

Final stage CO removal by oxidation or hydrogenation using supported PGM catalysts for fuel cell applications

By

ZIYAAD MOHAMED

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University of KwaZulu-Natal
Durban
South Africa

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As the candidate's supervisor/s I have approved this thesis/dissertation for submission.

Signed: _____ Prof. H.B. Friedrich Date: _____

Signed: _____ Dr. S. Singh Date: _____

ABSTRACT

Hydrogen has recently become a promising alternative fuel for small scale energy generation with the aid of fuel cells. The most preferred method for on-board production of pure hydrogen from methane is through a series of catalytic reactions. However, prior to entering the fuel cell stack, the CO concentration in the reformat gas must not exceed 10 ppm. Concentrations of CO greater than 10 ppm poison the Pt anode which results in the loss of activity and, the power output. Post water-gas shift reaction, two methods show promise for the effective CO removal to the desired levels of less than 10 ppm. In the first method, known as preferential oxidation (PROX), CO is oxidized to CO₂, whereas in the second method, known as selective methanation (SMET), CO is hydrogenated to CH₄. The catalysts for these reactions must be highly active and selective for the specific reaction (CO oxidation and/or CO hydrogenation), since unwanted side reactions could result in the additional loss of hydrogen.

This study presents the synthesis, characterization and testing of Pt, Ir and Ru supported on reducible oxides, TiO₂ and ZrO₂, for both the oxidation and hydrogenation of CO in H₂ rich streams. The effect of synthesis methods (wet impregnation and deposition precipitation), controlling the isoelectric points of the supports, the nature of the active metals (metal dispersion, particle sizes, CO chemisorption capacities) and the metal support interactions were investigated. The catalysts were characterized by ICP-OES, BET, XRD, XPS, temperature programmed studies, FTIR-CO, CO chemisorption and HRTEM. Catalytic testing of these materials included CO oxidation, CO oxidation in the presence of H₂ and the hydrogenation of CO in dry and realistic water-gas shift reformat feeds.

All the catalysts showed appreciable activity for the total oxidation of CO below 200 °C, but in the presence of H₂, the activity decreased significantly. The Pt and Ir catalysts, although showing low CO conversions, favoured the undesired oxidation of H₂, which was due to the strong metal support interactions of these materials, resulting in higher H₂ spillover on the supports, reducing them and thus forming H₂O. The Ru systems showed slightly better activity but tend to simultaneously hydrogenate CO and oxidize it, which is not selective or desired since increased H₂ consumption takes place.

CO hydrogenation, on the other hand, showed promising results for all the catalysts in the dry reactions. However, the Pt and Ir systems tested with realistic water-gas shift feeds, which included CO₂ and H₂O, favoured the forward and reverse water-gas shift reaction, as well as CO₂ hydrogenation. The Ru systems showed the best activity towards the selective methanation of CO with realistic feeds at a temperature 100 °C lower than the Pt and Ir systems, giving 99.9 % CO conversions and 99.9 % selectivity towards CH₄. CO₂ methanation was only observed once all CO in the feed was converted. The superior results of the Ru systems were attributed to the active metal which has a lower heat of CO adsorption and a higher CO dissociative adsorption energy compared to that of Pt and Ir. The CO content in the feed stream was effectively reduced to less than 10 ppm over the Ru catalysts which is crucial for fuel cell applications.

PREFACE

The experimental work described in this thesis was carried out in the School of Chemistry and Physics, University of KwaZulu-Natal, Westville Campus from June 2013 to December 2015, under the supervision of Prof. Holger B. Friedrich and the co-supervision of Dr. Sooboo Singh.

This study represents original work by the author and has not otherwise been submitted in any form for any degree or diploma to any tertiary institution. Where use has been made of the work of others, it is duly acknowledged in the text.

Ziyaad Mohamed

B. Sc (Honours)

M. Sc (Chemistry)

PLAGIARISM

I, Ziyaad Mohamed, declare that:

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PUBLICATIONS

1. **Publication 1:** Comparative studies for CO oxidation and hydrogenation over Pt supported catalysts prepared by different synthesis methods
Ziyaad Mohamed, Venkata DBC Dasireddy, Sooboo Singh and Holger B Friedrich*
Submitted for publication in Applied catalysis B: Environmental
2. **Publication 2:** TiO₂ and ZrO₂ supported Ru catalysts for CO mitigation following the water-gas shift reaction
Ziyaad Mohamed, Sooboo Singh and Holger B Friedrich*
Submitted for publication in Green Chemistry
3. **Publication 3:** The removal of CO present in the water-gas shift reformat gas over Ir-TiO₂ and Ir-ZrO₂ catalysts
Ziyaad Mohamed, Sooboo Singh and Holger B Friedrich*
In preparation for publication in International Journal of Hydrogen Energy

Contribution by authors

Holger B. Friedrich acted as research advisor and Sooboo Singh acted as co-supervisor.

Venkata D.B.C. Dasireddy assisted with the interpretation and the elucidation of XPS and FTIR-CO analyses and results.

All data generation, experimental work and its interpretation was carried out by me (Mr. Ziyaad Mohamed) and those who have assisted have been duly acknowledged.

CONFERENCE CONTRIBUTIONS

Parts of this work have been presented at conferences as detailed below:

1. **Poster presentation**, Catalysis Society of South Africa (CATSA) conference, Wild-coast Sun, RSA, November 2013, titled “The synthesis and characterization of supported PGMs for fuel cell applications”.
2. **Poster presentation**, International Syngas 2 convention, Cape Town, RSA, April 2015, titled “Hydrogen clean-up using precious metal catalysts following the water-gas shift reaction for fuel cell applications”.
3. **Poster presentation**, 24th North American catalysis society (NAM) conference, Pittsburgh, USA, June 2015, titled “Selective Oxidation and Hydrogenation of CO over precious metal catalysts for fuel cell applications”.

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"Glory be to You, we have no knowledge except what You have taught us. Verily, it is You, the All-Knower, the All-Wise."

(The Quran, 2:32)

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DEDICATION

My loving parents Akbar and Jamila Mohamed, and daughter Laylah Mohamed

ABBREVIATIONS

Å	: Angstrom
atm	: Atmosphere
BE	: Binding energy
BET	: Brunauer-Emmett-Teller
BDDT	: Brunauer-Deming-Deming-Teller
eV	: electron Volts
EDX	: Energy-dispersive X-ray spectroscopy
FTIR	: Fourier transformed infrared
GC	: Gas chromatography
GHSV	: Gas hourly space velocity
g	: gram
h	: hour
HySA	: Hydrogen South Africa
ICP-OES	: Inductively coupled plasma-optical emission spectroscopy
IEP	: Isoelectric point
kPa	: kilopascal
kV	: kilo-volts
L	: litre
LH	: Langmuir Hinshelwood
μ	: micron
mA	: milliamperes
mbar	: millibar
mg	: milligram
mL	: millilitre
M	: Molar (concentration in mole per litre)
MvK	: Mars and van Krevelan
nm	: nanometre
POX	: Partial oxidation
ppm	: parts per million
PSD	: Pore size distribution
PGM	: Precious group metal
PROX	: Preferential oxidation
PEMFC	: Proton exchange membrane fuel cell
RT	: room temperature
RWGS	: Reverse water-gas shift
SEM	: Scanning electron microscopy

SMET	: Selective methanation
SMSI	: Strong metal-support interaction
SR	: Steam reforming
TP	: Temperature programmed
TCD	: Thermal conductivity detector
HRTEM	: High resolution transmission electron microscopy
Vol	: volume
W	: watts
WGS	: Water-gas shift
wt	: weight
XRD	: X-ray diffraction
XPS	: X-Ray photon spectroscopy
λ	: wavelength
λ Value	: CO:O ₂ mole ratio of 1:0.5

DEFINITIONS AND CALCULATIONS

1. Gas hourly space velocity (GHSV):

GHSV of a reaction is calculated by using the following equation

$$GHSV (h^{-1}) = \frac{\text{Total flow rate in to the reactor}}{\text{Volume of the catalyst used}} \times 60$$

2. Conversion:

Conversion of substrate (i.e. CO/O₂/H₂/CO₂) is calculated by using the following equation

$$\text{Conversion (mol \%)} = \frac{\text{Moles of substrate in} - \text{Moles of substrate out}}{\text{Moles of substrate in}} \times 100$$

3. Selectivity:

Selectivity of a product is calculated by using the following equation

$$\text{Selectivity (mol \%)} = \frac{\text{Total moles product}}{\text{Total moles of all products}} \times 100$$

4. Carbon balance:

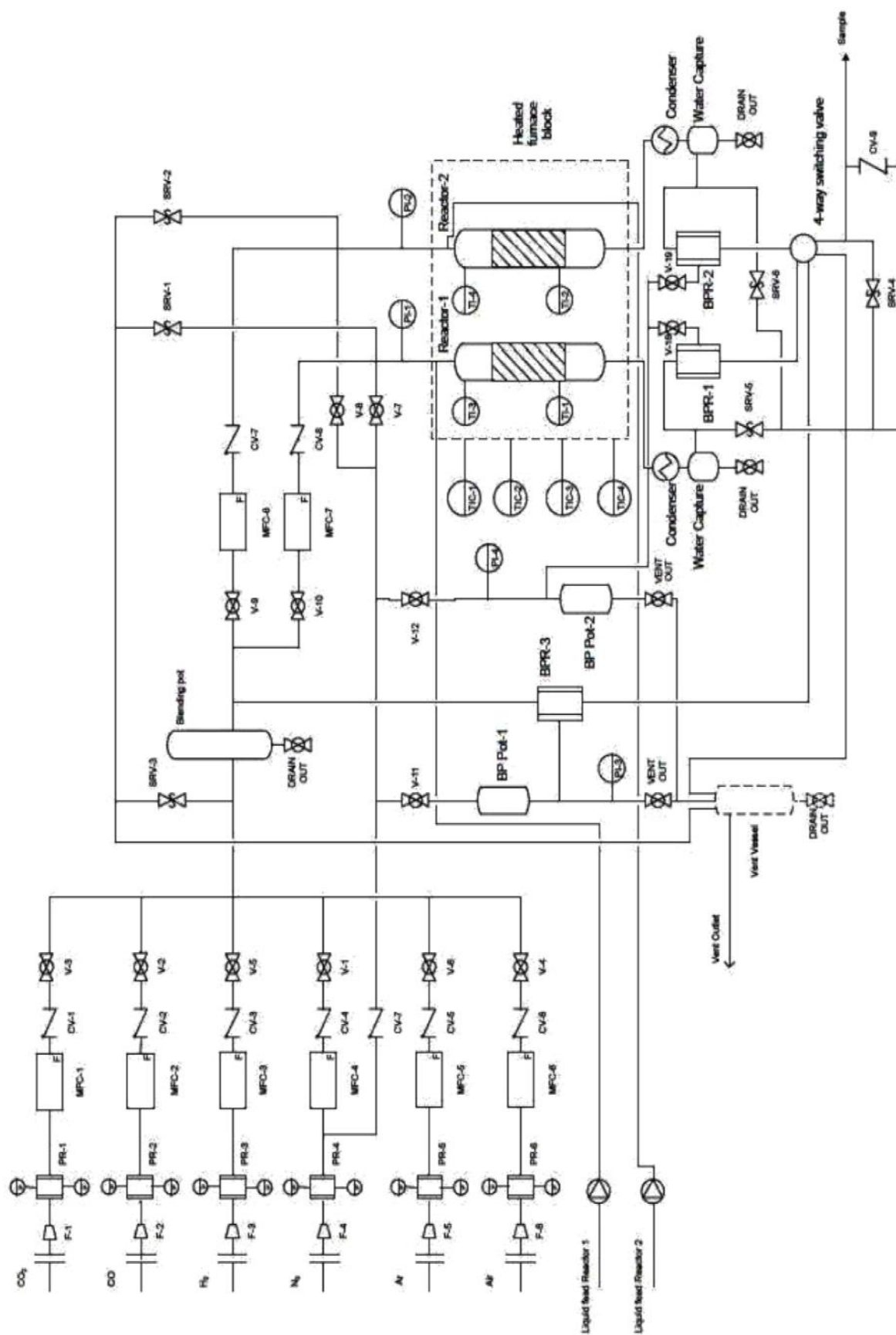
$$\text{Carbon balance} = \frac{\text{moles of carbon in}}{\text{moles of carbon out}} \times 100$$

The equation was modified to calculate O₂ and H₂ balances

TEST UNIT USED FOR THE CATALYTIC TESTING



TEST UNIT SCHEMATIC



Keys: V= Valve PR= Pressur regulator MFC= Mass flow controller BPR= Back pressure regulator CV= Check valve SRV= Safety release valve BP= Back pot TI= Temperature indicator

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CHAPTER 1

Introduction and literature survey

1.1. Background

The “man in the street”, who is a non-chemist, would likely consider a catalyst as something that is associated with the catalytic converter of a vehicle. Indeed, an automotive exhaust converter is a triumphant application with regards to catalysis. However, besides an automobile making use of this important application, catalysis has a broader scope than only pollution abatement. Living matter, for example, relies primarily on enzymes which are also catalysts by nature. The chemical industry, on the other hand, would not function without the existence of a catalyst which is a vital component in production facilities [1]. This field for scientists is multidisciplinary and extremely challenging. So, what is a catalyst? A universal definition of this term “catalyst” does not really exist, but an acceptable definition would be, “a substance that enhances the rate of a chemical reaction/system that is approaching equilibrium, without itself being consumed by the reaction” [2].

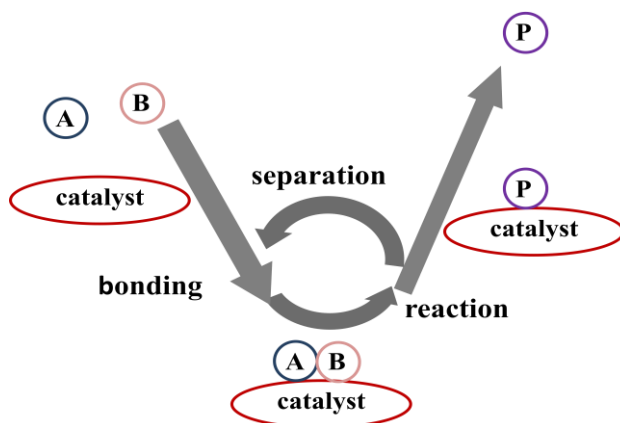


Figure 1.1: Steps involved in a catalytic reaction adapted from Chorkendorff and Niemantsverdriet, Concepts of modern catalysis and kinetics [1].

Following the steps of a catalytic reaction that takes place between molecules A and B, generating the product P (Figure 1.1.), the cycle usually commences with A and B adsorbing on the surface of the catalyst [1]. These then react with each other generating product P that is still

adsorbed on the catalyst. The final step involves the separation of product P from the catalyst which then (in its original state) exits the reaction cycle.

Many industrial processes such as the production of petrochemicals, bulk chemicals and pollution abatement involve some type of catalyst [3]. Currently the production of greenhouse gases has risen drastically due to automobiles, power stations and industrial plant exhaust systems. Therefore, catalysts are involved in reducing the gas emission from these sources. This study focuses on the mitigation of CO using heterogeneous catalytic systems.

1.1.1 The heterogeneous supported catalyst

Catalysts employed for heterogeneous catalytic reactions usually consist of a support and an active metal centre [4]. The support is generally present in higher amounts to the active metal and should be stable under both reaction and regeneration conditions. Metal oxides are used as supports because they have suitable physical, chemical and thermal properties with regards to electronic conductivity and hardness [5]. These types of supports allow for high dispersions of the active metal or active metal oxide components. This, together with their high abundance and cost efficiency, make metal oxides important in catalyst design. Of particular importance are the reactivity and interface properties of oxide surfaces that have been studied in relation to the presence of defects, such as oxygen vacancies created by strong metal support interactions [6, 7]. These defects could either reduce or improve the catalytic properties of the materials, depending on the specific reaction and the types of reactants present [6].

This study focuses on the inorganic supports, titania (TiO_2) and zirconia (ZrO_2) which provides ideal chemical and mechanical properties when used as supports for various reactions [6]. It is accepted that for TiO_2 and ZrO_2 , as supports for PGMs, the activity and selectivity enhancements are due to strong metal-support interaction (SMSI) effects [8-11]. These interactions alter the metal distribution and particle size of the catalyst, impacting on its activity, stability and selectivity. Other factors that are known to influence catalytic properties include the preparation methods and pre-treatments of the materials [8, 12]. ZrO_2 , commonly used in the three way automotive catalyst formulation for its oxygen storage capacity, is not as easily reduced as TiO_2 [13, 14]. However, when used as a support, compared to TiO_2 , it presents better mechanical and

thermal stability and its surface allows good metal dispersions when using ideal metal precursors [9, 15].

PGMs have received increasing attention as effective active metals due to their exceptional physiochemical properties and their application in catalysis [16]. The supported catalyst should be highly active for the particular process in which it is utilized, being easily reproducible, show high selectivity and stability for the desired product and process and it should be able to regenerate effectively if any deactivation should occur [5, 17]. This study focuses on Pt, Ir and Ru as active PGMs that are supported on TiO₂ and ZrO₂ for CO clean-up.

1.1.2 Oxidation catalysis

Oxidation is defined as the gain of an oxygen atom, loss of electron(s) or loss of hydrogen [18]. Oxidation reactions play vital roles in a majority of industrial processes as they account for more than 60 % of all chemicals synthesized through catalytic pathways. Centi et al. [19] reported that oxidation catalysis accounts for a net worth of between 20 – 40 billion dollars per annum. The oxygen source for this reaction is usually introduced into the feed as air. This reaction also plays a vital role in the automobile, chemical and power industries in mitigating the concentration of environmentally harmful pollutants, subsequently converting them to eco-neutral or less harmful emissions. PGMs are effective candidates for catalyzing these reactions, often showing excellent activity and stability [20-24].

1.1.3 Hydrogenation catalysis

Hydrogenation catalysis also plays a very important role in many catalytic fields of interest. An example would be the hydrogenation of α,β -unsaturated aldehydes to generate unsaturated alcohols that are used for the production of food, chemicals, fragrances, and pharmaceutical precursors [8, 25-27]. Many research efforts on these hydrogenation reactions have been primarily focused on supported catalysts involving PGMs [25, 27, 28]. Hydrogenation occurs via a reduction reaction which results from the addition of hydrogen. Recently, CO mitigation by this route to produce energy sources such as methane, methanol or other raw materials of C (1) chemistry via its interaction with hydrogen is of great interest [29].

1.2 Hydrogen: The future source of energy

Being the most abundant element on earth and in the universe, hydrogen is widely considered a promising fuel of the future, since it exposes high power density, deliverability and cleanliness [30-32]. The hydrogen economy typically involves hydrogen production, delivery and distribution, conversion and storage [30]. In transition to this economy, the first step is to develop a process that produces clean hydrogen from a variety of potential energy sources such as biofuels or fossil fuels [33]. This, currently, is of great interest globally and hydrogen is predicted to be the major energy carrier for the future [33-35]. This long-term project could change the current energy system to one that attempts to combine the cleanliness of hydrogen to the generation of energy with the aid of fuel cells (FCs) [21, 31, 36, 37].

Hydrogen is usually obtained from energy sources such as natural gas, gasoline or alcohols [33, 38]. For this future energy supply, three requirements must be fulfilled, viz. environmental protection, security in the energy supply, and the utilization of energy sources that promote the economic growth of societies [36]. For hydrogen production, amongst all current technologies, steam reforming is the major source of the world's total hydrogen, producing 80-85% of the hydrogen from natural gas [33, 39, 40]. Hydrogen is used in the chemical industries as a raw material in large quantities for processes such as methanol and ammonia synthesis [33, 40, 41].

While the hydrogen economy is still developing, safe and efficient storage has been identified as a major technological barrier when used for small-scale applications, such as transportation systems [21, 31, 38]. The on-board production of hydrogen could overcome this storage problem [21, 38, 42]. Reforming of natural gases, especially CH_4 , has been widely used due to its cleanliness, availability and ease of conversion to produce hydrogen [33, 43, 44]. Hydrogen production for fuel cell application is usually accomplished by a series of catalytic steps which include; steam reforming (SR), partial oxidation (POX), auto-thermal reforming (ATR) and water-gas shift (WGS) [21, 22, 31-33, 43].

1.3 Fuel cell technology

Fuel cell technology was discovered more than 100 years ago by Sir William Grove and Christian Friedrich Schoenbein. A fuel cell is an electrochemical device that converts chemical

energy directly into electrical energy. It has potential for highly efficient power generation through a potentially renewable and non-polluting route compared to other technologies [45-47]. This technology also avoids the thermodynamic mechanical cycle losses that are experienced by combustion in conventional power generations [22]. There are many fuel cells available and these are classified on the basis of the electrolyte employed [48]. Amongst these various fuel cell technologies, the development of the proton exchange membrane fuel cell (PEMFC) has rapidly accelerated during the last few years, becoming the primary candidate for elevating the commercial possibilities of producing cleaner and more efficient power for small scale applications [22, 49].

1.3.1 Proton exchange membrane fuel cells

Proton exchange membrane fuel cells (PEMFCs) are known to be superior over other fuel cells, offering high power outputs, fast start-up, dynamic response times with virtually little or no emissions of harmful pollutants [31, 35, 50]. PEMFCs utilize hydrogen as the fuel, which is known for offering maximum energy density (per unit mass) and the maximum cell voltage that can be derived in comparison to other fuels [51]. The fuel cell consists of a conducting polymer electrolyte membrane located between the two electrodes (Figure 1.3). Reactants are transported either by convection or diffusion to the electrode surfaces containing the catalyst. These act as a barrier between the bulk gas phase and the electrolyte. The electrode surfaces also provide the sites where oxidation and reduction reactions occur.

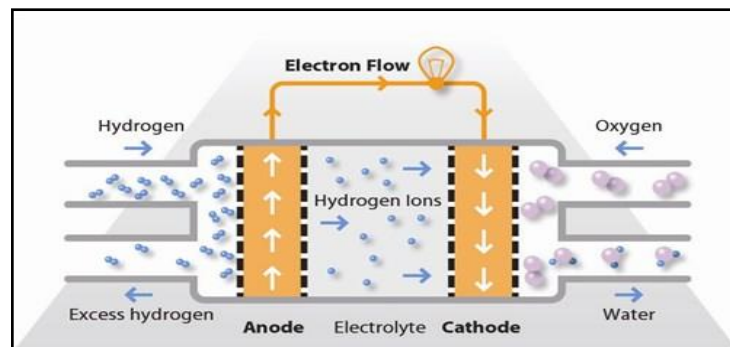
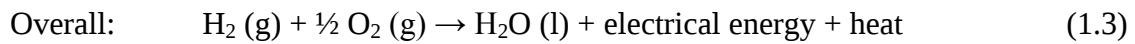
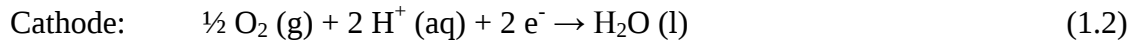


Figure 1.3: A typical fuel cell design [50] (not copyrighted).

Hydrogen is initially oxidized to produce hydrogen ions and electrons at the anode. These hydrogen ions then pass through the proton conducting electrolyte and the electrons through an

external circuit. The primary function of the electrolyte is the selective transport of hydrogen ions from the anode to cathode. At the cathode, the hydrogen ions, electrons and oxygen combine to produce water and waste heat which is constantly transported away from the cathode. Accordingly, the overall cell reaction in a PEMFC is the combination of hydrogen and oxygen to produce electricity, heat and water [34, 45] (Eqs. 1.1 – 1.3):



There are two major sources for producing hydrogen for PEMFCs, these are fossil fuels through reforming of natural gas or gasoline, coal gasification or partial oxidation of methanol [30, 33] and electrolysis of water [52]. However, at present hydrogen production for PEMFCs is mainly based on reforming of natural gas comprising of: SR, ATR, POX followed by the WGS reaction [32]. Electrolysis of water for hydrogen production is an alternative that offers a sustainable energy cycle and a clean source of hydrogen, however, it is not cost effective [52].

