkably improved the dispersion of the Ru compared to the un-functionalized support. The microwave polyol catalyst preparation technique resulted in almost uniformly sized Ru dispersed on the support.

The un-functionalized carbon had poorly dispersed large Ru particles with a wide size range distribution with poor CO conversion. Despite this drop in activity, it recorded the lowest reverse water gas shift activity which tended to generate extra CO in the reformat gas feed. This was explained as due to the absence of OH functional groups on the support which would enhance associative adsorption of  $\text{CO}_2$ . An insignificant percentage of higher hydrocarbons (mostly  $\text{C}_2\text{H}_6$ ) were observed at lower temperatures when the CO conversions were still below 10%.

## 7.9 Supplementary data

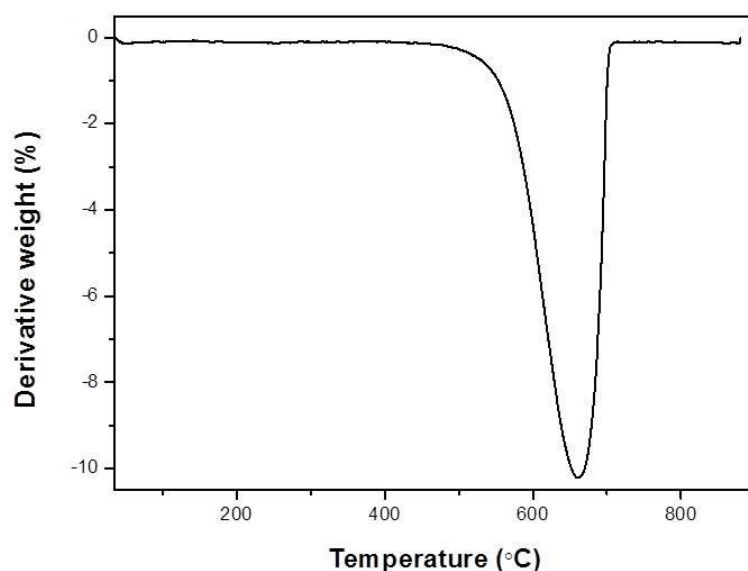


**Figure 7.S1.** Derivative weight loss plot for CSs-H.

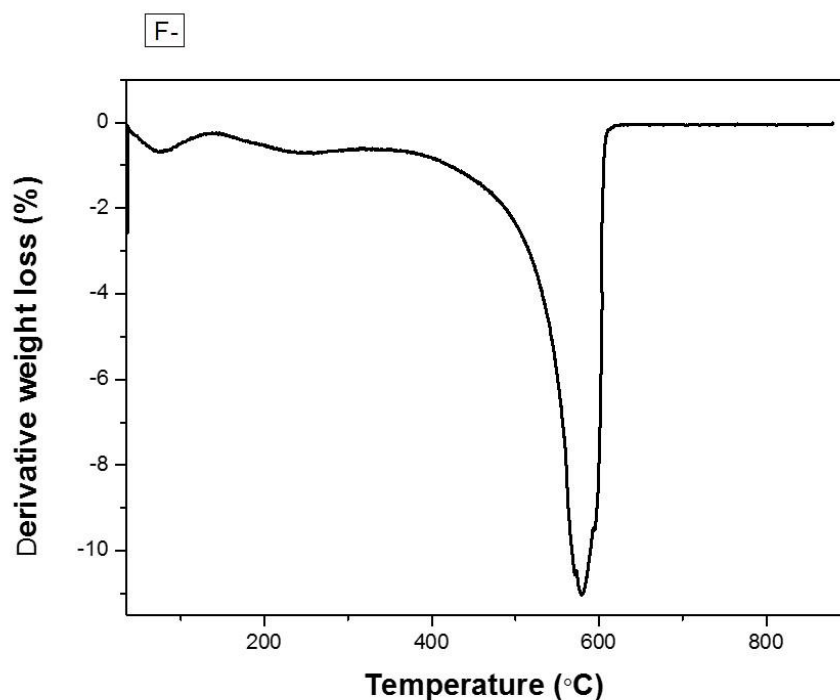


**Figure 7.S2.** Derivative weight loss plot for F-CSs-H.

## 7.10 References

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# Chapter 8

## 8.0 General Conclusions

The aim of this study was to study CO methanation and selective CO methanation reactions in the presence of excess CO<sub>2</sub> by exploring Ru supported on TiO<sub>2</sub> and carbon based supports. These supports and their respective catalysts were characterized using BET, Raman spectroscopy, TEM, SEM, both *in situ* and *ex situ* PXRD, TPR and chemisorption.

Thermally produced rutile (classic rutile) was compared to the novel dandelion-like rutile morphology prepared by a facile hydrothermal approach. Ru was loaded on the supports. These catalysts were applied in CO hydrogenation as well as selective CO hydrogenation in the presence of excess CO<sub>2</sub>. It emerged that the dandelion-like rutile morphology showed superior catalytic ability when compared to the thermally produced rutile. This was due to a particle size effect. The dandelion-like rutile had a relatively higher surface area which resulted in a high dispersion of the Ru specie relative to the thermally produced rutile. *In situ* PXRD showed that studies the dandelion-like supported catalyst showed better sinter resistance. This suggested this catalyst could be employed for use at high temperature reactions.