1.4 Reforming of hydrogen for the PEMFC

The reforming processes that have been proposed for the production of pure hydrogen from fossil fuels, such as natural gas or gasoline, are listed in Table 1.1 [41, 49, 53-55].

Table 1.1: Characteristic processes for hydrogen production from fossil fuels

Process	Feedstock	Temperature (°C)	Catalyst
Steam Reforming	Light hydrocarbons	500-900	Ni/ceramic support
Partial Oxidation	Light hydrocarbons	950-1050	Rh/ceramic support
Auto-Thermal Reforming	Light hydrocarbons	700-1050	Ni/Rh ceramic support
Water-Gas Shift	Syngas	230-500	Fe/Cr/Cu/Zn ceramic support

1.4.1 Steam reforming

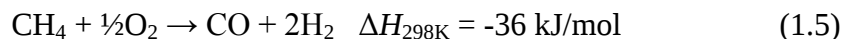
At present, steam reforming of hydrocarbons is the preferred process for industrial hydrogen production [32, 33, 56]. Methane has been proposed as a good source for hydrogen because of its availability, relatively low cost and because it can be easily processed [21, 32]. The process involves the conversion of two very stable molecules, water and methane, thus requiring the supply of heat [53] (Eq. 1.4). The reaction is known to generate high H₂/CO ratios and is highly endothermic for the production of hydrogen as a fuel [43].



Catalysts for this type of reaction are exposed to both high temperatures and steam partial pressures. Therefore, they must have high mechanical and thermal stability [53]. Ni catalysts are mostly employed for steam reforming reactions, since they are capable of withstanding these extreme conditions [43].

1.4.2 Partial oxidation

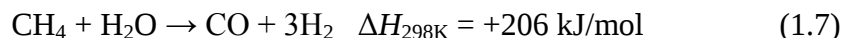
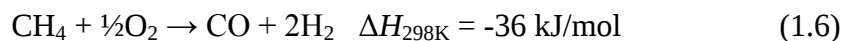
Partial oxidation is known to generate much lower H₂/CO ratios and is not as endothermic as steam reforming [43]. Here, the heat is provided by the partial combustion of the hydrocarbon, eliminating the need for a complex heated reactor system [53] (Eq. 1.5).



In this system, the hydrocarbon feedstock is mixed together with air (oxygen) and fed to the catalyst, which is usually rhodium [53, 54].

1.4.3 Auto-Thermal reforming

Auto-Thermal reforming is regarded as the best fuel processing option after steam reforming in terms of efficiency and heat integration within the PEMFC system [49]. This alternative process to generate hydrogen is a hybrid of steam reforming and partial oxidation of methane adiabatically to produce suitable H₂/CO ratios, and it does not require externally supplied energy (Eqs. 1.6 and 1.7) [43, 57]. The system allows for lower temperature operation, hence a low amount of oxygen is required [53].



Catalysts employed for this reaction are Ni based which are capable of withstanding the harsh operating conditions. The Ni based catalysts are often promoted with one or more of the PGMs, where Rh is most commonly used [43, 53, 57].

1.4.4 Water-gas shift

This reaction is applied for further conversion of syngas in order to increase cleaner hydrogen yields [58, 59]. The reaction is well established in hydrogen and ammonia production plants [41]. Recently, a renewed interest has emerged using this reaction for fuel cell applications [41, 58]. The reaction (Eq. 1.8) is usually carried out over Fe-Cr or Cu-Zn based catalysts [30, 53]. These reactions, in association with the former and latter catalysts, are referred to as the high temperature (HT) WGS, operating between 250-450 °C, and low temperature (LT) WGS, operating between 200-250 °C, respectively [30, 41, 60].



The WGS process utilizes the reaction between CO and H₂O to produce hydrogen [1], however, due to the thermodynamic limitation of the WGS reaction, trace amounts of CO (0.5-1 %) are still present in the outlet stream and could adsorb onto the platinum anode, decreasing the fuel cell efficiency [38, 61]. This results in significant loss of catalytic activity and power output of the fuel cell. Long term exposure to CO leads to electrode degradation, commonly referred to as CO poisoning [51]. Even trace amounts of CO (ppm levels) have been demonstrated to easily poison the Pt anode, and eliminating these traces to sub-ppm levels i.e. less than 10 ppm at the Pt anode in the hydrogen stream with minimal hydrogen loss is necessary [51, 61-63].

Since the conversion of CO is thermodynamically limited to levels of about 0.5–1%, further treatment for purifying the hydrogen stream is essential [21, 38]. To achieve this high purification level, various physical and chemical methods have been considered and are now being assessed for application [38].

1.5 Purification of the reformat

Technologies developed for the final cleaning process step to reduce the CO concentration to sub-ppm levels include membrane separation, pressure swing adsorption, selective methanation and preferential oxidation [31, 55, 62, 64].

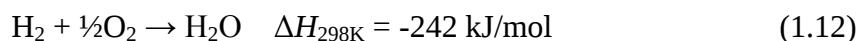
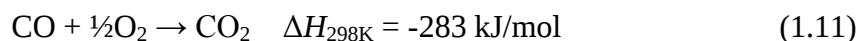
Pressure swing adsorption is more applicable to stationary fuel processing systems [31], utilizing multiple reactor vessels and pressurization. These require additional compressors to re-humidify H₂ prior to being used in the fuel cell, and a desiccant for adsorbing H₂O from the inlet wet gas stream [64].

Membrane separation also offers the possibility of producing clean H₂, but is coupled to the expense of high operating temperatures and very costly materials [64]. Together with this, the technique current cannot reduce the CO concentration to the desired levels suitable for the PEMFC.

Two promising techniques showing great potential for final CO cleanup following the water-gas shift reaction are the preferential oxidation and the selective methanation reactions. These offer ease of implementation, especially for on-board reforming of hydrogen [21, 62].

1.6 Preferential oxidation of CO

This technique of removing trace amounts of CO contaminants in H₂ rich streams is effective and offers ease of implementation, due to the small size, light weight, simple design, reliability and safety of the reactor for on-board fuel processing [37]. With regards to on-board application, the preferred operation temperature should ideally be within the range of the low water-gas shift exit temperature (± 250 °C) and that of the PEMFC operating temperature (± 80 °C) [61]. The reactions that take place in the preferential oxidation (PROX) reactor are shown below [45] (Eqs. 1.11 – 1.13):



These reactions should be closely monitored during the process, since only the first reaction (Eq. 1.11), the oxidation of CO to CO₂ is desired [45]. This reaction is usually accomplished at lower temperatures. The undesired H₂ oxidation reaction (Eq. 1.12) is the main competitive reaction and occurs at high temperatures. It must be avoided to minimize loss of H₂, while reducing CO to acceptable levels [31]. The formation of H₂O leads to a decrease in the selectivity towards CO₂, and also inhibits the catalyst activity.

PROX usually requires minimal amounts of surplus air corresponding to a CO/O₂ ratio, also called the λ value, between 0.5 and 2 [21, 45]. Making use of these conditions and achieving full conversion of CO, approximately 0.5 to 3 moles of H₂ is essentially lost for each mole of CO converted [21, 45]. The last reaction that could occur in the PROX reactor (Eq. 1.13), where low concentrations of CO are found, is the reforming of CO over the catalyst in an O₂ deficient environment by the reverse water-gas shift reaction [45, 61].

Catalyst design for the PROX reaction is of great importance and choice of active metal critical. Some PGMs are known to methanate CO at higher temperatures in the presence of H₂ and this hinders the preferential oxidation of CO to CO₂ [65]. Also, in the reformat feed stream, CO₂ is present. This may prove detrimental since CO₂ could be methanated, leading to the loss of additional hydrogen [66].

1.6.1 Catalysts used for the preferential oxidation of CO

Pioneers of the PROX reaction, Oh and Sinkevitch [20], investigated the performance of a number of noble metals and PGMs supported on alumina. Also, some other transition metal based catalyst compositions were investigated for this reaction. Results showed that among all the catalyst types tested, the precious metals Pt, Ru and Rh were the best candidates with regards to selectivity towards CO₂. Following the work of Oh and Sinkevitch, many catalytic formulations have been screened for the PROX reaction and among all the metals, Au, Rh, Ru, Pt, Ir and Pd supported on Al₂O₃, MgO, CeO₂, ZnO, TiO₂ and SiO₂ were the better performing catalysts [21, 35, 63, 64]. In these investigations, high CO oxidation rates together with high selectivity within the desired temperature ranges were obtained [67]. Based on the findings of these reports, Pt-Al₂O₃ catalysts seem to be the most promising for the PROX reaction, with

loadings above 1 wt. % the most active. The reducibility of well dispersed active sites on Al_2O_3 , however, remains a challenge.

Marino et al. [38] reported that Pt catalysts are the most comprehensively studied catalyst, compared to Au catalysts that are highly active at low temperatures (lower than 40 °C) for most reactions due to gold's weak interactions with most adsorbates. They studied a series of materials containing Pt, Ir, and Pd (2-3 wt. %) supported on CeO_2 , $\text{CeO}_2\text{-ZrO}_2$ and Al_2O_3 prepared by wet impregnation. Pt and Ir were found to be the most effective metals using a feed composition of 75 % H_2 , 2 % CO and varying quantities of O_2 . However, achieving low CO concentrations could not be accomplished over all these catalysts. Maximum CO conversions obtained were at 225 °C using $\lambda = 4$ and the CO concentration in the effluent gaseous mixture reduced to 700 ppm. These findings show that Pt catalysts are promising for CO oxidation in H_2 streams, but the undesired H_2 oxidation which occurs at higher temperatures needs to be avoided. Using lower Pt loadings could prove more cost effective in the long run. However, varying the O_2 concentration above that of 1 CO: 0.5 O_2 , could result in unwanted H_2 loss.

It was recently reported that mono-metallic Pt catalysts exhibit PROX activity only above 150 °C [21]. Catalytic activity at these temperatures increased with increasing O_2 content in the feed stream. The Pt- Al_2O_3 catalyst showed highest CO conversion of 56 % and 68 % selectivity toward CO_2 at 200 °C. Doping a NiO- Al_2O_3 catalyst, that showed very low activity, with 0.5 wt. % Pt (Pt-NiO- Al_2O_3) revealed synergistic effects, leading to a much higher CO conversions compared to both the mono-metallic catalysts. The highest CO conversion, of 99.9%, for this catalyst was at 200 °C, with a selectivity of 72.8% toward CO_2 using a C: O_2 ratio of 1:2. However, in obtaining these high conversions, the amount of O_2 that was additionally supplied to the reaction exceeded that of the stoichiometric ratio of 0.5 %. The cost of installing a device to additionally supply O_2 to the reaction isn't, ideally, recommended.

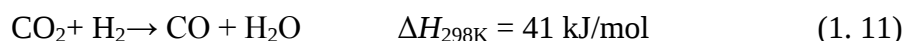
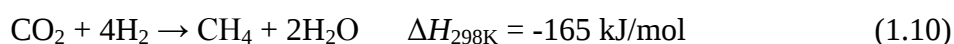
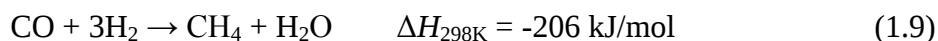
Other precious metal catalysts for the PROX reaction have also been studied and some of these catalysts show promise with increased stability and activity towards the reaction. Preparation methods, choice of metal precursors and reducibility of the support used for these catalysts are of key importance to give well dispersed active catalysts.

A study by Huang et al. [68] on supported Ir catalysts using a feed composed of 2 % CO, 1 % O₂ and 40 % H₂ evaluated the effects of catalyst preparation method, Ir loading, pre-treatments and the use of various supports such as CeO₂, Al₂O₃, TiO₂ and MgO. Results showed that the deposition method yielded highly active Ir-CeO₂ catalysts after reductive pre-treatment. The best activity was obtained over a catalyst containing 1.6 wt. % Ir, of 70 % at 80 °C with 70 % selectivity towards CO₂. Increasing the temperature resulted in a decrease in both CO conversion and CO₂ selectivity. Also, considering the amount of CO (2 %) and H₂ (40 %) used, effectively the conversion still remains low, since the concentrations do not optimally reflect the exit gas from the WGS reaction and the stability of these catalysts decrease rapidly with time. Water in the feed showed no noticeable influence on the catalytic activity, however, CO₂ in the feed negatively affected the performance of the catalyst. Thus, Ir showed promising activity for the reaction but the influence of the support could have negatively affected the performance. Consequently using other supports, such as ZrO₂, could improve the stability and performance of the material by tailoring the preparation methods to obtain well dispersed Cl⁻ free active sites.

Di et al. [69] synthesized a series of PGM supported on TiO₂ materials by the photo-deposition method. Amongst all catalysts, Ru-TiO₂ exhibited highest catalytic activity and revealed that the catalyst preparation method and pre-treatment conditions impact on performance. Characterization data revealed that surface reconstruction occurring during the pre-treatments could enhance performance. Isolated Ru⁰ species were identified as the preferred active sites, with linear mono-carbonyls on these Ru species being the key reaction intermediates in the PROX reaction. They associated the characterization with the catalytic results and proposed that the mechanism for PROX over this catalyst was: $\text{Ru} + \text{CO} \rightarrow \text{Ru-CO}$; $\text{Ru-CO} + \text{O}_2 \rightarrow \text{Ru-O} + \text{CO}_2$; $\text{Ru-O} + \text{H}_2 \rightarrow \text{Ru} + \text{H}_2\text{O}$. However, the feed composition used contained 1 % CO, 1% O₂ and 60 % H₂. Firstly, the amount of O₂ present exceeds the stoichiometric value and secondly, the catalyst containing 1 wt. % Ru on TiO₂ showed the best activity at 147 °C of 90 % and selectivity to CO₂ of 40 %. This indicated that H₂ oxidation was favoured over the best performing catalyst. Thus, Ru shows promising activity for the reaction and synthesizing materials with reducible supports (TiO₂ and ZrO₂) controlling the interaction of the metal and support could improve the catalytic activity for the PROX reaction.

1.7 Selective methanation of CO

Selective methanation (SMET) has also been identified as a reaction for lowering the CO levels in the reformat gas stream post WGS to acceptable levels. This reaction, unlike PROX, does not require an additional reactant. The reactants, H₂, CO₂ and CO are the products of the water-gas shift reaction [62, 70-72]. The selective methanation reactions are highly exothermic (Eqs. 1.9 and 1.10) [53, 73, 74]:



Obtaining high selectivity is important when eliminating CO by this reaction (Eq. 1.9), since simultaneous CO₂ methanation (Eq. 1.10) and the reverse water-gas shift (RWGS) reaction (Eq. 1.11) could consumed large amounts of H₂, as well as cause a temperature runaway in the reactor due to the highly exothermic nature of the CO₂ methanation reaction [62, 70, 73]. It is argued that a disadvantage of the reaction (Eq. 1.9) is that at 100 % selectivity to CO conversion, 3 moles of H₂ are consumed for every mole of CO removed. However, CH₄ produced is inert to the PEMFC and can be reused in the afterburner as a heating fuel [62, 70]. The H₂O is also required for cooling of the fuel cell stack and can also be recycled on-board [74].

1.7.1 Catalysts used for the selective methanation (SMET) of CO

Baker et al. [75] were among the first to report the selective CO methanation process. This was achieved by using Ru or Rh supported on Al₂O₃ to selectively hydrogenate CO in the presence of CO₂. However, during that early period, very low CO feed concentrations (less than 0.3 %) and low gas hourly space velocities (GHSV) were studied (500–2000 h⁻¹).

Dagle et al. [76], also reported CO removal over Ru based catalysts. The Ru metal loading and crystallite size were shown to affect catalyst activity and selectivity for the reaction. Results showed that when a GHSV of 13 500 h⁻¹ was employed, a 3wt. % Ru-Al₂O₃ catalyst with a crystallite size of 34.2 nm was capable of reducing the CO in the reformat gas to less than a 100 ppm over a wide temperature range (240 to 280 °C), keeping the hydrogen consumption under 10

%. The effect of preparation methods, crystallite size and metal loadings, on the performance of these Ru based catalysts was shown.

A study by Liu et al. [77] using a supported transition metal catalyst, Ni-ZrO₂, which was prepared by wet impregnation, investigated its activity and selectivity for the SMET of CO in hydrogen rich streams containing more than 20 vol % CO₂. Their results showed that the Ni loading significantly impacted the catalytic performances and a 1.6 wt. % Ni loaded catalyst showed the highest catalytic activity compared to all the other catalysts. The measured outlet CO concentration was reduced to less than 20 ppm and the hydrogen consumption was below 7 %, using a GHSV of 10 000 h⁻¹ and a temperature range of 260 to 280 °C. Characterization results indicated that on the ZrO₂ surface, if the Ni loading was less than 1.6 wt. %, even dispersions were obtained for these materials. When the Ni loadings were increased to 3 wt. %, free bulk NiO species started to assemble (agglomerate), which was not found to be favorable for increasing the selectivity of the catalyst.

Considering the activity of supported Ru and Ni catalysts for the SMET reaction, Tada et al. [78] recently reported results using both of these metals (varying wt. %) on a TiO₂ support. The bimetallic catalysts Ru-Ni-TiO₂ exhibited higher activity towards CO methanation at low temperatures and lower activity in CO₂ methanation at high temperatures than a mono-metallic Ru-TiO₂ catalyst. The best catalyst was a 0.2 wt. % Ru and 9 wt. % Ni-TiO₂. An increase in the Ru loadings, however, caused the RWGS reaction to be accelerated.

Increasing the selectivity of supported Ru catalysts for the SMET can be achieved in various ways, which include the use of different support materials such as Al₂O₃, TiO₂, SiO₂ [62] or by varying the particle size of the Ru [76]. The use of zeolites and other oxide supports were also investigated as promising alternatives to TiO₂ or Al₂O₃ [77]. These catalysts showed higher activity and selectivity for the SMET reaction compared to Ru-Al₂O₃ and Ru-SiO₂ catalysts, attributed to the strong metal-support interaction (SMSI) [79, 80]. Furthermore, other noble metals can also be investigated for activity that could be promising for this reaction.

From the literature, it is clear that developing a catalyst using low wt. % (± 1 %) PGMs (Pt, Ir, and Ru) supported on TiO₂ and ZrO₂, by tailoring the metal dispersions and metal support interactions could result in obtaining a highly active hydrogenation catalyst of relatively low

cost. These catalysts must effectively reduce CO concentrations to the desired low ppm levels (less than 10 ppm), and avoid unwanted RWGS and CO₂ methanation, with high stability.

Motivation and objectives of this study

Hydrogen as a future source of energy has become a promising alternative to conventional fuels. It is widely available, clean and can offer maximum power density as a fuel for fuel cell applications. It is evident that the vital component of the PEMFC's is the platinum based electrode which is poisoned by CO concentrations left in the gas feed after the production of hydrogen. Noble metals and PGM catalysts are currently emerging as promising candidates for the cleaning of hydrogen, producing an almost CO free feed for the PEMFC. These metals are known to show high activity and selectivity towards the oxidation and hydrogenation of CO.

According to the US Geological Survey [81], South Africa currently possesses more than 75 % of the world's known platinum reserves and also large quantities of other precious metals. Given the great potential use of PGM catalysts in fuel cells and the reforming steps for hydrogen production, participation in the growing hydrogen economy will enable the country to develop PGM based manufacturing activities. More importantly, numerous socioeconomic opportunities could be created to the benefit of its citizens. With this view, the South African Government has launched a major science and technology research, development and innovation strategy, which itself is embodied in the Hydrogen South Africa (HySA) program. The main focus of HySA is to generate income for the country by developing fuel cell technology. The ambition is that South Africa will supply at least 25% of the global requirement for PEM fuel cell catalysts in the near future.

The Hydrogen Catalysis Competence Centre at the University of Cape Town's Chemical Engineering Department is developing an on-board reformer together with the fuel cell stack. Their main focus is based on the stack design and the primary reforming techniques (steam reforming and water-gas shift). This study focuses on the exit gas from the water-gas shift reactor prior to entering the fuel cell itself.

At this early stage, developing a catalyst that can either oxidize or hydrogenate CO found in hydrogen and CO₂ streams is of great interest. The catalyst should be highly active and selective for these reactions, without undesired hydrogen consumption during the process. PGM catalysts are of increasing interest for many catalytic processes, since they can be used in much smaller quantities and show similar or better activity than many catalysts that don't use PGMs. PGM catalysts also often show excellent interactions with the supports used and this can be beneficial for the reactions. However, PGMs tend to be very expensive. Thus, using these highly active metals in lower quantities, and tailoring the synthesis methods to give catalysts with similar activity and better stability than their current higher loaded counterparts would improve cost effectiveness in the long run.

The objectives of the study are therefore:

Using reducible oxides TiO₂ and ZrO₂ with lower wt. % active metal, modifying the method of preparation giving well dispersed, easily reduced metal phases promoted by the strong metal-support interactions.

- To synthesize a low wt. % Pt supported on two reducible oxides (TiO₂ and ZrO₂) via two different preparation methods.
- To characterize these catalyst using various physisorption and chemisorption techniques, as well as temperature programmed studies, XRD, XPS and microscopy.
- To use the most appropriate synthesis technique and synthesize Ir and Ru (± 1 %) supported on TiO₂ and ZrO₂.
- To test these catalysts for the oxidation and/or hydrogenation of CO using a custom built reactor within the various required reaction temperature ranges in H₂ rich streams.

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Chapter 2

Comparative studies for CO oxidation and hydrogenation over Pt supported catalysts prepared by different synthesis methods

Ziyaad Mohamed, Venkata D.B.C Dasireddy, Sooboo Singh and Holger B. Friedrich*

Catalysis Research Group, School of Chemistry and Physics, University of KwaZulu-Natal,
Durban 4000, South Africa

Abstract

Pt supported on TiO_2 and ZrO_2 catalysts were synthesized via the wet impregnation and deposition precipitation methods and characterized by various physical and chemical techniques. The catalysts were tested for the removal of CO present in the reformat gas following the water-gas shift reaction for on-board fuel processors. The tests included the oxidation of CO to CO_2 , the oxidation of CO to CO_2 in the presence of H_2 (PROX), and the hydrogenation of CO to CH_4 . The influence of the synthesis methods, the redox properties of the supports, the nature of the active metal and the reaction conditions were evaluated on the catalyst activity and selectivity. Overall, Pt- ZrO_2 catalysts, regardless of the synthesis method, showed better metal dispersions, particle sizes and a lower degree of reduction than the TiO_2 catalysts. All the catalysts showed low activity for the oxidation of CO by the PROX reaction, since H_2 oxidation was favoured due to H_2 and O_2 spillover effects on the catalysts, resulting in H_2O formation. During the hydrogenation reaction, TiO_2 catalysts prepared by the deposition precipitation method showed better activity than the impregnated TiO_2 catalyst. However, ZrO_2 with its high reducing properties and strong metal-support interactions was found to be the more suitable support for hydrogenation of CO. Accordingly, ZrO_2 induced small well dispersed Pt particles that were shown to be the key parameters for the performance of the catalysts in the hydrogenation reaction. Both the Pt- ZrO_2 catalysts showed maximum CO conversions of over 99 % above 350 °C with high selectivities towards CH_4 (99 %). The CO concentration was effectively reduced to the desired ppm levels (<10 ppm) required for optimum fuel cell operation.

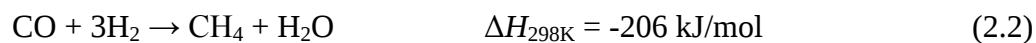
Keywords: Pt, CO, strong metal-support interactions, spillover, oxidation, hydrogenation

* Corresponding author: Tel.: +27 31 2603107, Fax.: +27 31 260 3091,

E-mail: friedric@ukzn.ac.za

2.1 Introduction

On-board reforming to produce hydrogen for fuel cell applications has received much attention during the last decade [1-3]. Proton exchange membrane fuel cells (PEMFCs), compared to other fuel cell systems, offer superior performance, ease of implementation and maximum power output using hydrogen as the fuel source [2, 4-6]. Hydrogen is usually obtained by steam reforming of fossil fuels, followed by partial oxidation and auto-thermal reforming, which is followed by high (300-500 °C) and low (200-300 °C) temperature water gas-shift (WGS) reactions for H₂ production [7-9]. However, following the subsequent WGS reaction the CO (±1 %) still remaining in the reformat gas is detrimental to the Pt anode of the fuel cell [1, 10]. This CO adsorbs strongly to the anode and poisons it, resulting in a loss of efficiency and hence decreasing its power output [2, 11]. A few methods have been postulated for removing these trace amounts of CO prior to entering the fuel cell. Each has their own advantages and disadvantages. Two reactions that currently seem to have greatest potential for removing this trace CO are the preferential oxidation (PROX) and selective methanation (SMET), which are shown below (Eq. 2.1-2.3) [1, 3-7, 12-15]:



In the first case PROX (Eq. 2.1), CO is oxidized to a less toxic green-house pollutant CO₂, whereas in the latter SMET (Eq. 2.2), CO is hydrogenated to CH₄. The major disadvantage in PROX is that the catalyst has to be highly active for the oxidation of CO and avoid the unwanted oxidation of H₂ which is a key competitive reaction (Eq. 2.3). Also, following the

WGS reaction for on-board reforming, extra O_2 has to be supplied for this reaction to proceed. Although the SMET does not require additional reactants, there is the situation where for every mole of CO converted, 3 mols of H_2 are consumed [3, 16]. However, considering the amount of CO present, only a very small fraction of the H_2 from the reformat gas will be consumed for this reaction. Also, the CH_4 produced can be recycled during the on-board reforming process [15, 17].

Previous work on PROX reactions were carried out using, Au, transition metals and PGMs supported on Al_2O_3 , MgO, CeO_2 , ZnO, TiO_2 and SiO_2 [1, 18-21]. The results of those studies showed that Au, Rh, Ru, Pt, Ir and Pd supported on these oxides were superior to all other catalyst formulations based on the CO oxidation rates and selectivity towards CO_2 within the desired temperature ranges. However, in terms of stability and activity, Pt- Al_2O_3 was the most promising for these reactions in the presence of H_2 .

Most of the studies involving the hydrogenation of carbon oxides to CH_4 use mainly catalysts where Ni, Ru and Rh are supported on various metal oxides [15, 16, 22-24]. Vannice [23] reported that for CO hydrogenation, the specific activity of Ru- Al_2O_3 was about one order of magnitude higher than that of Rh or Pd supported on Al_2O_3 and Pt- Al_2O_3 was shown to favour the reverse water-gas shift (RWGS) reaction instead of CO hydrogenation. Vannice [25, 26] also studied the kinetics of the strong metal-support interaction effects on CO adsorption and hydrogenation with Pt supported on TiO_2 , SiO_2 and Al_2O_3 . The effects of high and low reduction pre-treatments were investigated over these catalysts, focusing on the methane turn over frequency over varying Pt crystallite sizes. Despite these early studies, the hydrogenation of CO for on-board fuel cell applications over Pt- TiO_2 and Pt- ZrO_2 catalysts has, to the best of our knowledge, not been reported.

The activity of catalysts for both oxidation and hydrogenation of CO has been reported to depend strongly on the preparation method [7, 8, 11, 27], characteristics of the support [4, 8, 11, 18] and the conditions of catalytic testing [28-30]. For example, using reducible oxides as supports, the atmosphere of the reaction and the pretreatment conditions would control the degree of reducibility and this, in turn, would determine the nature of interaction of the support with the active metal and, hence, the overall reactivity of the system [8, 11, 27, 31]. The high

cost of Pt makes lower loadings desirable. Another weakness of the Pt-Al₂O₃ systems is the very strong metal-support interaction at lower loadings [32].

This study entails the synthesis of supported Pt ($\pm$ 1wt. %) catalysts, using commercial TiO₂ and ZrO₂, via the impregnation and deposition precipitation methods. The surface characterisations of these materials were studied by various physical and chemical techniques. For example, temperature programmed studies and CO chemisorption experiments were used to determine the effects of reducibility on the catalysts behaviour. These materials were tested for CO oxidation and hydrogenation activity within the stipulated temperature ranges using “dry” exit water-gas shift reformat feeds.

2.2 Experimental

2.2.1 Catalyst synthesis

Catalysts were synthesized using the wet impregnation and deposition precipitation techniques [1, 11, 12, 17, 27]. For wet impregnation, a solution containing approximately 1 wt % Pt from H₂PtCl₆.6H₂O (Alfa Aesar, Karlsruhe, Germany) dissolved in deionized H₂O was added dropwise to a slurry of either TiO₂ (Alfa Aesar, Karlsruhe, Germany) or ZrO₂ (Alfa Aesar, Karlsruhe, Germany). The slurry was stirred on a hotplate at 80 °C until a paste formed. The paste was oven dried at 110 °C, overnight and calcined at 400 °C for 4 h under a steady flow of air. These catalysts are denoted as PtIMP-TiO₂ and PtIMP-ZrO₂.

For the deposition precipitation preparation method Pt (1 wt. %) from H₂PtCl₆.6H₂O was dissolved in deionized H₂O and added dropwise to a slurry of the support (250 mL H₂O and TiO₂ or ZrO₂) at a pH of 7-7.5, maintained by the incremental addition of an ammonia solution. The mixture was aged for 2 h at the same pH and temperature. The precipitated material was filtered and washed with hot water (65 °C) until all Cl⁻ was removed. The decanted liquid was tested with AgNO₃ until no Cl⁻ was detected. The resultant paste was oven dried at 110 °C overnight and calcined at 400 °C for 4h under a steady flow of air. These catalysts are denoted as PtDP-TiO₂ and PtDP-ZrO₂.

2.2.2 Catalyst characterization

The Pt content of the samples was determined by ICP using an Optima 5300 DV PerkinElmer Optical Emission Spectrometer. Samples (± 0.05 g), were digested on a hotplate in 5 mL H_2SO_4 . ICP standards ranging from 0 to 50 ppm were prepared from a Pt stock standard of 1000 ppm (Industrial Analytical, RSA).

N_2 physisorption analyses of the materials were obtained using a Micromeritics TriStar II 3020. The samples (~ 0.2 g) were degassed under N_2 at 200 °C overnight prior to the analysis. Adsorption isotherms and pore size distributions were calculated using the instrument software.

X-ray diffraction (XRD) patterns of the catalysts were recorded on a Bruker D8 Advance instrument equipped with Diffracplus XRD Commander Software and a Bruker VANTEC detector. A Cu $\text{K}\alpha$ (λ 0.1540 nm) radiation source was used, operating on a long focus line at 40 kV and 40 mA respectively. Scans were obtained in a 2θ range from 10-90 ° at 0.5 °/min.

X-ray photon spectroscopy (XPS) was performed using a Kratos Axis Ultra DLD spectrometer. The achromatic Al K source was operated at 120 W, while the samples in the chamber were maintained at a pressure of around 1×10^{-9} mbar. For the regional scans, pass energies of 160 eV and 40 eV were used. Binding energy calibrations were done against the standard C 1s peak of contaminant carbon as a reference at a binding energy of 284.7 eV [1].

Temperature programmed (TP) studies were conducted using a Micromeritics Autochem II Chemisorption Analyzer 2920 on ± 0.05 g of sample. For TP reduction (TPR), the catalysts were first pre-treated by heating to 80 °C under a stream of He (10 mL/min) for 30 min and the temperature was decreased to 35 °C under the same stream. The reduction experiments were carried out using 5 vol % H_2 in Ar as the reducing agent with a flow rate of 5 mL/min to a temperature of 500 °C, ramped at 10 °C/min. The same method was used for TP oxidation (TPO), in this case using 5% O_2 in Ar as the oxidant.

FTIR-CO spectra were obtained using a Bruker Tensor 27 instrument with Harrick DRIFTS accessory fitted with a Harrick high temperature reaction chamber. Samples were

reduced under H_2 at 200 °C for 3 h prior to the analysis. Remaining H_2 was flushed out using Ar and CO gas was then pulsed over the samples through a VICI loop having a volume of 100 μL at a flow rate of 25 mL/min. Spectra were recorded at room temperature, 50, 100, 150 and 200 °C.

CO chemisorption experiments were carried out using fresh catalyst samples (~0.05 g) that were degassed under a flow of N_2 from RT to 200 °C. Upon reaching 200 °C, the samples were kept under vacuum for 12 h. These were analysed using a Micromeritics ASAP 2020 instrument. A quartz tube was used for housing the samples. These were initially reduced with H_2 at varying temperatures (200, 370 and 500 °C) for 2 h. The chemisorption analyses were carried out on the materials at 200 °C within a pressure range of 100–700 mmHg. The CO chemisorption capacity was determined by extrapolation of the CO uptake to zero pressure. The same methods were used to determine the metal dispersions, metallic surface areas, crystallite sizes and the chemisorption capacities using a stoichiometric ratio of CO/Pt of 1 [33], with the ratio of CO chemisorption capacity being defined as the total moles of CO chemisorbed/moles of Pt in the sample.

High-resolution transmission electron microscopy (HRTEM) was performed using a Jeol JEM-1010 TEM instrument, operated at 100 kV. Fresh catalyst samples were diluted in an Eppendorf tube with ethanol and sonicated to disperse the particles. Prior to viewing, the samples were coated on a formvar copper grid and air dried. Images were captured with a MegaView III Soft Imaging System and exported to JPEG. The particles were measured using iTEM software.

2.2.3 Catalytic testing

Catalytic reactions were carried out in a fixed bed stainless steel reactor at atmospheric pressure using 0.75 mL of catalyst diluted with 24 gritt carborundum (1:1). Prior to activity tests, samples were reduced under H_2 for 2 h at 200 °C. The temperatures ranged from RT to 200 °C for both the oxidation reactions, whereas the hydrogenation reaction was carried out from RT to 370 °C. The reaction mixture for CO oxidation consisted of 1% CO, 0.5 % O_2 and balance N_2 , for “dry” PROX 1% CO, 0.5 % O_2 , 50 % H_2 and balance N_2 and for “dry” methanation 1% CO, 70 % H_2 and balance N_2 . Reactions were carried out at a GHSV of 12

000 h⁻¹. The effluent gaseous products were analyzed using a 3 channel online Agilent Micro-GC CP-4900 TCD. Blank reactor studies were also carried out using the same feed compositions and conditions. Carbon, hydrogen and oxygen balances for all reactions ranged from 95 to 105 % and all data reported was obtained in triplicate.

2.3 Results and discussion

2.3.1 Catalyst characterization

2.3.1.1 Textural and ICP data of the synthesized catalysts

The textural and ICP data of the supported catalysts are shown in Table 2.1. From this, the ICP shows that Pt in all the catalysts was close to the desired loadings of 1 wt. %. Surface area data shows that TiO₂ has a higher surface area and pore volume than ZrO₂ and there was a subsequent decrease in both when Pt was added to the supports. However, the PtIMP-TiO₂ shows a slight increase in the pore volume.

Table 2.1. Surface area, pore volume and Pt loading of the catalysts

Catalyst	Pt (wt.%) ^a	Surface Area (m ² /g)	Pore Volume (cm ³ /g)
TiO ₂	-	151	0.35
ZrO ₂	-	57	0.25
PtIMP-TiO ₂	0.8	140	0.36
PtIMP-ZrO ₂	0.7	46	0.26
PtDP-TiO ₂	1.0	84	0.23
PtDP-ZrO ₂	0.7	51	0.24

^a ICP analysis

Nitrogen adsorption/desorption isotherms are shown in Fig. 2.1 and the corresponding pore size distributions are shown in Fig. 2.2. Based on the IUPAC classification, all samples show type IV isotherms with H1 hysteresis loops, which are characteristic for mesoporous materials [34]. For the ZrO₂ materials, there are slight shifts in the isotherms containing Pt, which is a common occurrence once metals at low loadings are added to the support [1]. These results correlate to the surface properties (Table 2.1) where no major changes are observed following

the addition of Pt on ZrO₂. Also, the pore size distributions of the samples in Fig. 2.2 show no evidence for changes in porosity following the addition of Pt and, hence, similar isotherm profiles are obtained.

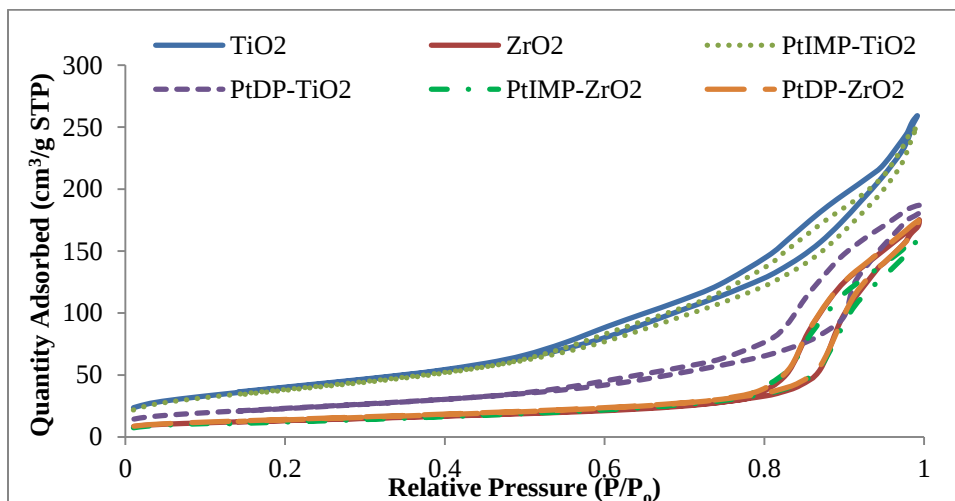


Figure 2.1. N₂-adsorption/desorption isotherms of the supported materials

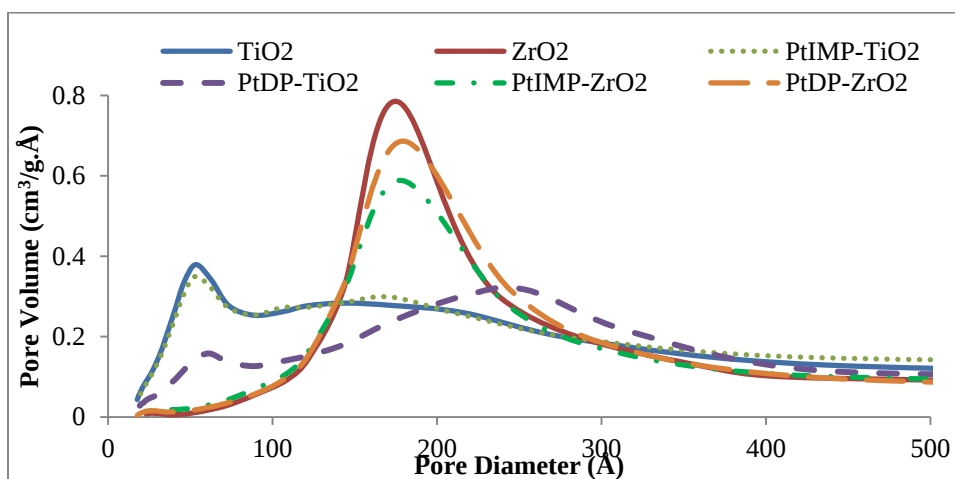


Figure 2.2. Pore size distributions for the supported materials

The TiO₂ support and the PtIMP-TiO₂ catalyst show similar trends for the adsorption isotherms and the pore size distributions which relate to the surface area and pore volume data where no drastic changes are observed. However, for the PtDP-TiO₂, the N₂ adsorption/desorption curve shifts to lower quantities of adsorbant values, whilst the pore size distribution profile indicates the formation of slightly larger pores. This result also correlates to those in Table 2.1 where

much lower surface areas and pore volumes were obtained following the addition of Pt. Additionally, following the addition of Pt to the supports the pore structure is not disrupted and Pt is preferably located on the surface of these supports.

2.3.1.2 Powder X-ray diffraction

The diffractograms of TiO_2 , ZrO_2 and supported Pt samples are shown in Fig. 2.3. The TiO_2 support showed the pure anatase phase (ICDD File No: 01-089-4921) with no diffraction peaks corresponding to the rutile phase. The ZrO_2 support appeared to be in the monoclinic and tetragonal phases (ICDD File Nos: 01-074-1200 and 01-080-255). The diffractions peaks characteristic of PtO are not observed due to the low Pt wt. loadings. The absence of the diffraction patterns of the Pt phases on the supports also indicate that its oxide is well dispersed on the support. This result correlates closely to that reported in literature where higher amounts of the active metal were used and also not detected by XRD [35].

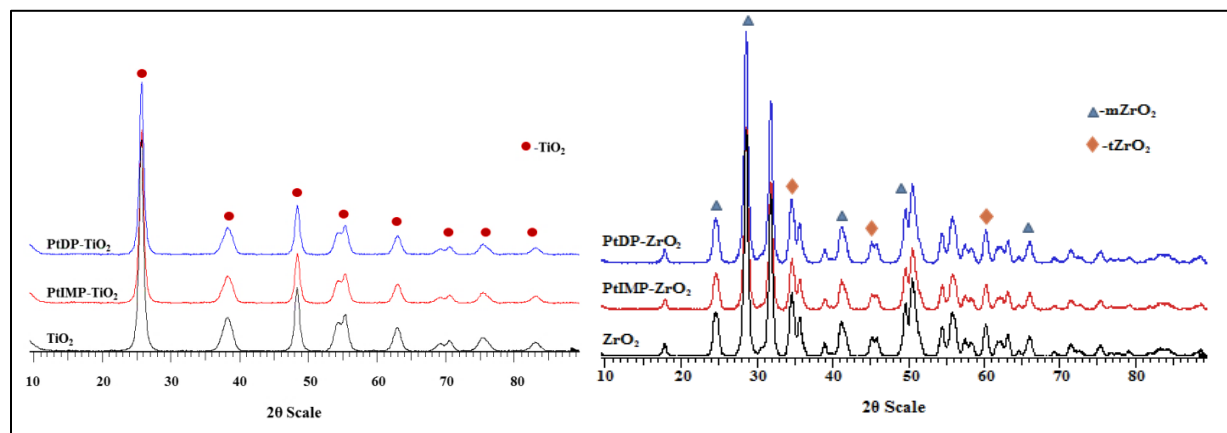


Figure 2.3. XRD diffractograms of the materials

2.3.1.3 X-ray photon spectroscopy

XPS was employed to study the Pt on the supports. The $\text{Pt}4f_{7/2}$ photoelectron spectra of the supported catalysts are shown in Fig. 2.4. After the $\text{Pt}4f_{7/2}$ curve fitting, the spectra show two characteristic peaks at eV ~ 72 -73 and ~ 76 for all the samples, with the binding energies corresponding to those of Pt^{2+} species [1, 36]. Slight shifts for the $\text{Pt}4f_{7/2}$ are seen when comparing the binding energies of bulk platinum oxide at eV ~ 72 . This is probably due to the electron transfer from the support to Pt generating strong metal–support interactions [37].

Table 2.2. XPS data of the supported materials

Catalyst	Binding Energy (eV)				Pt wt. %
	Pt ($4f_{7/2}$)	O (1s)	Ti ($2p_{3/2}$)	Zr ($3d_{5/2}$)	
PtIMP-TiO₂	73.0	529.2	458.8	-	1.0
	76.2		464.9	-	
PtIMP-ZrO₂	72.8	529.8	-	185.5	0.9
	76.5		-	187.6	
PtDP-TiO₂	72.5	529.1	458.3	-	0.9
	76.1		464.2	-	
PtDP-ZrO₂	72.8	530.1	-	185.8	0.8
	76.4		-	188.3	

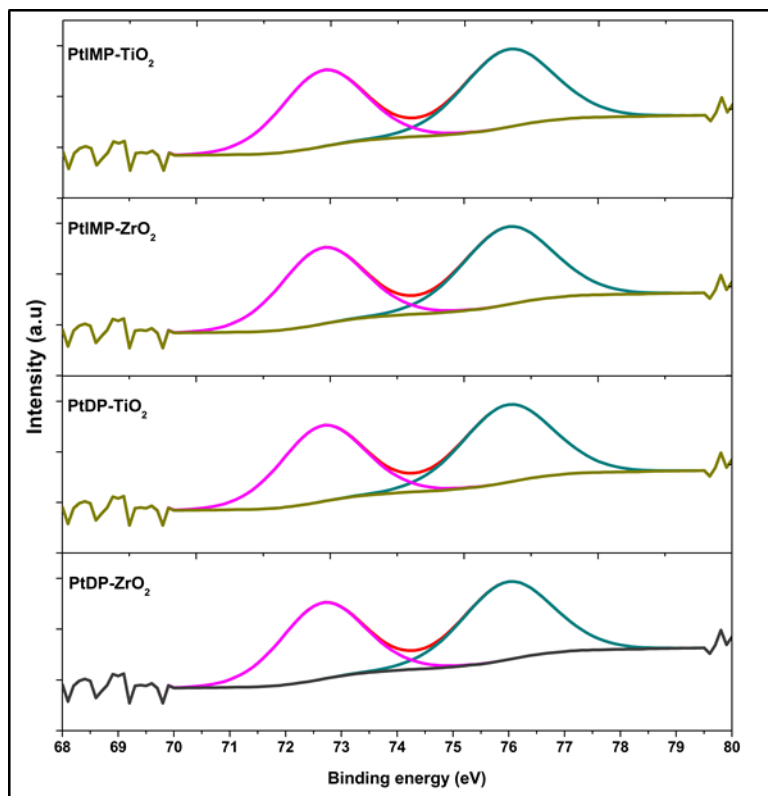


Figure 2.4. The Pt $4f_{7/2}$ photoelectron spectra of the supported Pt catalysts

The binding energies of all the phases present in the materials corresponding to Pt4f $_{7/2}$, Ti 2p $_{3/2}$, Zr 3d $_{5/2}$ and O 1s are presented in Table 2.2. The O1s peaks for all the catalysts show similar binding energies which closely correlate to Pt-O phases of the materials [1]. The estimated wt. % of Pt for these materials are slightly different to the ICP values, probably due to the difference in the analytical techniques.

2.3.1.4 Temperature programmed reductions and oxidations

The supports showed no reduction in the temperature range used for this experiment which agrees with reported studies [32, 38]. All reductions presented in Fig. 2.5 are due to the Pt metal and/or Pt catalysed reductions of the supports. Reduction peaks below 100 °C are due to some loosely interacting PtO $_x$ on the supports and appear before the signals could be detected on the instrument used (minimum temperature 35 °C) [32, 39]. Reduction peaks at 112-140 °C for the PtIMP-TiO $_2$ and 122 °C for the PtDP-TiO $_2$ are associated with the reduction of PtO $_x$ to metallic Pt.

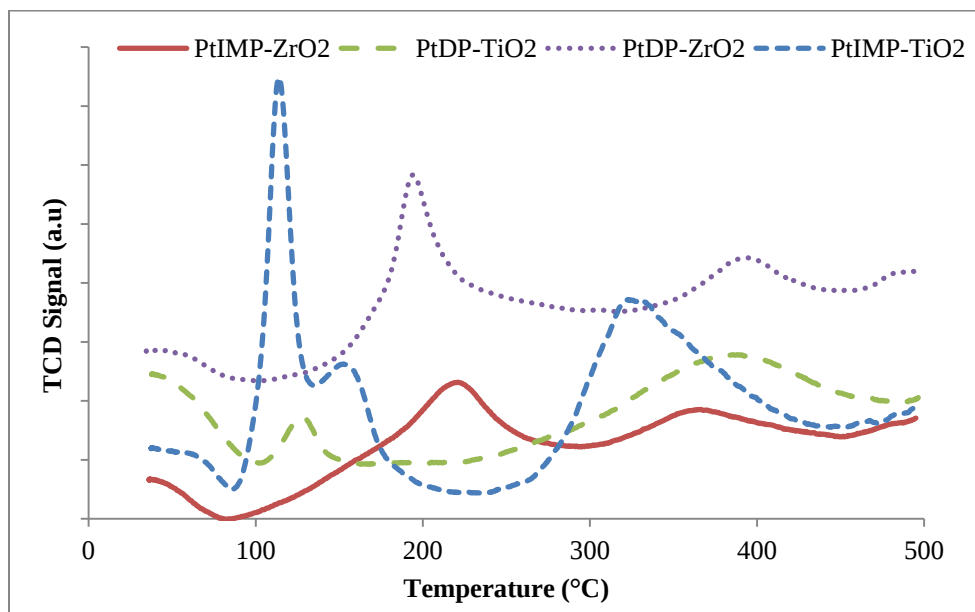


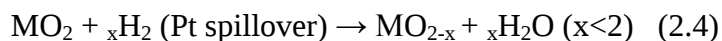
Figure 2.5. H $_2$ -TPR profiles of the supported catalysts

The peaks at 320 °C for the PtIMP-TiO $_2$ and 380 °C for the PtDP-TiO $_2$ could be due to the surface capping oxygen of TiO $_2$ [39, 40]. TiO $_2$ on its own partially starts to reduce under H $_2$ at temperatures above 500 °C [40, 41]. However, dispersed Pt strongly interacting with the

support is known to promote this reduction of the Ti^{4+} ions that are in close proximity to the active metal particle to Ti^{3+} at lower temperatures ($<500\text{ }^{\circ}\text{C}$) [29, 40, 41].