Carbon nanotubes were synthesized using CVD and a Fe-Co/CaCO<sub>3</sub> catalyst. Functionalization by acid refluxing removed the bulk of the residual catalyst. A microwave polyol catalyst preparation technique was employed and compared with the traditional impregnation method. Ru particle sizes could be tuned by altering the microwave temperature used on and the time without increasing metal loading or calcination by conventional heating. These Ru particles were observed to have a very narrow size distribution which could not achieved by the impregnation preparation method. Smaller particles also yielded the highest activity. The carbon supported Ru catalyst showed that it promoted the reverse water gas shift reaction alongside CO methanation, which was an undesired reaction.

To address the issue high reverse water gas shift activity the effect of modifying the carbon nanotube support by doping with nitrogen in the carbon nanotube domains or by coating the carbon nanotubes with titania nano anatase to form NCNT-TiO<sub>2</sub> and CNT-TiO<sub>2</sub> was

undertaken. The nitrogen doping was achieved *via* a CVD process by bubbling a carbon source through acetonitrile. The coated CNTs were also made by a hydrothermal method using titania butoxide as anatase source this same method generated nano anatase in the absence of CNTs. The incorporation of nitrogen into the CNTs compromised the thermal stability of the support i.e. it decomposed in air at much lower temperatures than found for the un-doped CNTs. The thermal stability was significantly improved after it was coated with nano TiO<sub>2</sub> anatase and the effect was explained as the TiO<sub>2</sub> shielding carbon from the oxygen. BET analysis also revealed that modifying the CNTs improved the surface, especially the NCNT-TiO<sub>2</sub> and CNT-TiO<sub>2</sub> composites. It was noted that N-CNTs had a high defect content which increased anchorage sites for active metal species. The pyridinic nitrogen found on the surfaces also served as anchorage site as well as donating extra electrons to the Ru which increased the back bonding leading to a higher rate of methanation than found for the un-doped CNT as support. The coated sample had a relatively higher surface area with smaller Ru particles and well dispersed and showed a higher methanation activity than the anatase support. Coating significantly retarded the reverse water gas reaction and this was attributed to the presence of the TiO<sub>2</sub> covering the NCNTs and CNTs.

Carbon spheres were hydrothermally synthesized from sucrose. This spheres were mono dispersed, with mesopores and had a high surface area after annealing at 900 °C for 4 h. A portion of the spheres were functionalized (acid treated HNO<sub>3</sub>) to modify the surface of the spheres. The functionalized spheres was observed to have slightly larger pores sizes due to the high defects in the carbon matrix as revealed by Raman analysis and recorded a high surface area than the un-functionalized from BET data. The impregnated Ru catalyst on the un-functionalized support showed poor dispersion and larger agglomerated Ru particles which was reverse for the functionalized support. It was attributed mainly to the absence of functional groups such as OH. Another catalyst was prepared using the functionalized support made by the microwave polyol technique. This catalyst demonstrated good dispersion of the Ru and had a very narrow Ru size distribution which made it more effective for methanation reaction than the impregnated sample. Even though the un-functionalized catalyst showed low catalytic activity it did not promote reverse water gas reaction as seen in the other catalyst.

## 8.1 Recommendations

This study focused on reformates gas composition without steam. It is highly recommended further studies be done that focuses on the addition of steam to the CO (CO/CO<sub>2</sub>) see if the catalyst behavior under the present experimental conditions is enhanced.

The carbon supports demonstrated that they promote the reverse water gas shift reaction which occurred at the same time as the selective CO methanation reaction. To understand the exact role played by the carbon support in the reverse water gas shift, this catalyst should be subjected to TGA-MS studies to monitor and quantify the possible amount of CO emerging from catalyzed oxidation reaction on the carbon supports to be sure if excess CO generated is not from the oxidation reaction. Attention should be paid to in situ IR (DRIFT) to unravel the mechanism involving the support toward reverse water gas shift reaction.

Further studies using both high resolutions TEM and the normal TEM should be conducted to reveal actual size distribution of Ru particles on the individual components in the TiO<sub>2</sub> and NCNTs /CNTs composites. To gain better understanding of the reduction behaviour of Ru/TiO<sub>2</sub>-A (which was unexpectedly reduced at lower temperature), NCNTs/CNTs and its composites (CNT-TiO<sub>2</sub> and NCNT-TiO<sub>2</sub>), TPR studies should focus on experiment using the same catalyst bed height to eliminate the possibility of density affecting the reduction profile. Again to confirm the presence of functional groups altered the reduction temperatures of Ru/NCNT and Ru/CN. This can possibly be achieved by;

1. Diluting Ru/TiO<sub>2</sub>-A catalyst with SiC to achieve the same catalyst bed height with the carbon supported catalyst.
2. Calcining the NCNTs/CNTs under nitrogen at relatively elevated temperatures (400 to 500 °C to remove functional groups or calcine the Ru loaded support at similar temperatures also under nitrogen.