For the Pt-ZrO₂ catalysts, peaks at 190 °C and 214 °C are due to the PtO_x reduction to metallic Pt [38]. These occur at higher temperatures than for the TiO₂ supported catalysts due to ZrO₂ having a stronger metal-support interaction and it is also not as reducible as TiO₂ [42-44]. Reduction peaks at 356 °C and 381 °C on these samples, similar to those of the TiO₂ supported materials, could be due to the reduction of surface oxides on the support or possibly reduction by H₂ spillover [38, 45]. These TPR results of the supported materials can be correlated to the textural properties and N₂ adsorption/desorption isotherms which imply that Pt particles are preferably located on the surfaces of these supports and not blocking the pores.

Also, these results can be related to reports which show that under increasing reduction environments, highly reducible supported Pt materials that have strong metal-support interactions tend to form interstitials (O₂ vacancies) in close proximity to the active metal. These interstitials tend to migrate toward and over the active metal. Reported results for supported Pt materials indicated the following order of reduction: Pt-TiO₂ > Pt-ZrO₂ > Pt-Al₂O₃ [32, 38-40, 46]. The results of this study and previous work [1] show the same trends comparing the reduction profiles of Pt supported on TiO₂, ZrO₂ and Al₂O₃. Also, it can be seen that at higher temperatures ($>450\text{ }^{\circ}\text{C}$) H₂ consumption is still evident for these materials, indicating the reduction of the supports (TiO₂ or ZrO₂). These are catalysed by Pt and described as MO_x, (2-x) species (M = Ti or Zr) migrating towards, or on to, the Pt active sites as follows (Eq. 2.4) [32, 38, 39, 41]:



Following the TPR experiments, it is shown that for all the catalysts, re-oxidation (Fig. 2.6) takes place readily from 40 °C onwards. For the Pt-TiO₂ samples, there are two oxidation peaks in the ranges 40-160 °C and 160- 350 °C. The Pt-ZrO₂ catalysts showed almost the same oxidation profiles with one broad peak from 40-150 °C. The lower temperature oxidation peaks for all the materials correspond to Pt metal being oxidized to PtO_x (40-150 °C) [38]. These lower oxidizing temperatures could be evident of the degree of crystallinity as well as the degree of reduction of these supported Pt materials [40, 45]. The higher temperature oxygen

consumptions (150-350 °C) are attributed to the support re-oxidations [29, 38, 40, 47] as observed for the TiO₂ supported catalysts. ZrO₂ supported materials, on the other hand, do not show any peaks above 150 °C, suggesting a lower degree of reducibility [44].

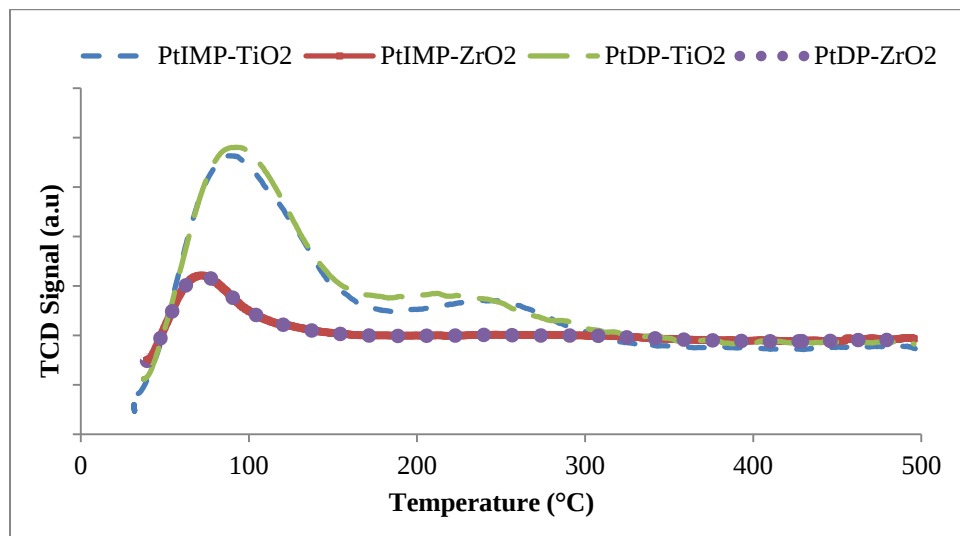


Figure 2.6. TPO profiles of the supported catalysts

2.3.1.5 FTIR-CO

Variable temperature FTIR-CO analyses over the supports showed no intense bands at any of the temperatures screened. Fig. 2.7 shows the FTIR-CO analyses of all the samples at 200 °C. The adsorption of CO on the samples gives a series of bands in the region between 1850-2200 cm⁻¹. CO adsorption on the catalysts is said to be reversible, and the bands obtained at 2083 and 2175 cm⁻¹ can be assigned to carbonyls formed with two kinds of coordinated unsaturated states of Ti³⁺ or Zr³⁺ cations on the surfaces [48]. These can be related to the TPR studies that indicate the formation of Ti³⁺ or Zr³⁺ interstitials. Bands at 1820, 1951, 2053 and 2088 cm⁻¹ are a reflection of Pt⁰ carbonyls present on the materials [1, 49]. Accordingly, the band at 2088 cm⁻¹ together with its shoulder at 2073 cm⁻¹ can be attributed to linear carbonyls of Pt⁰, whereas, bands at 1850 cm⁻¹ correlate to bridged Pt⁰-CO-Pt⁰ species. Additionally, bands at 2185 cm⁻¹ could also be assigned to linear Pt⁰-CO species, since these carbonyls of Pt⁰ are expected at higher wavenumbers [32, 50].

The FTIR spectra of the catalyst samples at increasing temperatures are shown in the supplementary information (Fig. S2.1). As the temperature increases, the capacity of CO

adsorption and desorption tends to increase on the supported Pt samples. ZrO₂ supported catalysts display similar CO adsorption bands, whilst the TiO₂ supported catalysts differ slightly. For the PtIMP-TiO₂ catalyst the band located at 2096 cm⁻¹ is slightly shifted to higher wavenumbers compared to all the other catalysts. These results, according to literature [51-54], may be attributed to CO adsorption on a Pt⁰ atom with larger particles. This can be correlated to the particle size determinations from TEM, as well as the metal dispersion obtained for this sample. The other TiO₂ supported catalyst shows a higher intensity band at 2035 cm⁻¹ which is characteristic for CO adsorption on weakly coordinated Pt atoms in smaller particles [48]. These results also correlate to those obtained from TEM and chemisorption studies.

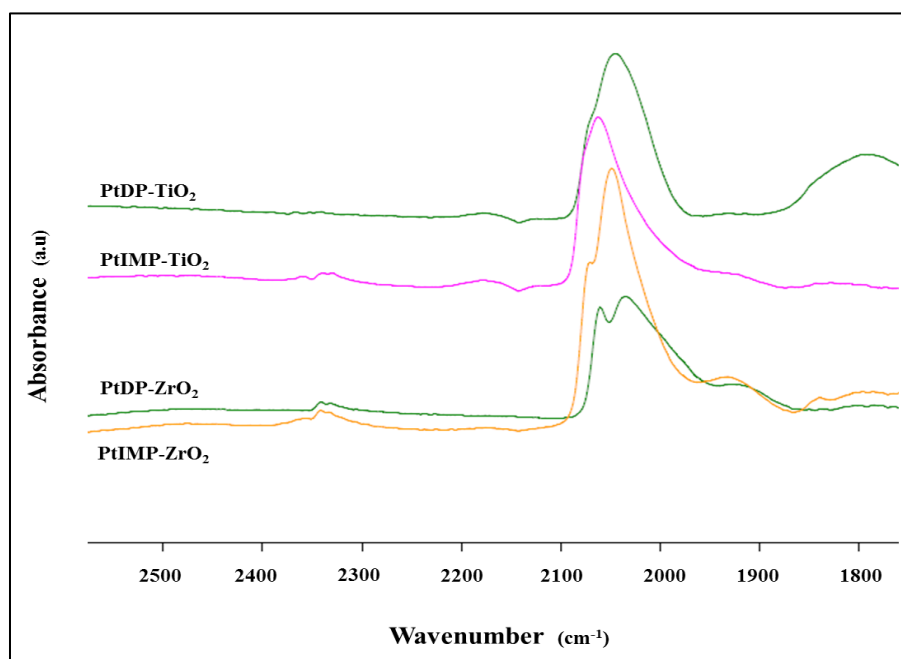


Figure 2.7. FTIR-CO spectra of the supported Pt catalysts recorded at 200 °C

2.3.1.6 CO chemisorption

Table 2.3 shows the CO chemisorption properties of the synthesized catalysts. The supports on their own showed almost no ability to chemisorb CO and the results presented are mainly due to the active metal (Pt) present on these supports. Results obtained show that both the ZrO₂ supported materials have higher CO chemisorption ability than the TiO₂ materials. Furthermore, the PtDP-TiO₂ catalyst showed higher CO chemisorption than the PtIMP-TiO₂ catalyst.

Table 2.3. CO chemisorption properties of the supported catalysts

Catalysts	Properties	Temperature of reduction		
		200 °C	370 °C	500 °C
PtIMP-TiO ₂	Metal dispersion (%)	24.7	17.2	10.8
	Metallic surface area (m ² /g metal)	42.4	34.7	19.3
	Crystallite size (nm)	11.2	11.3	13.1
	Chemisorption capacity (CO/Pt)	0.14	0.11	0.09
PtDP-TiO ₂	Metal dispersion (%)	58.2	32.5	25.2
	Metallic surface area (m ² /g metal)	152.3	98.7	60.9
	Crystallite size (nm)	10.2	11.8	12.9
	Chemisorption capacity (CO/Pt)	0.38	0.25	0.18
PtIMP-ZrO ₂	Metal dispersion (%)	69.5	55.5	42.2
	Metallic surface area (m ² /g metal)	154.3	125.2	118.9
	Crystallite size (nm)	6.2	6.1	6.7
	Chemisorption capacity (CO/Pt)	0.68	0.54	0.41
PtDP-ZrO ₂	Metal dispersion (%)	68.4	53.2	40.2
	Metallic surface area (m ² /g metal)	147.2	121.0	100.8
	Crystallite size (nm)	6.4	7.0	7.1
	Chemisorption capacity (CO/Pt)	0.67	0.52	0.39

According to Siddiquey et al. [55] variations of the zeta potentials of a support can lead to variations in metal dispersions. The isoelectric point (IEP) is the pH where the zeta potential of a substance is zero. The IEP of TiO₂ is 6.2 and during the synthesis by the deposition precipitation method (pH 7-7.5) a basic medium was maintained in which the acidic H₂PtCl₆.6H₂O (Cl⁻) precursor (pH 5.5) could interact with the support. During the wet impregnation technique, however, this controlled pH was not maintained and hence this resulted in weaker interactions with the metal and support which gave the poor metal dispersion, metallic surface area, particle size and CO chemisorption capacity of the catalyst. For the Pt-ZrO₂ catalysts, on the other hand, the IEP of ZrO₂ is 7.4, and during both the

synthesis methods, the controlled medium allowed Pt particles to interact strongly with the support. This was due to the high attracting affinity of the $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Cl^-) precursor (pH 5.5) and also, ZrO_2 is more electropositive than TiO_2 [43]. Hence, Pt- ZrO_2 catalysts showed higher CO chemisorption.

Increasing the reduction temperature of these materials reveals a decrease in the metal dispersions, metallic surface area and hence the CO chemisorption capacity (Table 2.3). Bitter et al. [33] reported that for the chemisorption capacities for Pt- ZrO_2 and Pt- TiO_2 catalysts with strong metal-support interactions, Pt is decorated by partially reduced oxides that suppress the chemisorption capacity, but do not alter the particle size. These results correlate closely to the TPR experiments, as well as reported data [32, 33, 38, 40, 41, 45]. Reductions at higher temperatures lead to the migration of the support towards or over the active metal and the reducibility of supported materials relate closely to the size and dispersion of the active metals. Also, these metals (Pt) are not completely encapsulated at maximum reduction temperatures (500 °C) since CO chemisorption capacities are still evident.

2.3.1.7 High resolution transmission electron microscopy

The particle sizes of Pt distributed over the supports generally have strong effects on the catalytic activity of the materials [56]. The HRTEM micrographs of the supported Pt catalysts presented in the oxide phases show that all materials display crystalline properties which are observed in the selected electron diffraction areas of the images (Fig. 2.8). The particle size of the measured PtO was dependant on the synthesis method and the nature of the supports. Both supports can be clearly distinguished by the lattice fringes in the images obtained. For the TiO_2 supported catalysts, the impregnated material showed larger PtO particles (~12 nm) than those synthesized by the deposition precipitation method (~10 nm). The ZrO_2 supported materials, on the other hand, irrespective of the synthesis method showed similar particle sizes (~6 nm). These results correlate closely to the CO chemisorption results of the materials, with ZrO_2 giving rise to smaller dispersed particles than the TiO_2 support, which is mainly due to the strong metal-support interaction between the metal precursor used and the electro-positivity of the support.

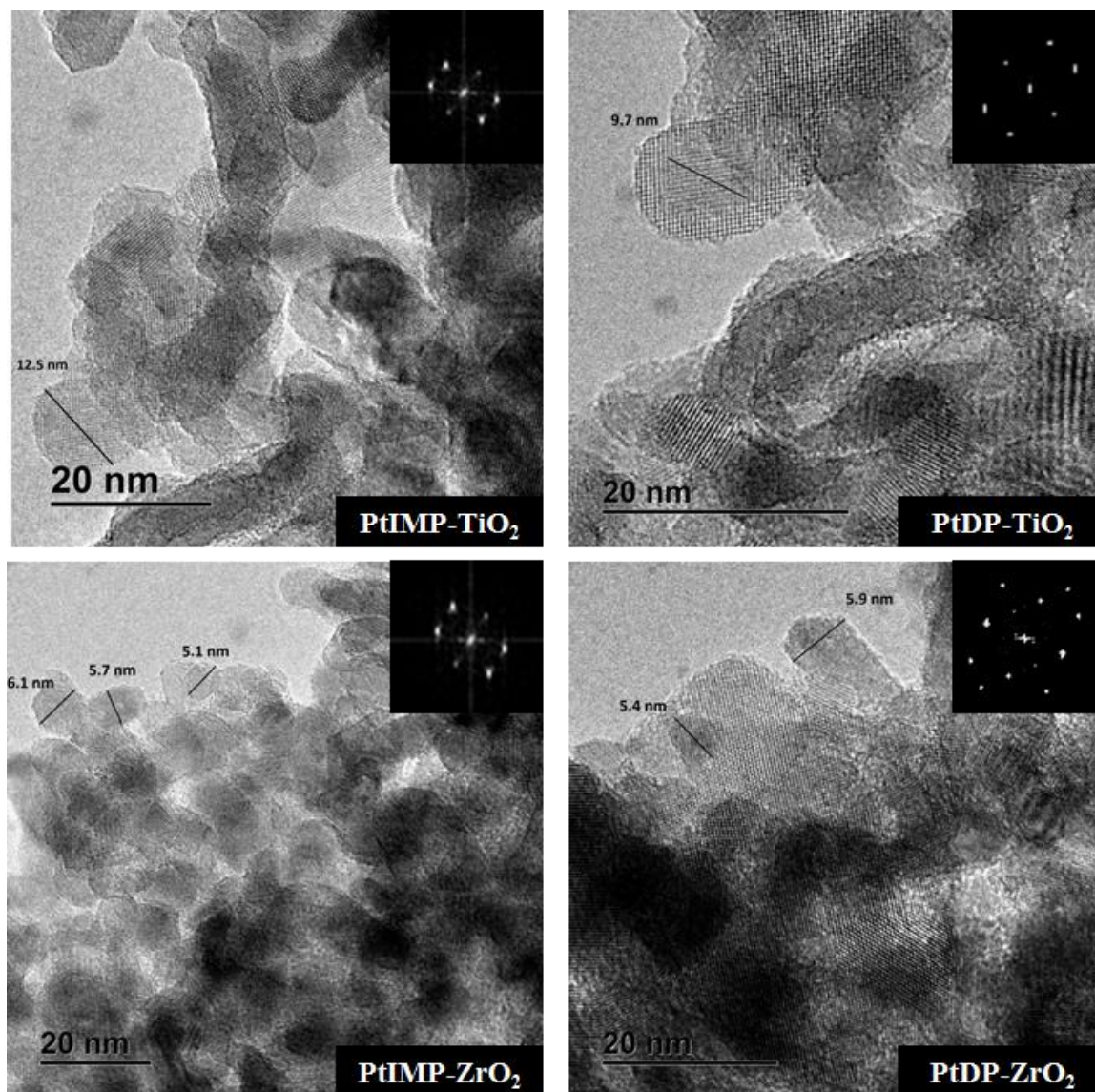


Figure 2.8. HRTEM images of the supported Pt catalysts (Inset: selected diffraction areas)

2.3.2 Catalytic testing

TiO₂ and ZrO₂ showed no activity within the temperature ranges tested for the various reactions examined. The supported Pt catalysts were tested for CO oxidation, preferential oxidation and hydrogenation by varying the temperature with the GHSV fixed at 12 000 h⁻¹. Additionally, analysis carried out while the catalysts in the reactor were cooled, showed similar activity to those taken during temperature ramping at the same temperature.

2.3.2.1 CO oxidation reactions

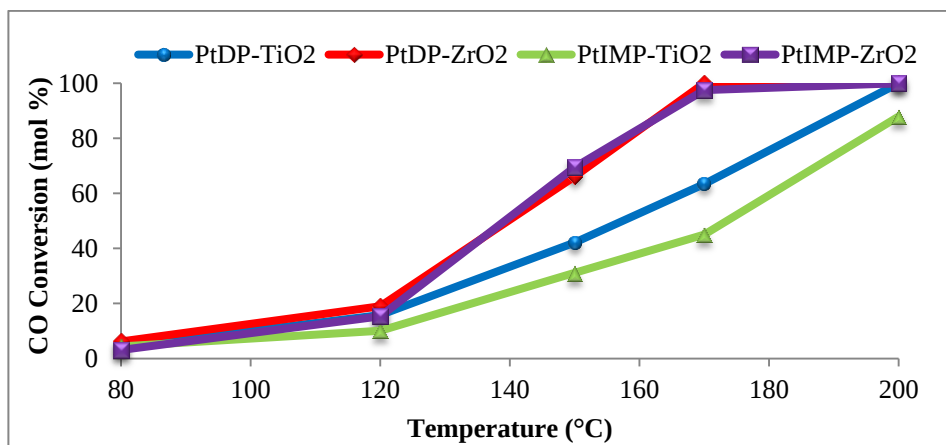


Figure 2.9. CO conversion as a function of temperature for the supported catalysts in the absence of H₂ (GHSV of 12 000 h⁻¹)

Figure 2.9 shows the oxidation of CO over the catalysts in the absence of H₂, with corresponding O₂ conversions provided in the supplementary information (Fig. S2.2). The onset temperature for the oxidation of CO over all the catalysts was ~80 °C. Both ZrO₂ based catalysts achieved 99.9 % conversion to CO₂ at ~ 170 °C, 30 °C lower than over the PtDP-TiO₂ catalyst. The PtIMP-TiO₂, compared to the other catalysts, only achieved a maximum conversion of 87.9 %, perhaps due to its lower metal dispersion. It is clear, however, that all these catalysts are active in removing CO in the absence of other reformat gases.

2.3.2.2 PROX reactions

The materials in the PROX reaction (Fig. 2.10) showed distinct differences in behaviour when compared to CO oxidation. Firstly, they all showed low CO conversion up to 200 °C. Secondly, the TiO₂ supported systems have much lower activity than the ZrO₂ supported systems. The ZrO₂ supported catalysts reach a maximum CO conversion of 20-22 % at 180 °C which remains fairly constant up to 200 °C, where the selectivity towards CO₂ for both these catalysts was ± 26 % (Fig. 2.11). The only other product observed was H₂O. For the TiO₂ supported catalysts, maximum CO conversions were obtained at 80 °C of ± 5% and remained very low for all temperatures tested thereafter. It is also noted that the CO₂ selectivity for these catalysts did not exceed 5 % for temperatures other than 80 °C. Results obtained for

all the catalysts show that the oxidation of H₂ is favoured over that of CO. This is supported by the H₂ conversion data for the catalysts (supplementary information Fig. S2.3), which show an increase with an increase in temperature.

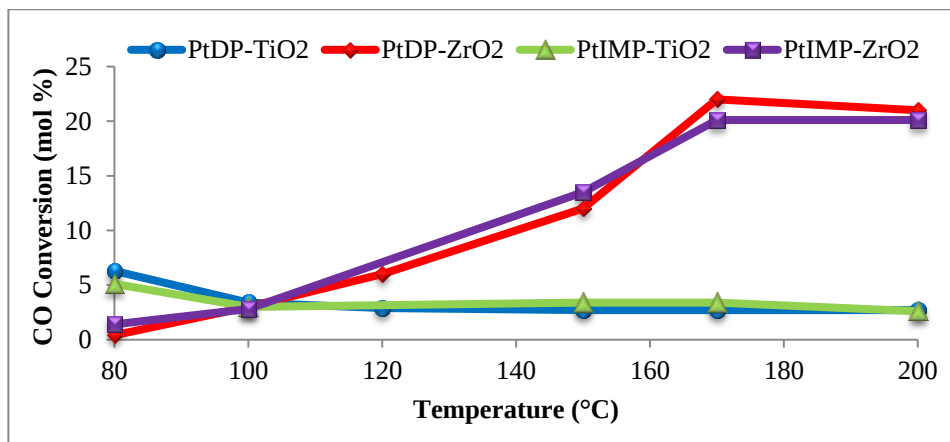


Figure 2.10. CO conversion as a function of temperature for the catalysts in the presence of H₂ (GHSV of 12 000 h⁻¹)

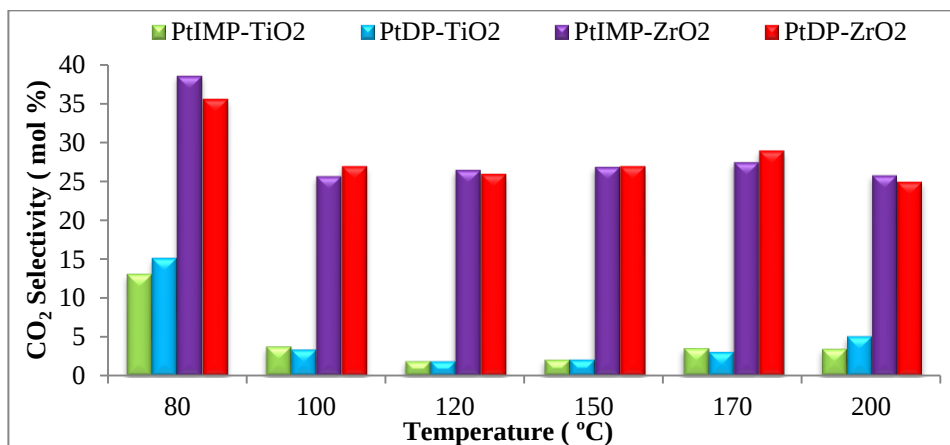


Figure 2.11. CO₂ Selectivity as a function of temperature over the supported Pt catalysts

The postulated reactions taking place on the surface of the catalyst are shown schematically in Fig. 2.12. During the pre-treatment of the catalysts under pure H₂, the active metal is reduced to its metallic form Pt⁰. However, the support is also reduced ($M^{4+} \rightarrow M^{3+}$, where M = Zr or Ti) in close proximity to the active metal by H₂ spillover (from Pt). This is catalysed by Pt due to the strong metal-support interaction, thus creating oxygen vacancies in close proximity to the reduced metal sites [57]. This postulate matches results obtained in the TPR experiments. On

the other hand, since Pt is an active metal for O_2 dissociation, O_2 spillover also takes place; in one of two ways [58]. Firstly, O_2 adsorbs onto the active metal, dissociates into O^- species which then spill over to the support to re-oxidize the O_2 vacancy created, or alternatively the O_2 molecule adsorbs on the support surface, migrates towards the Pt metal where it rapidly dissociates thus re-oxidizing the vacancy created. This in turn results in H_2 , that is in excess, interacting with the newly oxidized surface layer, thus re-reducing it to form H_2O , rather than allowing CO to interact with the oxygen to form CO_2 . This phenomena is more prominent over the TiO_2 catalysts compared to the ZrO_2 catalysts, which correlates closely to the lower CO chemisorption capacities measured, the higher degree of reduction and the larger particle sizes of the TiO_2 systems, which are all key parameters affecting the PROX reaction [1, 32, 33, 40, 51, 54, 56].

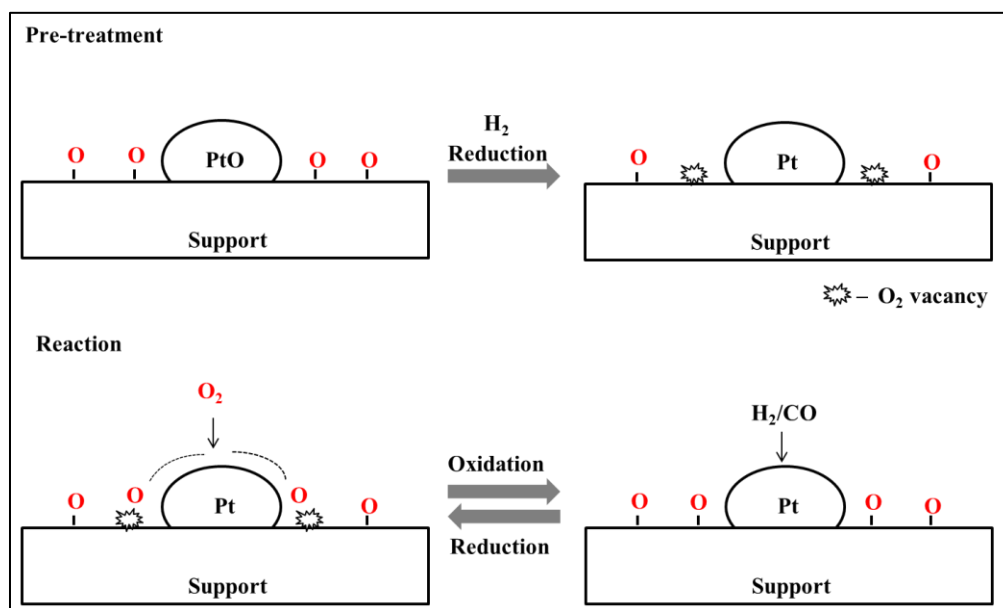


Figure 2.12. Schematic diagram showing the plausible mechanism of the PROX reaction

Furthermore, the low CO conversions over these catalysts could be due to either the occurrence of a redox cycle between CO and O_2 , following the Mars and van Krevelan (MVK) mechanism [1], or also CO could directly interact with molecular O_2 on the surface of Pt prior to spillover following the Langmuir Hinshelwood (LH) mechanism. These findings can be supported with the O_2 conversions obtained for the catalysts (supplementary information Fig. S2.2). Both the TiO_2 supported catalysts show very high O_2 conversions, but with very low CO conversions,

indicating that O_2 in this case is not contributing much to CO oxidation, but rather H_2 oxidation, thus following the MVK pathway. O_2 oxidizes the reduced support and does not interact directly with CO on the active metal. The ZrO_2 supported catalysts, on the other hand, only reach maximum O_2 conversion at 200 °C. This implies that at lower temperatures the LH mechanism is probably favoured, and O_2 conversions are attributed to CO_2 formation on the active metal (Pt). At higher temperatures (200 °C) a combination of the LH and MVK mechanisms could be possible for these catalysts, where all of the O_2 is consumed showing that H_2 oxidation is favoured.

The oxidation of CO in the presence of H_2 over these catalysts is thus not favoured and increasing the temperature above 200 °C for this reaction increases the reducibility of the supports catalysed by Pt, leading to greater spillover and hence H_2 oxidation. Also, above 200 °C, the O_2 balances of the catalysts during the reaction decrease. This indicates that the degree of reduction of the support is higher and the O_2 in the feed is utilized to re-oxidize the support vacancies (created by H_2).

2.3.2.3 CO hydrogenation reactions

Since the PROX reactions over these catalysts were ineffective in reducing CO to acceptable levels, and also considering that an additional supply of O_2 for the reaction is required, the catalysts were screened for hydrogenation activity to aid in the removal of CO. Fig. 2.13 shows the CO conversion profiles of the catalysts and Fig. 2.14, the CH_4 selectivity. This selectivity is based on only CH_4 and CO_2 being formed. Both Pt- ZrO_2 catalysts achieve maximum CO conversions of over 99 % just above 350 °C with high selectivity towards CH_4 (99 %). Also, the loss of H_2 by this reaction (supplementary information Fig. S2.4) is minimal at the highest CO conversion, ~1.8 % considering a 1% CO feed and the reaction proceeding stoichiometrically. Additionally, no other products were observed during the reactions besides CH_4 , CO_2 and H_2O .

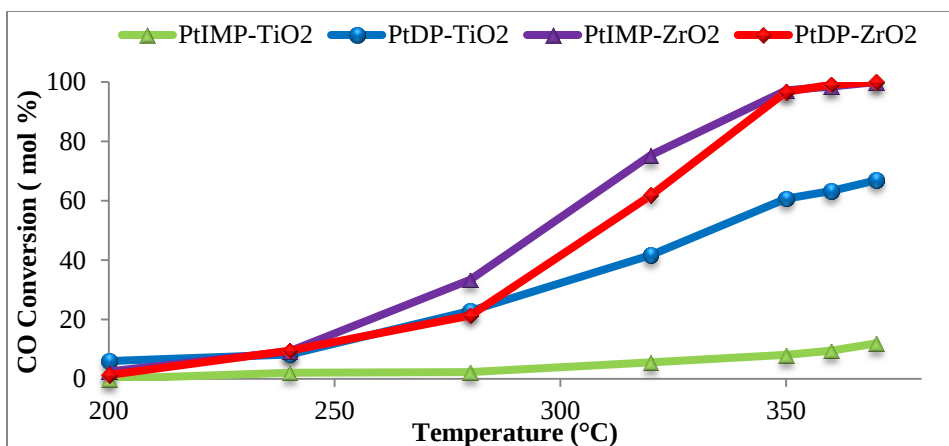


Figure 2.13. CO conversion over the supported Pt catalysts during CO hydrogenation using a GHSV of 12 000 h⁻¹

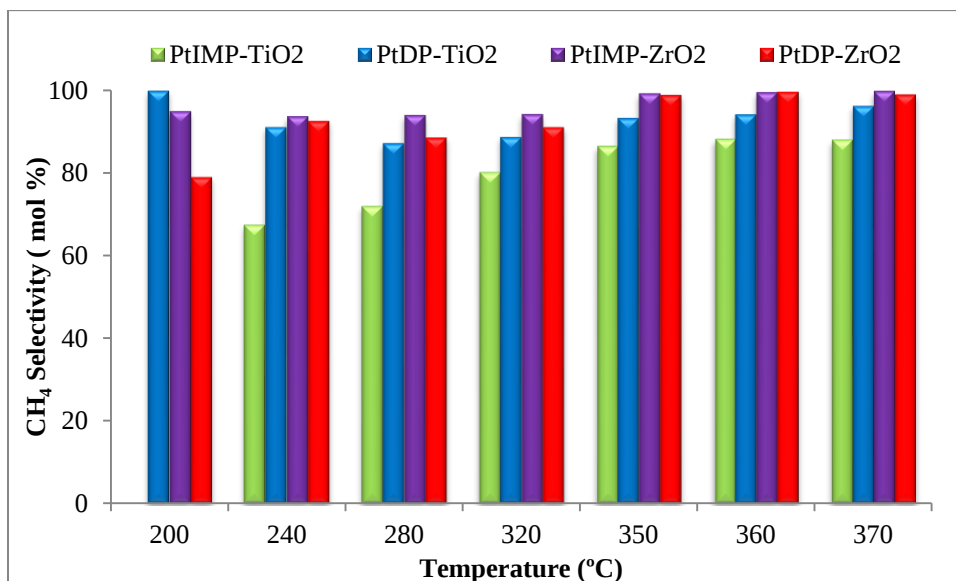


Figure 2.14. Selectivity towards CH₄ over the prepared catalysts

The PtDP-TiO₂ catalyst gave a maximum CO conversion of 67 % and a selectivity towards CH₄ of 96 % at the highest temperature tested. The PtIMP-TiO₂, on the other hand, showed very low activity towards the reaction and only reached a maximum CO conversion of 12 % at 370 °C with a selectivity towards CH₄ of 88 % and CO₂, via the water-gas shift (WGS) reaction, of 12 %. According to Hwang [38] and Azzam et al. [45] the WGS is mainly due to the nature of the active metal in terms of the size of the active particles, dispersions of these particles and also the metal-support interaction with the oxide support. The formation of

interstitial titanate species, $\text{TiO}_{(2-x)}$ ($0 < x < 2$) over the TiO_2 supported Pt catalysts is also a probable reason. CO chemisorption properties of the materials can be correlated to these activity measurements. For the Pt- TiO_2 catalysts at 370 °C, the metal dispersions are much lower than those of the Pt- ZrO_2 catalysts, which were very similar (Table 2.3). Also, the CO chemisorption capacity for the Pt- TiO_2 catalysts is less than half those obtained for the Pt- ZrO_2 catalysts. The amount of metal sites available (metal dispersion) to chemisorb the reactant (CO) at these high temperatures for the Pt- TiO_2 catalysts is important and relates directly to the activity of these two catalysts compared to the Pt- ZrO_2 catalysts. Similarly the catalytic activities of the Pt- ZrO_2 catalysts correlate closely to the similar characterization properties (N_2 adsorption/desorption profiles, pore size distributions, TPR, TPO, CO chemisorption and HRTEM) obtained for these catalysts. Thus, from these catalytic hydrogenation reactions it can be assumed that the LH mechanism is the preferred pathway.

The ZrO_2 supported materials thus performed much better than the TiO_2 supported materials for the hydrogenation reaction due to the metal-support interaction of ZrO_2 and Pt. The Pt- ZrO_2 catalysts have smaller particle sizes and higher metal dispersions compared to the TiO_2 systems. At higher temperatures, the availability of active metal (metal dispersion) for the hydrogenation of CO over the ZrO_2 supported materials is greater than for TiO_2 . CO chemisorption data reveals that even at temperatures beyond the hydrogenation reaction (500 °C) there is still CO adsorption taking place, revealing the availability of Pt, but with lower metal dispersions. Furthermore, both the ZrO_2 supported catalysts are similar materials and showed similar activity for both the oxidation and hydrogenation reactions, whilst for the TiO_2 supported catalysts, PtDP- TiO_2 , showed better activity than the PtIMP- TiO_2 catalyst. These similarities or variations in both the material properties and activity measurements correlate closely to the isoelectric point (IEP) of the supports. ZrO_2 supported catalysts have a stronger interaction with Pt, resulting in highly dispersed small particles with very similar characteristic properties and hence catalytic activity. TiO_2 catalysts, on the other hand, showed distinct differences between each other in both the characteristic properties and activity measurements.

2.4 Conclusion

All the catalysts showed appreciable activity towards the oxidation of CO in the absence of H_2 . However, the PROX reaction over these catalysts favoured H_2 oxidation rather than the

desired CO oxidation. Characterization of the materials revealed that the reduction of the supported catalysts with well dispersed Pt particles resulted in the formation of interstitials (O₂ vacancies) on the support surface. During the PROX reaction, H₂ reacts with O₂ spilled over onto the support forming H₂O.

Importantly, the hydrogenation of CO, for on-board fuel reformers, over the Pt-ZrO₂ catalysts was shown to be excellent for the removal of trace amounts CO in H₂ rich streams. These catalysts lowered the amount of CO to < 10 ppm at temperatures above 350 °C. The activity of these materials related closely to the synthesis techniques with strong Pt support interactions. The redox data of these materials showed that Pt catalyzes the reduction of the support due to this strong metal-support interaction, leading to the formation of these well dispersed active metal particles on ZrO₂. Following the catalytic reaction/s and data obtained for these catalysts for on-board fuel processing reactions, Pt-ZrO₂ catalysts prepared by either the wet impregnation or deposition precipitation methods could be suitable catalysts following the high temperature water-gas shift reaction to remove the trace CO. Also, ideal exit water-gas shift reformat feeds can be investigated since these catalysts show promising stability and activity towards CO hydrogenation. Further work continues to evaluate the performance and stability of these catalysts in the presence of CO₂ and H₂O.

Acknowledgements

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Supplementary information

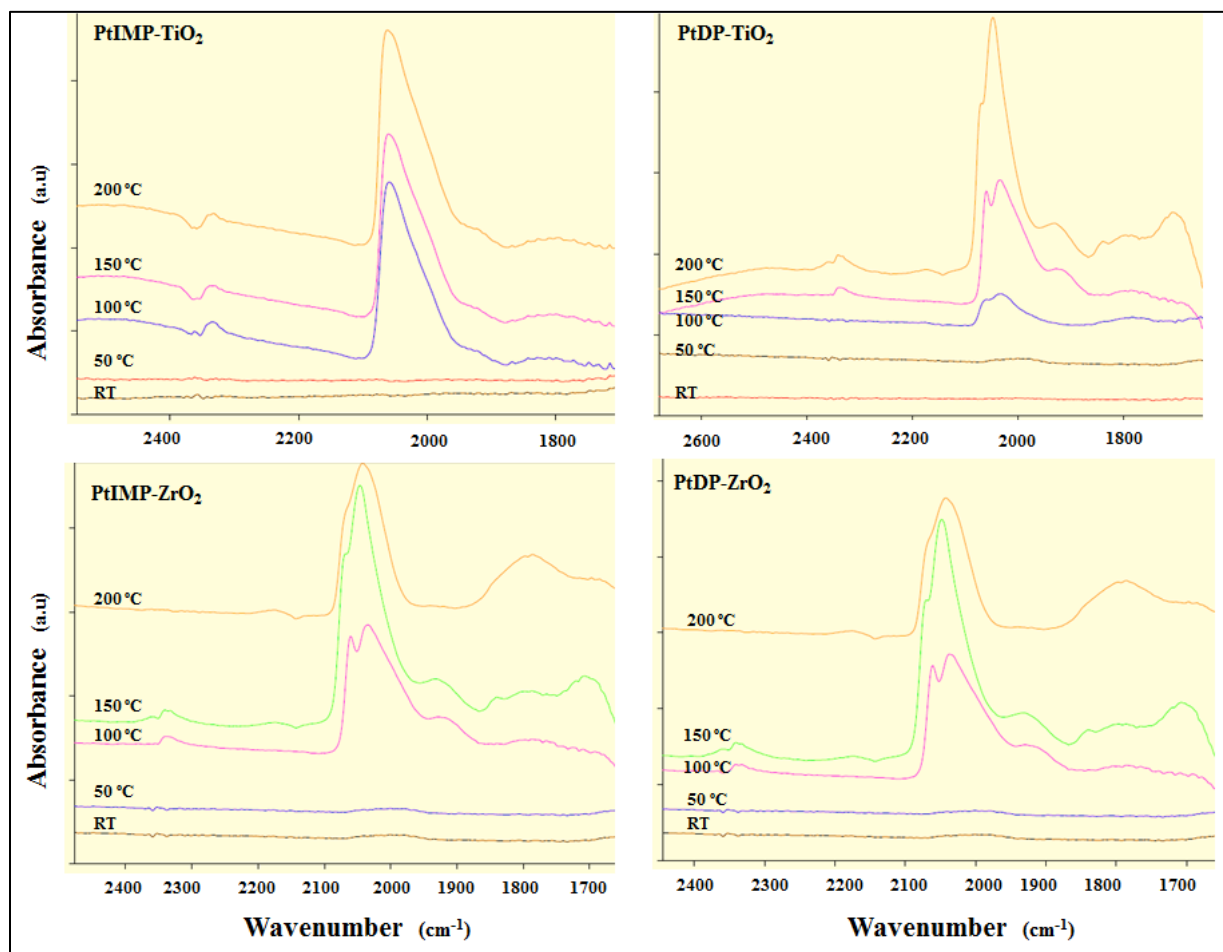


Figure S2.1. FTIR-CO analyses of the catalysts at varying temperatures

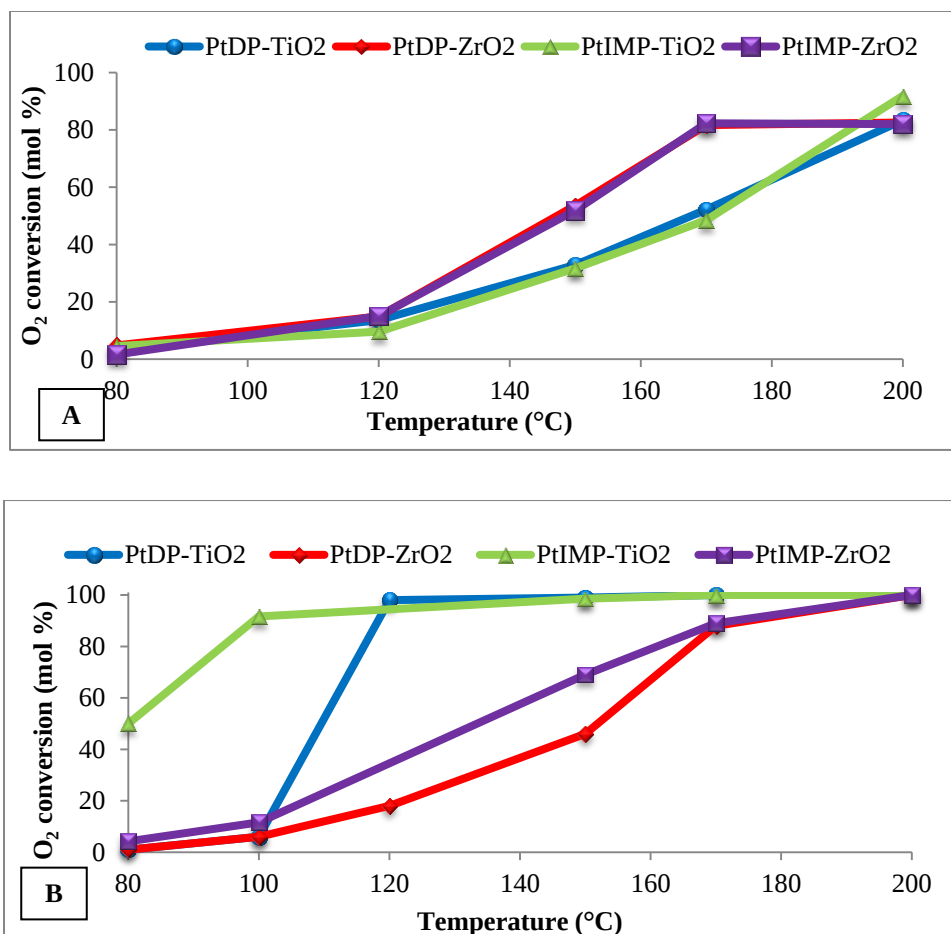


Figure S2.2. O₂ conversions of the supported Pt catalysts (A: CO oxidation and B: PROX)

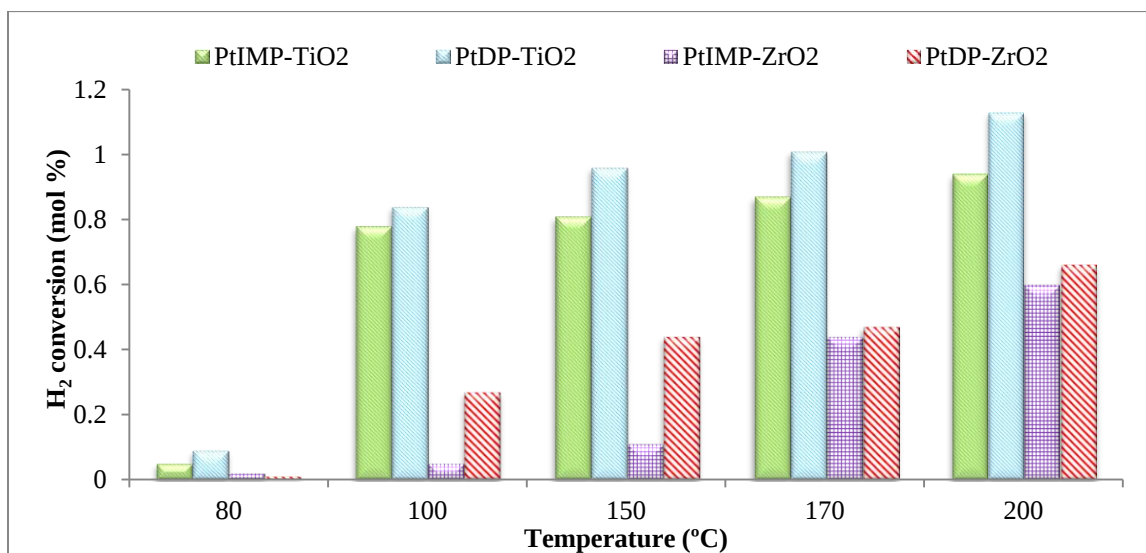


Figure S2.3. H₂ conversions of the supported Pt catalysts during the PROX reaction

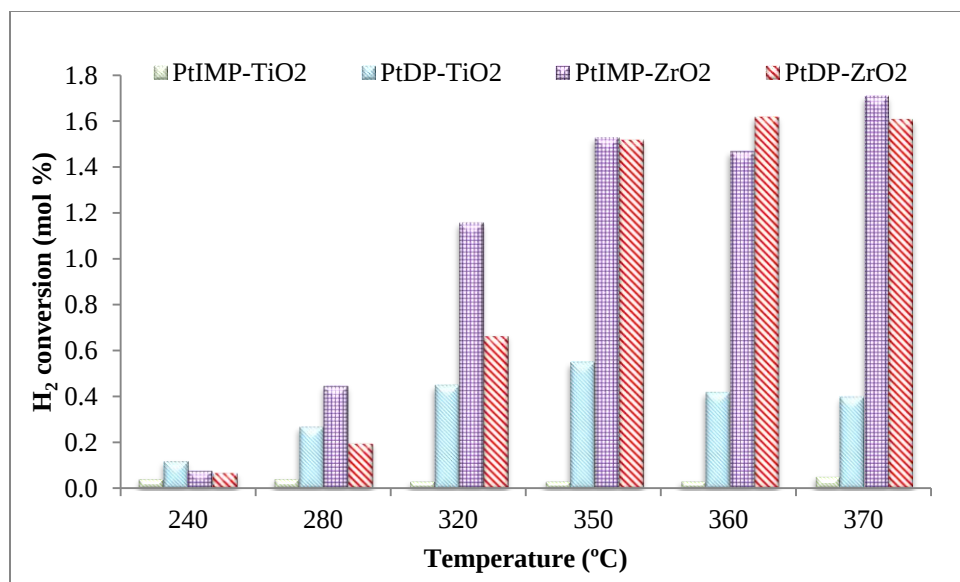


Figure S2.4. H₂ conversions of the supported Pt catalysts during the hydrogenation reaction

Chapter 3

The removal of CO present in the water-gas shift reformat gas over Ir-TiO₂ and Ir-ZrO₂ catalysts

Ziyaad Mohamed, Sooboo Singh and Holger B. Friedrich*

Catalysis Research Group, School of Chemistry and Physics, University of KwaZulu-Natal,
Durban 4000, South Africa

Abstract

Ir supported on TiO₂ and ZrO₂ catalysts were tested for the oxidation and hydrogenation of CO using a feed mimicking the water-gas shift reformat stream. The influence of the support interaction with Ir and the catalyst's redox and CO chemisorption properties on activity and selectivity were evaluated. Both the catalysts showed appreciable activity towards the total oxidation of CO in the absence of H₂ and a conversion of 70 % was obtained at 200 °C. For the oxidation of CO in the presence of H₂ over these catalysts, the oxidation of H₂ was favoured over CO, due to H₂ spillover occurring at the interface of the support and active metal, resulting in the formation of interstitials catalyzed by Ir. Both catalysts showed promising activity for the hydrogenation of CO. Ir-ZrO₂ was more active giving 99.9 % CO conversions from 350 to 370 °C with high selectivity towards CH₄ using minimal H₂ from the feed. Furthermore, results in the Ir-ZrO₂ catalyst showed that the superior activity compared to the Ir-TiO₂ catalyst was mainly due to the reducibility of the support and its interaction with the active metal. Controlling the isoelectric point during the synthesis allowed for a stronger interaction between Ir and the ZrO₂ support which resulted in higher catalytic activity due to better metal dispersions and higher CO chemisorption capacities than obtained for the Ir-TiO₂ catalyst.

Keywords: Iridium, preferential oxidation, hydrogenation, spillover and isoelectric point.

* Corresponding author: Tel.: +27 31 2603107, Fax.: +27 31 260 3091,

E-mail: friedric@ukzn.ac.za

3.1 Introduction

In transition to the hydrogen economy from current power sources, proton exchange membrane fuel cells (PEMFC) are considered as good candidates for portable power generation [1]. During on-board reforming of hydrogen for these fuel cells, trace amounts of CO are still present in the reformat feed following the water-gas shift (WGS) reaction. Preferential oxidation (PROX) and methanation (MET) of CO are viable processes employed to reduce the CO concentration to acceptable levels, to feed on-board PEMFCs with pure hydrogen, thus avoiding unwanted poisoning by CO of the Pt anode [2-6].

These reactions have been widely studied using Au, Pt, Ru, Rh, Pd, Ir, Ni, Cu and Co supported on non-reducible oxides [1, 4, 7-11]. Among these catalytic formulations, supported Ir catalysts have not been widely explored for the PROX reaction [10, 12, 13]. Nguyen et al. [13] showed that Ir supported on Al_2O_3 was less active than its ceria supported counterparts (Pt, Pd and Ir) for the PROX reaction. Also, the stability of the ceria supported Ir, compared to Rh and Ru, was much higher above 200 °C, since Rh and Ru, although encouraging CO dissociation, followed the methanation pathway.

Huang et al. [12] reported that Ir-CeO₂ catalysts prepared by the deposition precipitation method with no Cl⁻ residue gave the highest activity for the preferential oxidation reaction compared to the other prepared materials on metal oxides (Al_2O_3 and TiO_2). Also, reductive pre-treatment of the catalyst was found to be essential for obtaining high activity on a sample containing 1.60 wt. % Ir. The catalyst as obtained gave the highest oxidation activity of 60 % which decreased after 120 °C.

Ir supported on ZrO₂ has not been reported for these oxidation reactions and also, to the best of our knowledge, no data has been reported for Ir supported on TiO₂ and ZrO₂ for the CO hydrogenation reaction. Additionally, the effect of controlling the isoelectric point of the two supports during synthesis of these catalysts has not been mentioned. This motivated the present

study in which TiO_2 and ZrO_2 supported Ir (1 wt. %) was tested for both the oxidation and hydrogenation of CO in a feed mimicking the water-gas shift reformat. In addition to metal benchmarking for each reaction, we emphasize the strong metal-support interaction effects on both the supports during these reactions. For catalyst preparation, the deposition precipitation method was used. The effects shown by controlling the isoelectric points during catalyst synthesis were investigated.

3.2 Experimental

3.2.1 Catalyst synthesis

All catalysts were prepared by the deposition precipitation technique [14, 15]. A 1 wt. % of Ir loading was attempted using an aqueous solution of IrCl_3 (Sigma-Aldrich, USA). The metal salt was dissolved in minimal amount of deionized H_2O and added to a slurry of the support (TiO_2 or ZrO_2 in 250 mL H_2O) with the pH maintained between 7-7.5 using a 10 % solution of NH_3 . The mixture was aged for 2 hours with constant stirring at 65 °C, filtered and washed repeatedly with hot water (65 °C) to remove any traces of Cl^- . The precipitate was oven dried overnight at 110 °C, and calcined at 400 °C for 4 h under a steady flow of air. The materials were denoted as Ir- TiO_2 and Ir- ZrO_2 .

3.2.2 Catalyst characterization

Using an Optima 5300 DV PerkinElmer Optical Emission Spectrometer, the active metal content of the samples were determined by ICP. Approximately, 0.50 g of sample (accurately weighed) was digested using 5 mL H_2SO_4 on a hotplate. The ICP standards were prepared ranging from 0 to 50 ppm from a stock standard of Ir 1.000 $\mu\text{g/mL}$ in 10 wt. % HCl (Fluka Analytical, USA).

The specific surface areas of the catalysts were determined by N_2 physisorption using a Micromeritics TriStar II 3020. Prior to the analysis, the samples (~0.2 g) were degassed under N_2 at 200 °C overnight.

X-ray diffractograms (XRD) of the materials were recorded using Diffracplus XRD Commander Software and a Bruker VANTEC detector on a Bruker D8 Advance instrument.

Scans of the materials were obtained within a 2θ range of 10-90 ° (0.5 °/ min) using a Cu K α (λ 0.1540 nm) radiation source that was operated at 40 kV and 40 mA respectively.

Temperature programmed reduction and oxidation (TPR and TPO) studies were conducted using a Micromeritics Autochem II Chemisorption Analyzer 2920. The samples ($\pm$ 0.05 g) were loaded in a U-shaped quartz tube and pre-treated at 80 °C under He (10 mL/min) for 30 min and then cooled to 35 °C. The reduction (5 vol % H₂ in Ar) and oxidation (5% O₂ in Ar) experiments were conducted using a flow rate of 5 mL/min from 35-500 °C with a ramp rate of 10 °C/min.

Using a Bruker Tensor 27 with Harrick DRIFTS accessory fitted with a Harrick high temperature reaction chamber, the FTIR-CO spectra of the catalysts were obtained. Prior to the analyses, the samples were reduced at 200 °C under H₂ for 3 h. Ar was used to flush out residual H₂ over the samples and CO was then pulsed through a 100 μ L VICI loop using a flow rate of 25 mL/min.

X-ray photon spectroscopy (XPS) scans of the materials were obtained using a Kratos Axis Ultra DLD spectrometer. An achromatic Al K source was used and operated at 120 W while maintaining the pressure of the samples in the chamber at 1×10^{-9} mbar. For the regional scans, pass energies of 160 eV and 40 eV were used. Binding energy calibrations were done against the standard C 1s peak of contaminant carbon as a reference at a binding energy of 284.7 eV [1].

Using fresh catalyst samples ($\sim$ 0.05 g) that were degassed under N₂ overnight (200 °C) and then placed under vacuum for 12 h prior to the analyses, CO chemisorption experiments were carried out using a Micromeritics ASAP 2020 instrument. The samples were housed in a quartz tube and reduced under H₂ at varying temperatures (200, 370 and 500 °C) for 2 h prior to the analyses. Data were recorded at 200 °C within a pressure range of 100–700 mmHg. The CO chemisorption capacities were determined by extrapolation of the CO uptake to zero pressure. Accordingly, the crystallite sizes, metal dispersions, metallic surface areas and ratios of CO chemisorption capacities were calculated using a stoichiometric ratio of 1 for CO:Ir [16].

3.2.3 Catalytic Testing

The catalytic testing was performed at atmospheric pressure on a custom built, stainless steel fixed bed reactor using 0.75 mL of catalyst diluted with 24 gritt carborundum (1:1). Catalysts were pre-treated at 200 °C under H₂ for 2 h. Activity measurements were recorded from RT-200 °C for the oxidation reactions and from RT to 370 °C for the hydrogenation reaction. The reactant flow mixture for CO oxidation was 1% CO, 0.5 % O₂ and balanced with N₂; for “dry” PROX, 1% CO, 0.5 % O₂, 50 % H₂ and balanced with N₂ and for “dry” SMET it was 1% CO, 70 % H₂ and balance N₂, with the GHSV fixed at 12 000 h⁻¹. The effluent gaseous products were analyzed on an online Agilent Micro-GC CP-4900 TCD housing 3 channels. Data were recorded in triplicate with O₂, C and H₂ balances ranging between 95 and 105 % for all the reactions. Only CO₂, H₂O and CH₄ were observed under the conditions tested.

3.3 Results and discussion

3.3.1 Catalyst characterization

3.3.1.1 BET and ICP data of the materials

Table 3.1. BET and ICP data of the supported Ir catalysts

Catalyst	Ir wt. (%) ^a	Surface area (m ² /g)	Pore volume (cm ³ /g)
TiO ₂	-	151	0.35
ZrO ₂	-	57	0.25
Ir-TiO ₂	1.1	95	0.23
Ir-ZrO ₂	1.1	50	0.23

^a ICP analysis

ICP and N₂ adsorption/desorption isotherms were obtained for the materials. The results are shown in Table 3.1. The Ir wt. % loadings were the same for both catalysts and close to the nominal loading of 1%. The surface areas and pore volumes of the catalysts show a decrease compared to the supports. The decrease in pore volume could be evidence of the metal being

not only on the surfaces of the support, but it also occupies the pores to a degree. This effect is larger in the TiO_2 supported catalyst.

Fig. 3.1 shows the N_2 adsorption/desorption isotherms for the supports and catalysts studied. These isotherms correspond to type IV with H1 hysteresis, indicative of cylindrical bottle pores which are characteristic for mesoporous materials [17, 18]. No significant changes can be observed with regards to the shape of the isotherm following the addition of Ir which confirm that the metal is located mainly on the surface of the supports and not disrupting the pore structures.

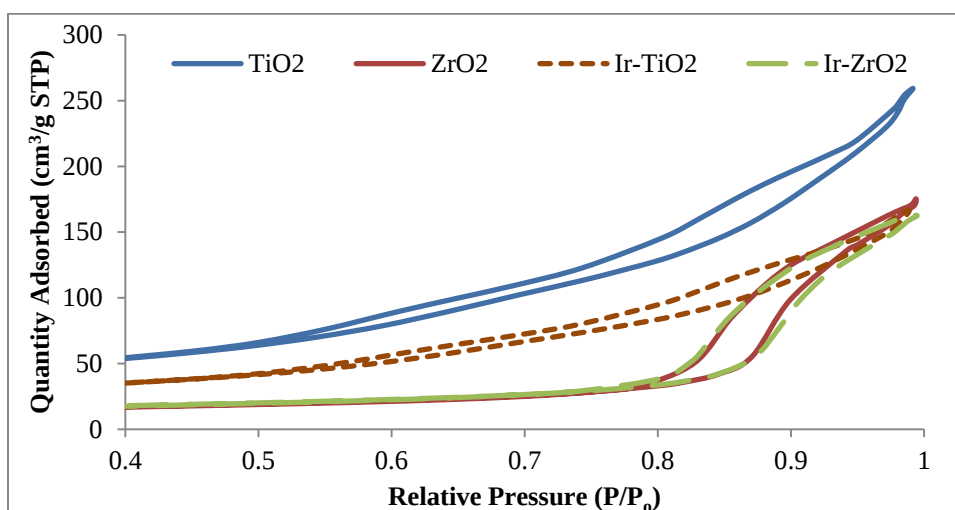


Figure 3.1. N_2 adsorption/desorption profiles of the materials

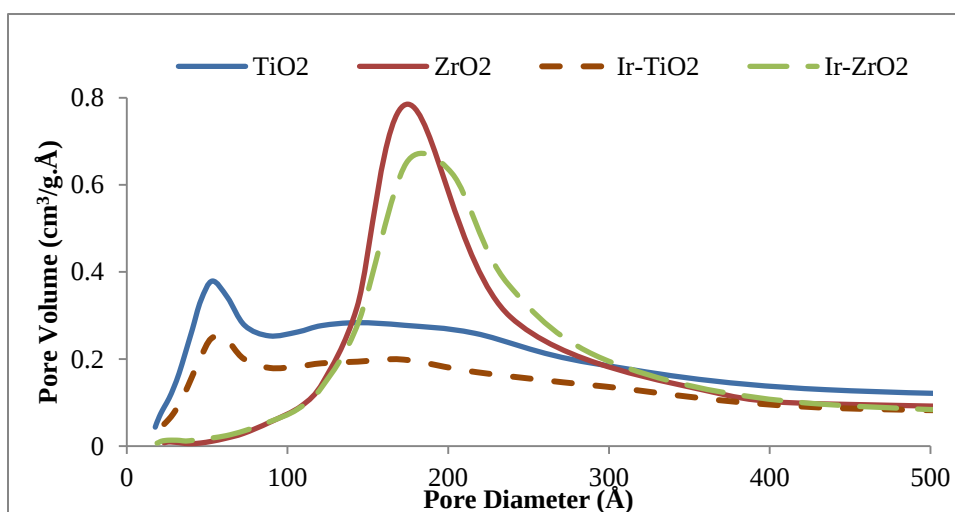


Figure 3.2. Pore size distributions of the materials

The pore size distributions in Fig. 3.2 show no evident peaks that correspond to micropores or macropores for these materials, indicating that all materials have uniform mesoporosity. Slight shifts in the pore volumes are indicative of the presence of the metal on the supports.

3.3.1.2 Powder X-ray diffraction

The XRD diffractograms of the supported Ir catalysts (supplementary information Fig. S3.1) show no phases for Ir at these low weight loadings. This is generally the case for well dispersed active phases, which are not detected by XRD. The supports show characteristic peaks of pure anatase TiO_2 (ICDD File No: 01-089-4921), and the monoclinic and tetragonal phases of ZrO_2 (ICDD File Nos: 01-074-1200 and 01-080-255).

3.3.1.3 X-ray photon spectroscopy

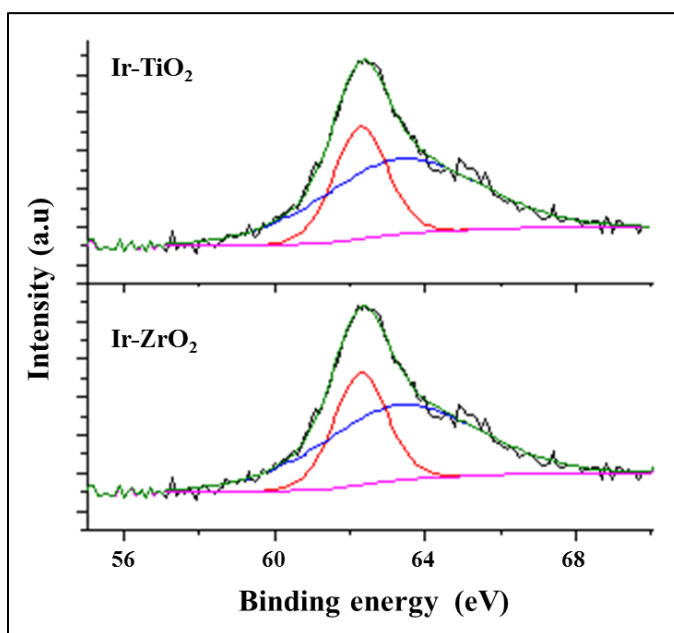


Figure 3.3. XPS spectra of the $\text{Ir}4f_{7/2}$ transition of Ir-TiO_2 and Ir-ZrO_2

Peaks representative for the iridium oxide phases that were not detected by XRD were confirmed using XPS. Fig. 3.3 shows the deconvoluted $\text{Ir}4f_{7/2}$ XPS scan for the supported oxide catalysts. No peaks were observed at binding energies of ~ 60 eV corresponding to Ir^0 . Peaks observed at binding energies of ~ 62 eV and ~ 64.7 eV are attributed to iridium oxide phases respectively [19, 20].

Table 3.2 summarizes the binding energies observed for the Zr $3d_{5/2}$, Ti $2p_{3/2}$, Ir $4f_{7/2}$ and O 1s for the supported Ir catalysts. The binding energies of Zr $3d_{5/2}$ at 184-188 eV and Ti $2p_{3/2}$ at 458-464 eV are the expected values for the oxide supports [20, 21] (Supplementary information Fig. S3.2). The O 1s spectra (supplementary information Fig. S3.2) of the supported Ir catalysts, and the binding energies obtained, correspond to two types of oxygen species, assigned to M-O-M (M= Ti or Zr) and Ir-O species on the support [18, 20]. The Ir loadings obtained are also in agreement with the ICP values.

Table 3.2. Binding energies of the supported Ir catalysts

Catalyst	Binding Energy (eV)				Ir wt. %
	Ir ($4f_{7/2}$)	O (1s)	Ti ($2p_{3/2}$)	Zr ($3d_{5/2}$)	
Ir-TiO ₂	62.3	529.3	458.8	-	0.9
	64.6		464.1	-	
Ir-ZrO ₂	62.3	534.3	-	184.3	1.0
	64.8		-	188.1	

3.3.1.4 Temperature programmed studies

Fig. 3.4 shows the TPR profiles of the supported Ir catalysts. The catalysts have their main reduction peak at 113 °C (Ir-TiO₂) and 117 °C (Ir-ZrO₂), respectively. These peaks are attributed to the reduction of IrO₂ to metallic Ir. The Ir-ZrO₂ catalyst has a shoulder peak at 167 °C with a broad reduction zone which could be the reduction of Ir oxide species with differing interactions with the support [22]. The reduction of these species on the TiO₂ support occurs at a slightly higher temperature (240 °C), probably due to the larger particle size of IrO₂ (HRTEM and CO chemisorption, Sections 3.3.1.6 and 3.3.1.7) [22]. Reduction peaks observed for both the catalysts above 300 °C could be attributed to the surface capping O₂ of the supports or reduction by H₂ spillover [23-25]. Yoshida et al. [19] reported the formation of partially reduced TiO₂ by H₂ in Ir-TiO₂ catalysts which is a well-known phenomenon referred to as the strong metal support interaction effect.

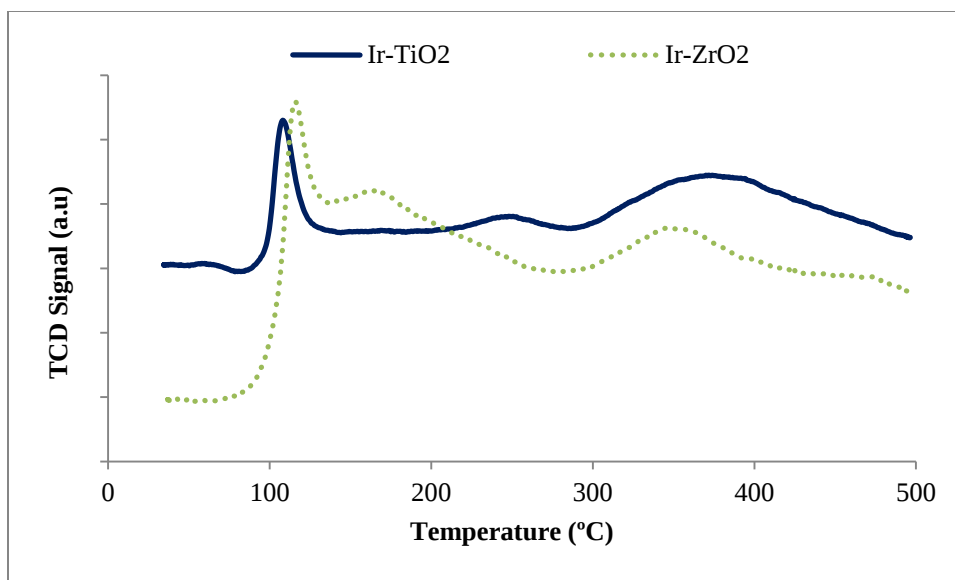


Figure 3.4. H₂-TPR profiles for the supported Ir catalysts

Similarly to what has been seen previously (Chapter 2 and literature [24-28]), under reducing environments reducible supported PGM metals with strong metal support interactions tend to become partially decorated by support interstitials that migrate towards and/or over the active metal at the metal support interface. These migrations are not evident on bare supports but rather are catalysed by the active metal (Ir) as $\text{MO}_{x(2-x)}$ species ($\text{M} = \text{Ti}$ or Zr), as explained in Chapter 2.

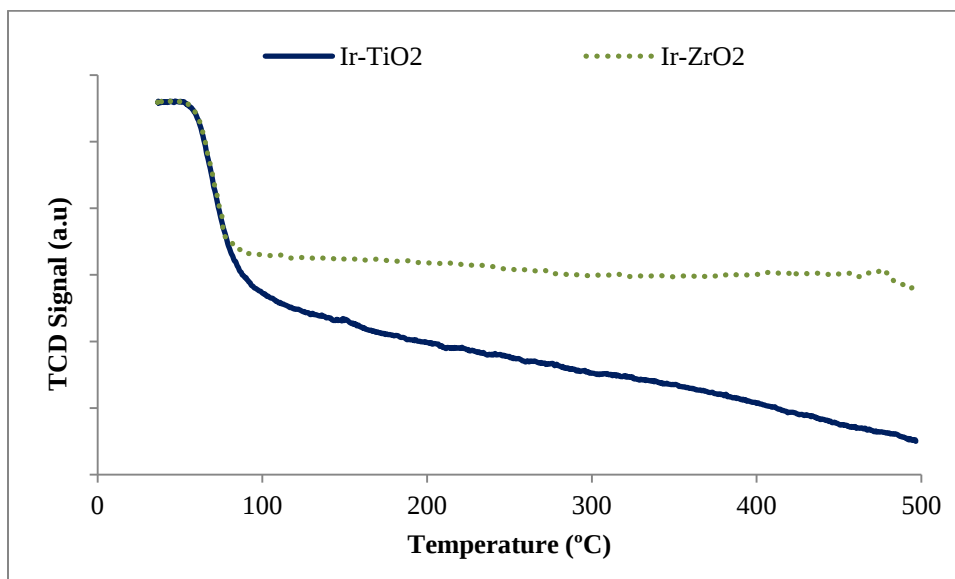


Figure 3.5. O₂-TPO profiles for the supported Ir catalysts

Fig. 3.5 shows the TPO profiles of the reduced catalyst samples. As with the Pt catalysts (Chapter 2), the oxidation of these materials occurs readily at low temperatures even before the TCD records the signal. Also, according to literature highly dispersed Ir samples were found to be easily oxidized at low temperature, from Ir^0 to IrO_2 [29]. O_2 consumption still visible at higher temperatures could be evidence for the oxidation of the supports in close proximity to the metal that forms interstitials, which was also evident for the Pt systems (Chapter 2).

3.3.1.5 FTIR-CO

FTIR-CO analysis of the catalysts was used to determine the interaction of the metals with CO as the probe molecule. Analyses conducted at increasing temperatures are shown in the supplementary information (Fig. S3.3). The analyses of the catalysts at 200 °C are shown in Fig. 3.6. Both spectra show broad peaks for both the supported catalysts at wavenumbers $\sim 2050\text{ cm}^{-1}$ (Ir-ZrO_2) and $\sim 2060\text{ cm}^{-1}$ (Ir-TiO_2), and a smaller shoulder band at $\sim 1950\text{ cm}^{-1}$. These bands indicate adsorption of CO over different metallic species of Ir present on the materials. According to reports [22, 30], CO adsorbing on Ir crystals present a single band between $2000\text{--}2100\text{ cm}^{-1}$ and can be assigned to linearly adsorbed CO species ($\text{Ir}^0\text{--CO}$). Also, bands in the region of 2080 and 2010 cm^{-1} (seen as shoulders on the main peak) could be assigned for simultaneous adsorption of two CO molecules on Ir^0 sites [30]. The shoulder peak located at $\sim 1950\text{ cm}^{-1}$ has been reported as being due to bridge CO molecules adsorbed on supported Ir^0 sites [31].

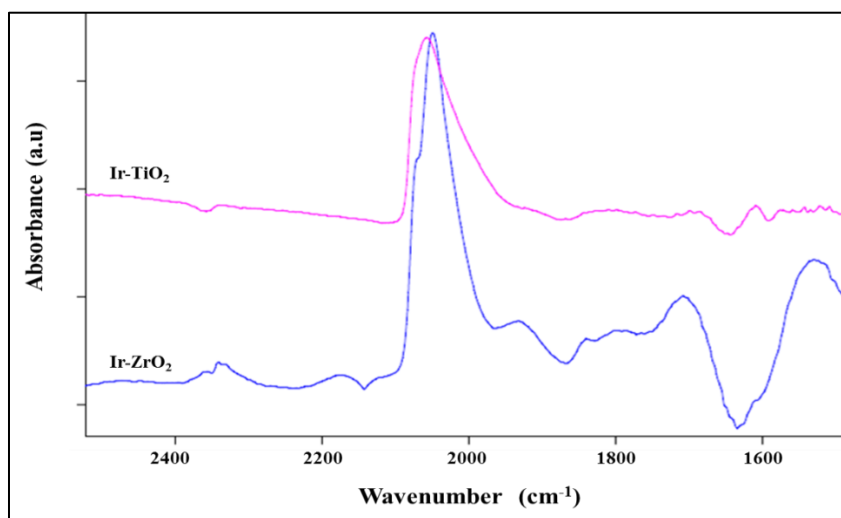


Figure 3.6. FTIR-CO of the supported Ir catalysts at 200 °C

3.3.1.6 CO chemisorption

Table 3.3. CO chemisorption data of the supported Ir catalysts

Catalysts	Properties	Temperature of reduction		
		200 °C	370 °C	500 °C
Ir-TiO ₂	Metal dispersion (%)	61.4	52.1	36.3
	Metallic surface area (m ² /g metal)	107.9	89.4	73.3
	Crystallite size (nm)	6.4	7.0	7.0
	Chemisorption capacity (CO/Ir)	0.49	0.31	0.24
Ir-ZrO ₂	Metal dispersion (%)	91.4	77.5	54.0
	Metallic surface area (m ² /g metal)	160.6	133.0	109.1
	Crystallite size (nm)	5.3	5.8	5.9
	Chemisorption capacity (CO/Ir)	0.69	0.44	0.35

The CO chemisorption properties of the supported Ir catalysts at different reducing temperatures are depicted in Table 3.3. The supports showed no chemisorption properties and the results obtained are attributed to the Ir present on the supports. Similarly to the data presented for the Pt systems (Chapter 2), the metal dispersion, metallic surface area and CO chemisorption capacity decrease with increasing reduction temperature. The Ir-ZrO₂ catalyst showed much better metal dispersion, metallic surface area, CO chemisorption capacity and hence smaller crystallite sizes than the TiO₂ supported catalyst. This result is also possibly due to the acidic Ir precursor (IrCl₃) used for the synthesis of these catalysts which results in stronger interactions with the ZrO₂ support since it is more electropositive and basic than TiO₂ [32]. Also, the synthesis pH plays an important role in controlling the zeta potential of these two supports, whereby the ZrO₂ at its isoelectric point (IEP) (pH 7.4) has a higher affinity for interacting with the metal (pH 5.5) than the TiO₂ (pH 6.0) [33]. As a result the metal dispersions, metallic surface areas and the CO chemisorption values of the Ir-ZrO₂ catalyst are higher than those of the Ir-TiO₂ catalyst. Increasing the reduction temperature results in lower values, which are also likely due to reduction of the supports in close proximity to the active metal attributed to the strong metal-support interactions as observed for the Pt systems [16]. The Ir metal becomes decorated by partially reduced oxides that migrate towards/onto the

metal, suppressing the chemisorption capacity which is seen in Table 3.3 at higher reduction temperatures. The results obtained can be related to those from TPR experiments, where at higher reduction temperature the support shows reduction that is catalyzed by Ir. These supports on their own showed no reductions and according to reported data these reductions occur at temperatures beyond 500 °C [26, 28].

3.3.1.7 Electron Microscopy

Fig. 3.7 shows TEM images of the supported Ir catalysts with the selected area diffraction inserts indicating that the samples are crystalline in nature. Particles sizes presented for the oxide phases were measured using iTEM software and found to be similar on both supports at ± 7 nm. These were clearly distinguished from the supports by the lattice fringes in the images presented. These particles are also within a reported particle size range (6-7 nm) for supported Ir catalysts calcined at 400 °C [29].

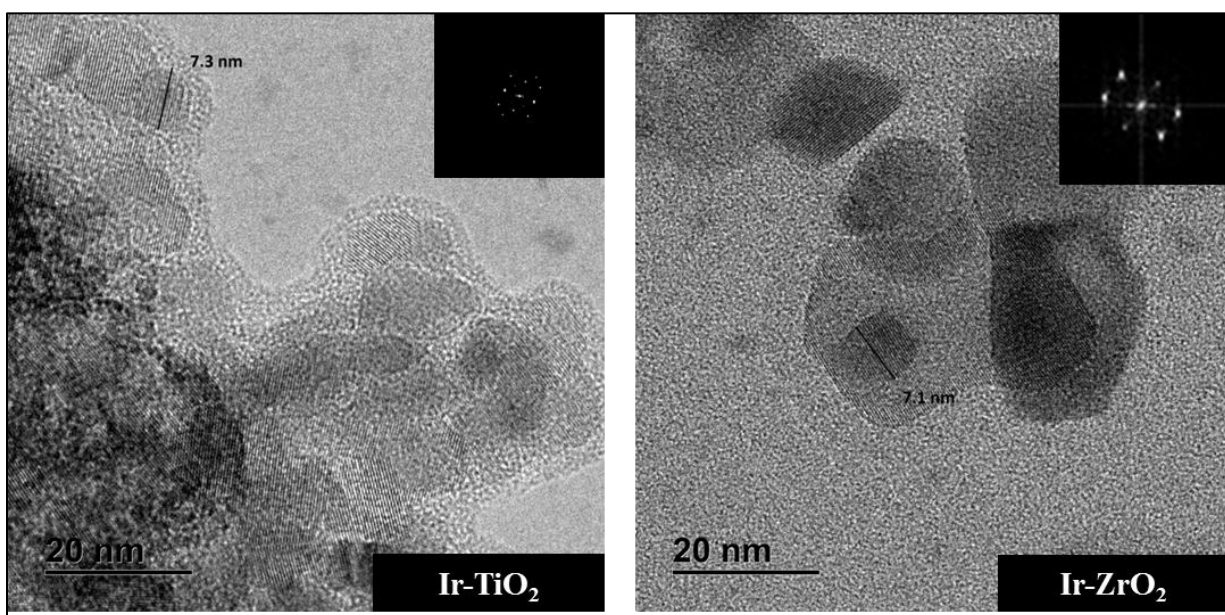


Figure 3.7. HRTEM images of the Ir catalysts (Inset: selected area diffractions)

3.3.2 Catalytic testing

3.3.2.1 CO oxidation

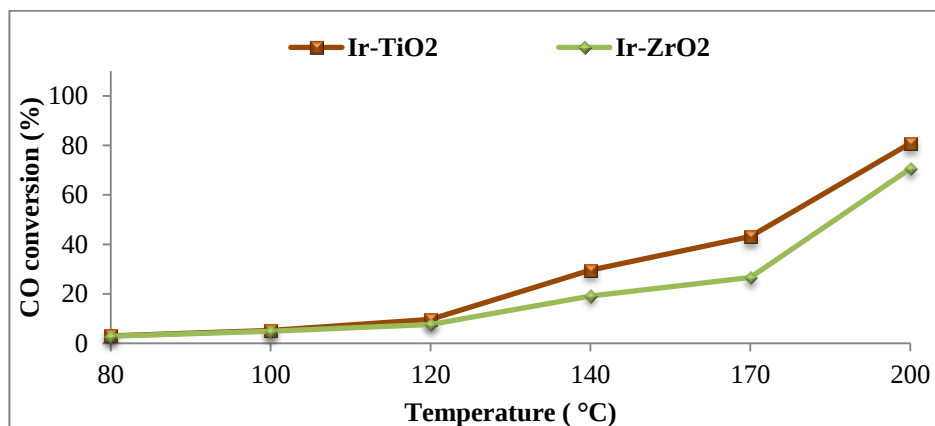


Figure 3.8. CO oxidation reactions over the catalysts with increasing temperatures (GHSV 12 000 h⁻¹)

The activity for the catalysts towards the oxidation of CO in a H₂ free feed is shown in Fig. 3.8. The onset temperature for the oxidation reaction starts at 80 °C. After 120 °C the Ir-TiO₂ catalysts shows slightly higher conversions than the Ir-ZrO₂ catalyst. Both catalysts reach maximum CO conversions at 200 °C, using stoichiometric amounts of O₂ in the feed (O₂ conversions, supplementary information Fig. S3.4). The Ir-TiO₂ catalyst gave a CO conversion of ~80 %, whilst the Ir-ZrO₂ catalyst showed a slightly lower conversion of ~70 %.

3.3.2.2 PROX reaction

The activity of the catalysts for the PROX reaction with high H₂ concentrations (50 %) is presented in Fig. 3.9, with the accompanying O₂ conversions shown in the supplementary information Fig. S3.4. Both the catalysts are active at temperatures lower than 80 °C (Fig. 3.9). The Ir-TiO₂ catalyst shows a maximum CO conversion at 80 °C of 6.4 % with a selectivity towards CO₂ of ~20 %. At temperatures higher than 80 °C, the CO conversion decreases to ~1 % and remains constant, whilst the CO₂ selectivity decreases significantly. The Ir-ZrO₂ catalyst, on the other hand, shows an increase in CO conversion with increasing temperature from 80 °C and reaches a maximum of ~20 % at 200 °C. The selectivity towards CO₂ for this catalyst was at its highest at 80 °C and thereafter also decreases with increasing temperature,

indicating that the oxidation of H_2 becomes more favourable. This is also evident from the O_2 conversions shown for the catalysts (supplementary information Fig. S3.4).

The results obtained for the PROX reaction over the supported Ir catalysts relate to those obtained for the supported Pt-TiO₂ catalysts (Chapter 2). The trends based on the supports are almost identical, indicating that the behaviour of these supported catalysts is controlled by the redox properties of the active metals present on them. These results match those obtained from TPR, TPO and CO chemisorption, where the Ir-TiO₂ catalyst with lower reducibility profile, higher oxidation profile and lower chemisorption values than those of the Ir-ZrO₂ catalyst, was inferior for the PROX reaction. These findings relate closely to reports where ZrO₂, being a “hardier” (less easily reduced) support compared to TiO₂, is shown to have a stronger interaction between the support and the active metal [16, 26, 32-34].

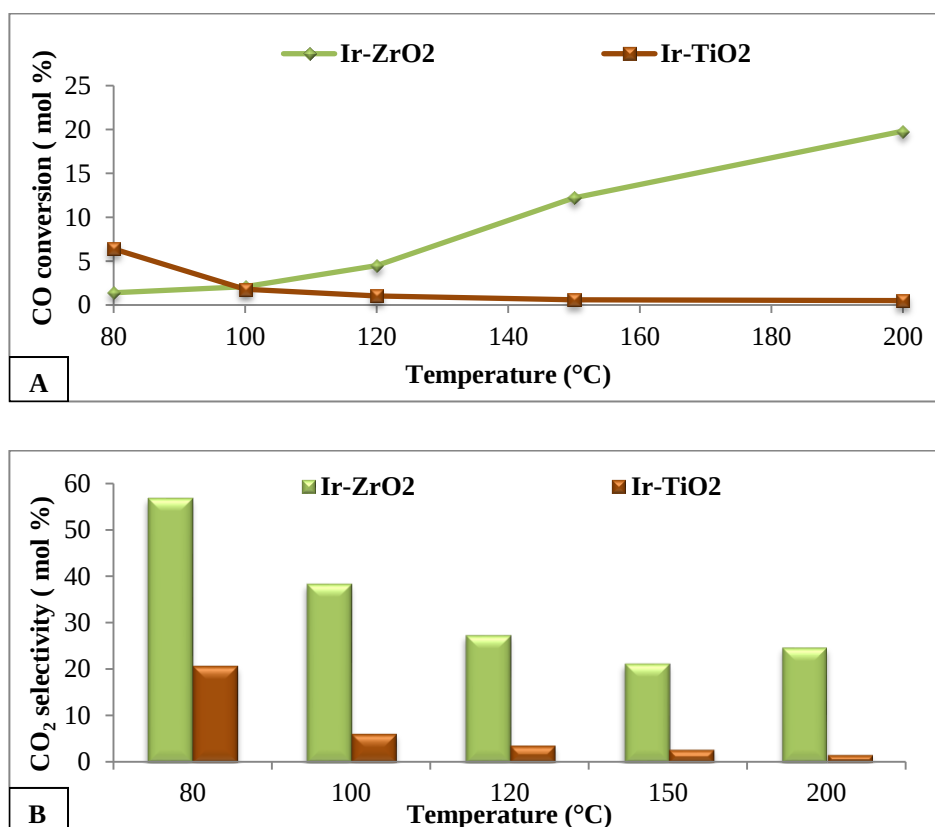


Figure 3.9. CO conversions (A) and selectivity towards CO₂ (B) for the supported Ir catalysts (GHSV 12 000 h⁻¹)

The low activity found for these catalysts, indicating similar behavior as for the Pt systems (Chapter 2) could likely be occurring by a redox mechanism between CO and O₂, similar to that of H₂, over the Ir-TiO₂ catalyst following the Mars and van Krevelan (MvK) mechanism. This result is confirmed by the O₂ conversion for the catalyst (supplementary information Fig. S3.4), where high conversions > 90 % are observed, but with very low CO conversions.

The Ir-ZrO₂ catalyst on the other hand, allows adsorbed CO to interact with molecular O₂ from the feed following the Langmuir Hinshelwood (LH) mechanism similar to that of the Pt-ZrO₂ catalysts shown in Chapter 2. A study by Huang et al. [12] reported a non-competitive LH mechanism for a 1.6 wt. % Ir-CeO₂ catalyst, where Ir particles themselves were involved in both the CO and H₂ oxidation pathways. However, with increasing temperatures Ir becomes too active to selectively oxidize CO and favours H₂ oxidation instead, which is also evident in this study where CO₂ selectivity decreases with increasing temperature (Fig. 3.9). This is confirmed by the H₂ conversions of the catalysts (supplementary information Fig. S3.5) which shows an increase with temperature. Ir-TiO₂ shows a higher H₂ conversion than the Ir-ZrO₂ catalyst, though the CO conversions were much lower.

Another study by Okumura et al. [35] reported that for a 1.8 wt. % Ir-TiO₂ catalyst synthesized at pH 7, where the point of zero charge of TiO₂ was controlled (negatively charged) for a better interaction with an Ir⁴⁺ salt, resulted in higher stabilities of the catalysts at 27 °C using a feed consisting of 1% CO and balanced with Air. However, this catalyst still deactivated rapidly after 7 h. Comparing these findings with this study, firstly the amount of O₂ used is too high for fuel cell application where this catalysts would give much higher H₂ oxidation. Secondly, the catalyst was not stable for the reaction and showed rapid deactivation early in the reaction. Lastly, the temperature at which maximum CO conversions were obtained was 27 °C, and an on-board fuel cell operates at 80 °C, therefore additionally to the O₂ that is supplied, a heat exchanger would need to be introduced.

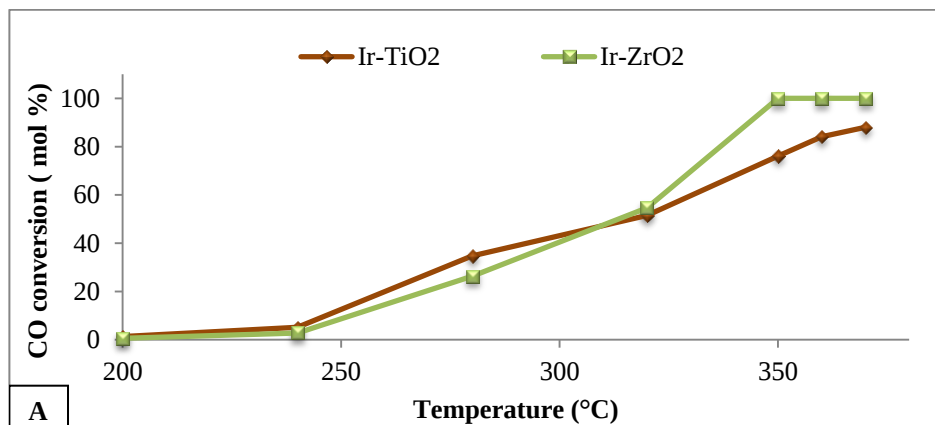
For the reactions carried out in this study irrespective of the low CO conversions, the catalysts were stable over the entire heating cycle and upon cooling the results obtained were very similar showing no signs of deactivation. However, the Ir-ZrO₂ catalyst was much more effective than the Ir-TiO₂. Future work on these materials, such as varying the particle size,

support and pre-treatments could show promising results towards the oxidation reaction in the presence of H₂.

3.3.2.3 Hydrogenation reactions

CO hydrogenation reactions over the supported catalysts were performed and the results obtained are shown in Fig. 3.10. It is seen that these catalysts are active for the hydrogenation reaction with the onset of activity following 200 °C over both the catalysts. Temperatures above 200 °C for these reactions, unlike from the PROX reaction, pose no complications such as the unwanted oxidation of H₂ since no O₂ is present in the feed. As the temperature increases, the CO conversions of both the catalysts increase accordingly. The Ir-ZrO₂ catalyst reached maximum CO conversions of 99.9 % at 350 °C and thus remained constant to 370 °C. The Ir-TiO₂ catalyst on the other hand reached a maximum CO conversion at 370 °C of ~88 %. The selectivities towards CH₄ for both these catalysts were above 90 % for all the reaction temperatures investigated, indicating that these catalysts are not active for the WGS reaction. Hydrogen conversions, shown in Fig. 3.10, indicate that at these high CO conversions only a small fraction of the H₂ is used. Also, the CH₄ formed by CO conversion can be reused in the reformer for on-board applications, therefore H₂ usage remains minimal [36].

The activity of these catalysts are very similar to those obtained for the PtDP-TiO₂ system (Chapter 2), with Ir-TiO₂ showing slightly better activity due to the better metal dispersions, particle sizes and redox properties. Similarly, the Ir-ZrO₂ catalyst showed better redox and CO chemisorption properties than Ir-TiO₂, and therefore, showed better activity for the hydrogenation reaction.



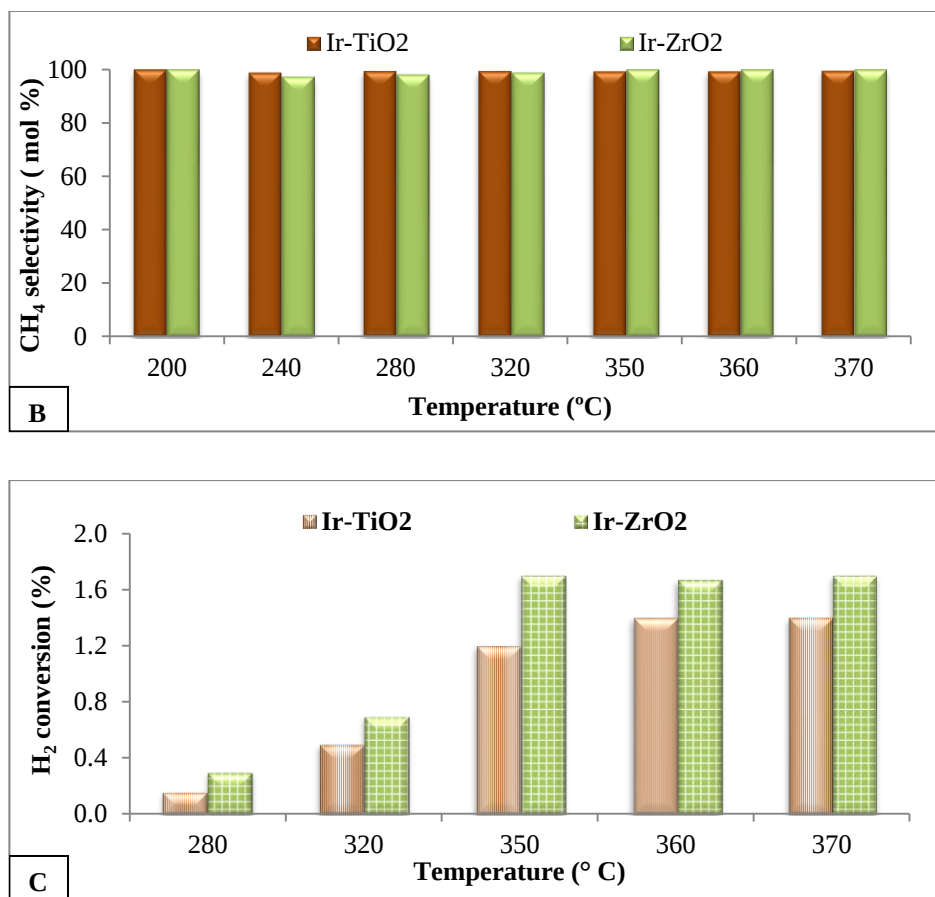


Figure 3.10. CO hydrogenation reaction over the supported catalysts with increasing temperatures (GHSV 12 000 h⁻¹), CO conversion (A), CH₄ selectivity (B) and H₂ conversion (C)

Based on these results of the supported Ir catalysts, the Ir-ZrO₂ catalyst showed better metal dispersion, metallic surface area, CO chemisorption capacity and smaller particle sizes and hence better catalytic activity than for the Ir-TiO₂ catalyst, due to the strong metal support interactions of ZrO₂ and Ir which resulted from controlling the IEP during the synthesis which gave better metal support interactions. The availability of the active metal (metal dispersion) for the hydrogenation of CO on the Ir-ZrO₂ catalyst at higher temperatures was higher than that for the Ir-TiO₂ catalyst. Also, at higher temperatures, even beyond the hydrogenation reaction at 500 °C, evidence of CO adsorption (CO chemisorption) still taking place on both the catalysts reveals that Ir active sites are still available and not completely embedded in the support.

Following the high temperature WGS reaction, these Ir catalysts may have promise for removing the trace CO that is present in the reformat gas.

3.4 Conclusion

All catalysts were active for the oxidation of CO, showing significant activity within the temperature range screened (80-200 °C). However, both the catalysts showed low activity for the PROX reactions, since the oxidation of H₂ was favoured rather than the desired CO oxidation. Characterization of the prepared catalysts revealed that supports with well dispersed Ir particles result in the formation of interstitials (O₂ vacancies) due to the strong metal-support interactions at the interface. These interactions allow for partial reduction of the supports which are catalyzed by the Ir on the surface. Therefore, during the PROX reaction H₂ reacts with O₂ forming H₂O instead of CO₂.

The Ir-TiO₂ catalyst follows the Mars and van Krevelan pathway using lattice O₂ for the oxidation reaction, whilst the Ir-ZrO₂ catalysts follows the Langmuir Hinshelwood pathway instead.

Both the catalysts showed promising results for lowering the amount of CO present in the reformat gas to low ppm levels by CO hydrogenation. Ir-ZrO₂ gave 99.9 % CO conversion above 350 °C with high selectivities toward CH₄. Controlling the IEP of the catalysts during the synthesis resulted in better dispersion of Ir over the supports, thus favoring the interaction between metal and support. TiO₂ and ZrO₂ supported Ir catalysts prepared by the deposition precipitation method show promising activity for the hydrogenation of CO following the high temperature WGS reaction for removing trace amounts of CO. These catalysts need to be subjected to ideal exit WGS reformat feeds for further investigation to determine the catalyst's stability in the presence of CO₂ and H₂O.

Acknowledgements

We thank NRF and HySA for financial support during this study, Dr J.W. Smith CSIR for the microscopic analyses, Dr. D. Morgan, Cardiff Catalysis Institute, for XPS studies, Dr P. Mohlala and Dr M. duToit at SASOL R&D for the FTIR-CO analyses.

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Supplementary information

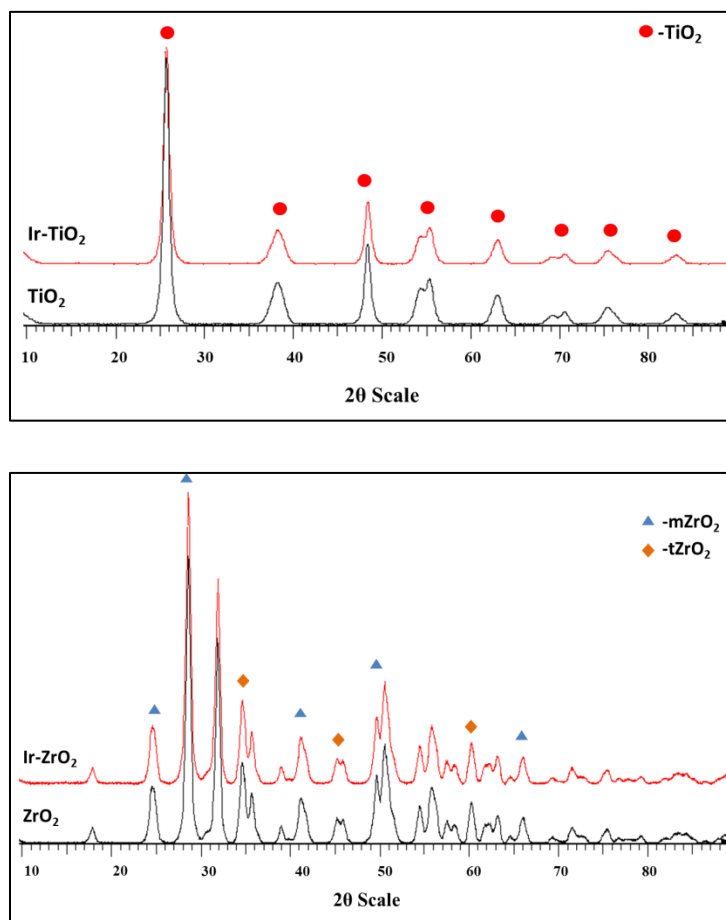


Figure S3.1. XRD diffractograms of the supports and catalysts

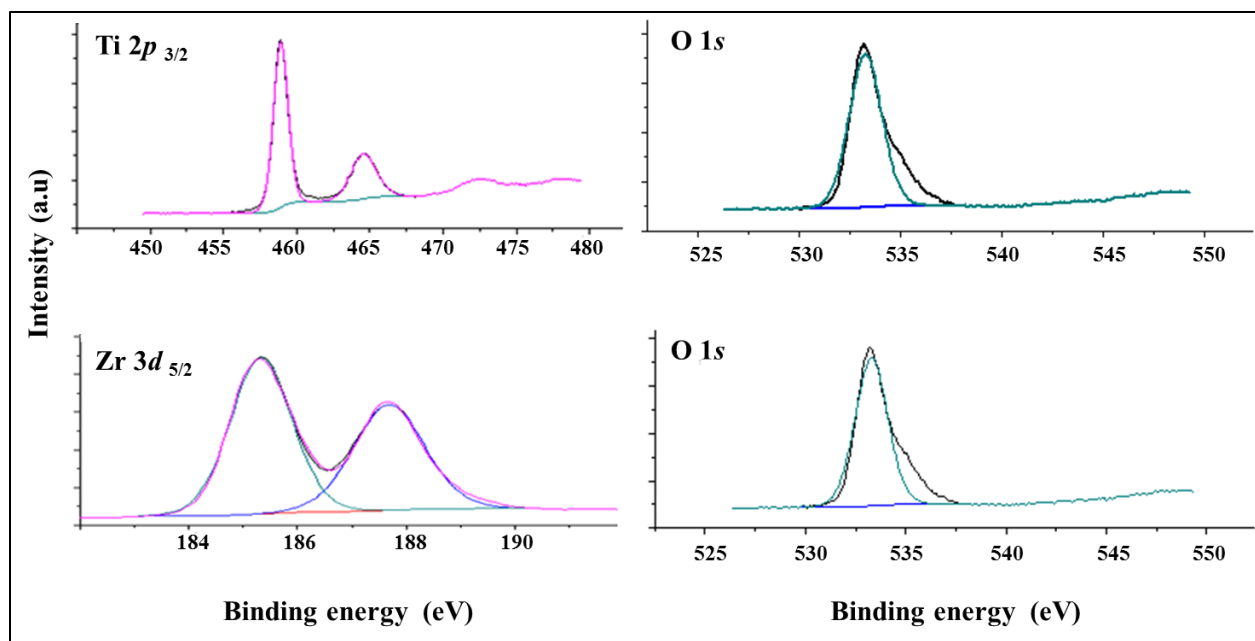


Figure S3.2. XPS spectra showing the Zr 3d_{5/2}, Ti 2p_{3/2} and the O 1s levels for the catalysts

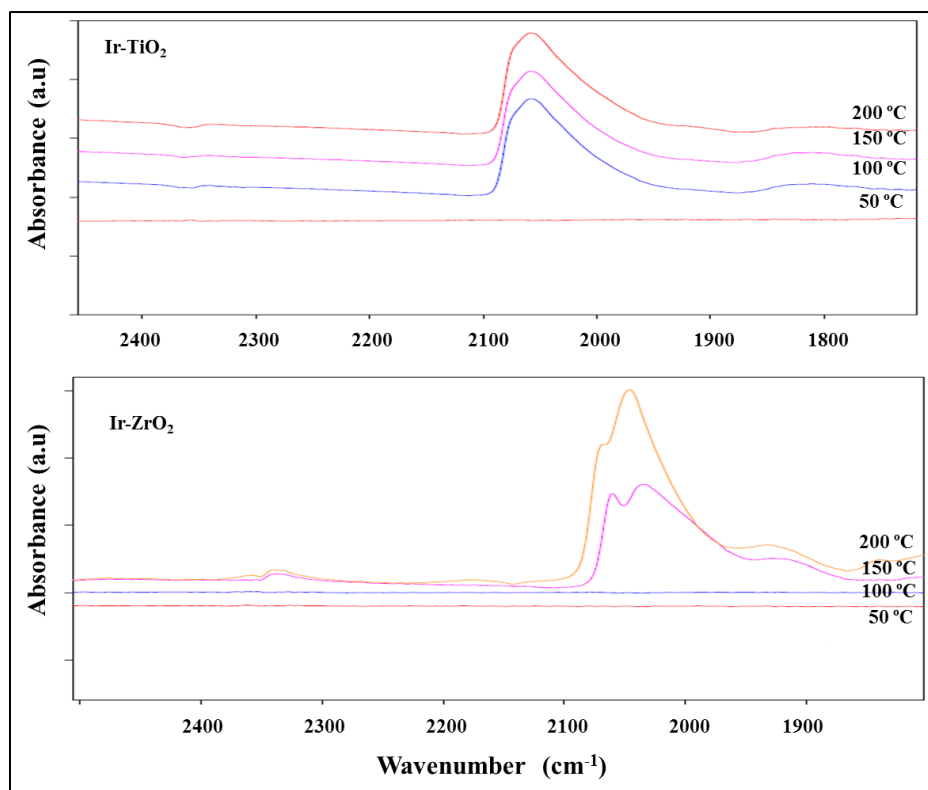


Figure S3.3. FTIR-CO analyses of the catalysts with increasing temperatures

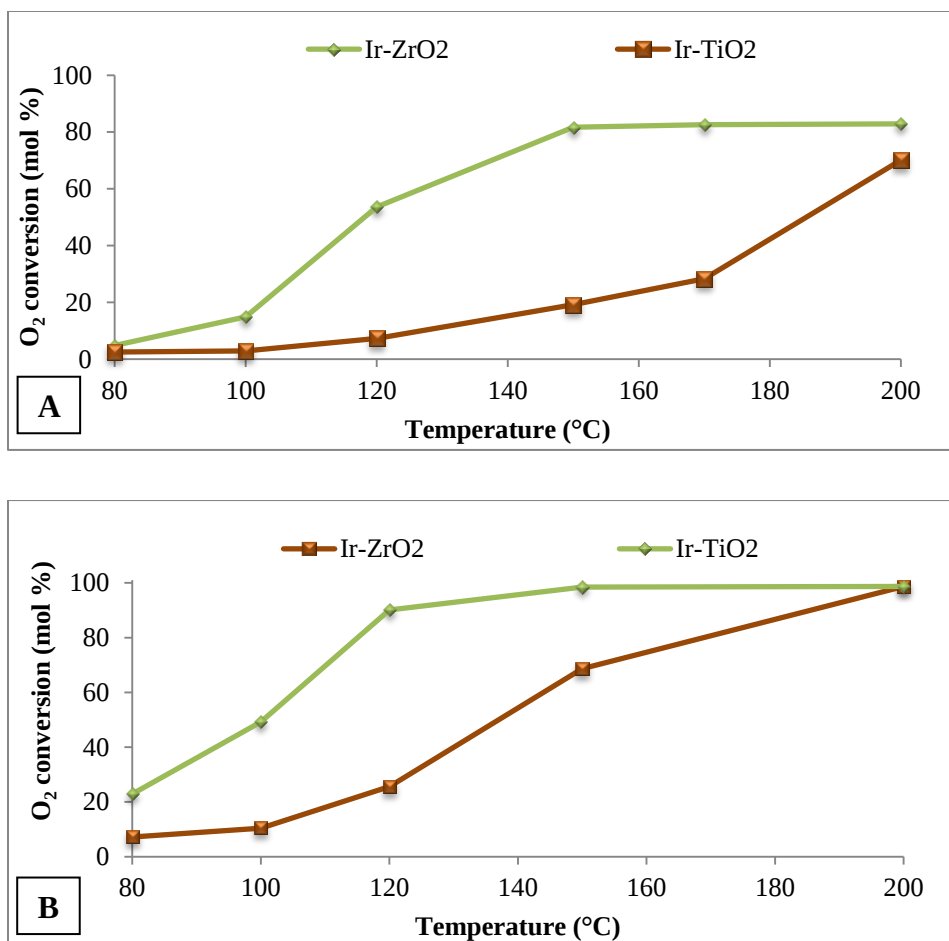


Figure S3.4. O₂ conversions of the supported Ir catalysts for A: Total oxidation and B: PROX

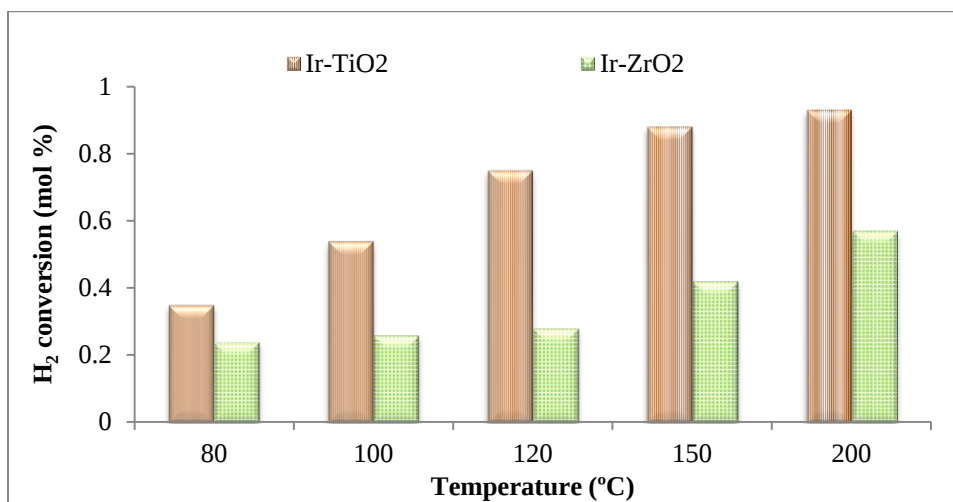


Figure S3.5. H₂ conversions of the supported Ir catalysts for the PROX reaction

Chapter 4

TiO₂ and ZrO₂ supported Ru catalysts for CO mitigation following the water-gas shift reaction

Ziyaad Mohamed, Sooboo Singh and Holger B. Friedrich*

Catalysis Research Group, School of Chemistry and Physics, University of KwaZulu-Natal,
Durban 4000, South Africa

Abstract

CO oxidation and methanation over Ru-TiO₂ and Ru-ZrO₂ catalysts were investigated for CO removal for applications in proton exchange membrane fuel cells. Characterization experiments including TPR, XPS, FTIR-CO, CO chemisorption and HRTEM were conducted to reveal the physio-chemical properties of Ru on the supports. Both the catalysts showed excellent activity for the total oxidation of CO, however, with the addition of H₂, the catalysts activity to CO oxidation decreased significantly. Higher temperatures for the preferential oxidation reaction indicated that the Ru catalysts not only oxidize CO, but hydrogenate it as well. Furthermore, H₂ oxidation was favoured over the catalysts. Hydrogenation of CO over these catalysts gave high CO conversion and selectivity towards CH₄. Both the catalysts showed similar activity across the temperature range screened and gave maximum conversions of 99.9 % at 240 °C with 99.9 % selectivity towards CH₄. These similarities in the catalyst's activity were attributed to the well-dispersed Ru metal over the supports. H₂ consumption remained below 2 % throughout.

Keywords: Ruthenium, TiO₂, ZrO₂, CO, oxidation, CO hydrogenation

* Corresponding author: Tel.: +27 31 2603107, Fax.: +27 31 260 3091,
E-mail: friedric@ukzn.ac.za

4.1 Introduction

On-board reforming of natural gas to generate hydrogen for proton exchange membrane fuel cells (PEMFC) is currently an emerging field of research [1]. PEMFCs offer higher power density, deliverability, cleanliness and ease of implementation compared to other fuel cell types used for mobile or portable power generation [2-5]. At present, the development of a fuel processor that is capable of converting CH_4 into H_2 via a series of on-board catalytic steps is the preferred route [6-8]. In these systems, following the water-gas shift (WGS) reaction, where unacceptable levels of CO are still present in the reformat gas, oxidation or hydrogenation reactions could be employed to reduce CO to acceptable levels (<10 ppm) or obtain a CO free feed gas [7, 9-11].

Studies on the preferential oxidation (PROX) reaction over supported Ru catalysts were carried out using Al_2O_3 , CeO_2 , SiO_2 and multi-walled carbon nanotubes as supports [7, 9, 12]. Compared to the amount of work already carried out using Au and Pt based catalysts for this reaction, Ru also shows promise for the PROX reaction, where factors such as the preparation techniques, pre-treatments and particle size have been investigated [7, 13]. To date, no comparative study on Ru supported on TiO_2 or ZrO_2 , with regards to CO chemisorption properties and support effects, have been carried out.

In contrast, hydrogenation of CO over Ru based catalysts has been extensively reported [2, 11, 14]. Vannice [15-18] reported kinetic studies on the reaction over transition metals and PGMs supported on oxides such as Al_2O_3 , SiO_2 and TiO_2 . These studies show that among all the catalysts tested, those containing Ru were best. Later studies also involving monometallic (Ni/ TiO_2 , Ru/carbon nanofiber, Ni/ CeO_2 and Ru/mesoporous supports) and bimetallic (Ru- $\text{Al}_2\text{O}_3/\text{TiO}_2$ and Ni- $\text{Al}_2\text{O}_3/\text{TiO}_2$) catalysts were also proposed for the CO methanation reaction [2, 6, 10, 11, 14, 19]. Reports on these systems showed that the reaction proceeded through the dissociation of CO on the active metal, followed by sequential hydrogenation. In spite of the previously mentioned studies, the CO methanation reaction for on-board fuel cell applications using ZrO_2 as a support has not been examined. Furthermore, a comparative study involving the CO chemisorption properties of TiO_2 has, to date, not been reported.

This study presents the synthesis of Ru-TiO₂ and Ru-ZrO₂ catalysts by the deposition precipitation method. The catalysts were characterized by a number of physical and chemical techniques to elucidate the nature of the Ru on the supports which give high efficiency in both PROX and hydrogenation. The reactions were studied within the stipulated temperature ranges for fuel cell applications using a feed mimicking the water-gas shift (WGS) reformat stream.

4.2 Experimental

4.2.1 Catalyst synthesis

The supported Ru catalysts (~1 wt. % loaded) were prepared by the deposition precipitation method [20, 21]. An aqueous solution of RuCl₃.xH₂O (Merck, Germany) was dissolved in a minimum of deionized water and added to a slurry of the support (TiO₂ or ZrO₂ in 250 mL H₂O) at a maintained pH of 7-7.5 using a 10 % solution of NH₃. The mixture was aged for 2 hours at 65 °C and filtered. This was then washed repeatedly with water (65 °C) to remove all Cl⁻. The resultant precipitate was oven dried at 110 °C overnight and calcined for 4 h under a steady flow of air at 400 °C. The catalysts are denoted as Ru-TiO₂ and Ru-ZrO₂.

4.2.2 Catalyst characterization

Using an Optima 5300 DV PerkinElmer Optical Emission Spectrometer, the active metal content of the samples were determined by ICP. Approximately, 0.50 g of sample (accurately weighed) was digested using 5 mL H₂SO₄ on a hotplate. The ICP standards used were prepared in the range 0 to 50 ppm from a stock standard of Ru (1.000 µg/mL in 10 wt. % HCl, Fluka Analytical, USA).

The BET specific surface areas of the catalysts were determined by N₂ physisorption analyses using a Micromeritics TriStar II 3020. Prior to the analysis, the samples (~0.2 g) were degassed overnight under N₂ at 200 °C.

X-ray diffractograms (XRD) of the materials were recorded using Diffracplus XRD Commander Software and a Bruker VANTEC detector on a Bruker D8 Advance instrument. Scans of the materials were obtained within a 2θ range of 10-90 °(0.5 °/ min) using a Cu Kα (λ 0.1540 nm) radiation source that was operated at 40 kV and 40 mA respectively.

Temperature programmed reduction and oxidation (TPR and TPO) studies were conducted using a Micromeritics Autochem II Chemisorption Analyzer 2920. The samples (± 0.05 g) were loaded in a U-shaped quartz tube and pre-treated at 80 °C under He (10 mL/min) for 30 min and then cooled to 35 °C. The reduction (5 vol % H₂ in Ar) and oxidation (5% O₂ in Ar) experiments were conducted using a flow rate of 5 mL/min from 35-500 °C with a ramp rate of 10 °C/min.

Using a Bruker Tensor 27 with Harrick DRIFTS accessory fitted with a Harrick high temperature reaction chamber, the FTIR-CO spectra of the catalysts were obtained. Prior to the analysis, the samples were reduced at 200 °C under H₂ for 3 h. Ar was used to flush out residual H₂ over the samples and CO was then pulsed through a 100 μ L VICI loop using a flow rate of 25 mL/min.

X-ray photon spectroscopy (XPS) scans of the materials were obtained using a Kratos Axis Ultra DLD spectrometer. An achromatic Al K source was used and operated at 120 W while maintaining a pressure of 1×10^{-9} mbar in the chamber. For the regional scans, pass energies of 160 eV and 40 eV were used. Binding energy calibrations were done against the standard C 1s peak as a reference at a binding energy of 284.7 eV [1].

CO chemisorption experiments were carried out (on catalysts samples (~ 0.05 g) that were degassed under N₂ overnight (200 °C) followed by being kept under vacuum for 12 h) using a Micromeritics ASAP 2020 instrument. Similar to the TPR experiments, samples were loaded into a quartz tube and reduced under H₂ at different temperatures (200, 240, 280 and 320 °C) for 2 h prior to the analyses. Data were recorded at 200 °C within a pressure range of 100–700 mmHg. The CO chemisorption capacities were determined by extrapolation of the CO uptake to zero pressure. Accordingly the crystallite sizes, metal dispersions and metallic surface areas were calculated from the software using stoichiometric ratios of CO:Ru of 1.

4.2.3 Catalytic testing

The catalytic testing was performed at atmospheric pressure on a custom built stainless steel fixed bed reactor using 0.75 mL of catalyst diluted with 24 gritt carborundum (1:1). Catalysts were pre-treated at 200 °C under H₂ for 2 h. Activity measurements were recorded from RT to 200 °C for the oxidation reactions and from RT to 260 °C for the hydrogenation

reactions. The reactant flow mixtures were: for CO oxidation 1% CO, 0.5 % O₂ and balance N₂; for “dry” PROX: 1% CO, 0.5 % O₂, 50 % H₂ and N₂ balance and “dry” SMET: 1% CO, 70 % H₂ and balance N₂ with the GHSV fixed at 12 000 h⁻¹. The effluent gaseous products were analyzed online using an Agilent Micro-GC CP-4900 TCD housing 3 channels. Results were recorded in triplicate with O₂, C and H₂ balances ranging between 95 and 105 % for all the reactions. No products except CO₂, H₂O and CH₄ were observed under these conditions.

4.3 Results and discussion

4.3.1 Catalyst characterization

4.3.1.1 Surface area, porosity analyses and Ru loadings

Table 4.1. BET surface area, pore volume and Ru loadings of the materials

Catalyst	Ru wt. (%) ^a	Surface Area (m ² /g)	Pore Volume (cm ³ /g)
TiO ₂	-	151	0.35
ZrO ₂	-	57	0.25
Ru-TiO ₂	0.8	144	0.37
Ru-ZrO ₂	0.7	52	0.25

^aICP analysis

Results of specific surface area measurements and ICP data for the supports and Ru catalysts are presented in Table 4.1. The actual loadings of Ru obtained from ICP are lower than expected, but both catalysts show similar loadings. Following the addition of Ru to the supports, lower specific surface areas are obtained, whilst the pore volumes appear to be unchanged.

N₂ adsorption/desorption isotherms shown in Fig. 4.1, show typical type IV isotherms with H1 hysteresis loops that are characteristic for mesoporous materials. These isotherms also show that the addition of Ru to TiO₂ and ZrO₂ does not change the shape and hysteresis of the isotherms, suggesting that the Ru particles are present over the surface of the supports and do not affect its pore structure or porosity.

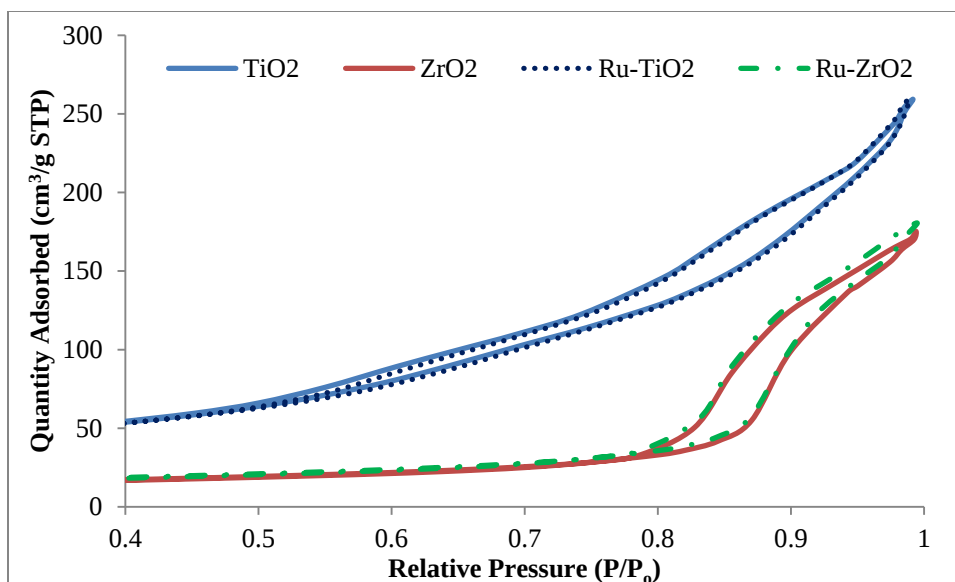


Figure 4.1. N₂-adsorption/desorption isotherm profiles of the supported Ru catalysts

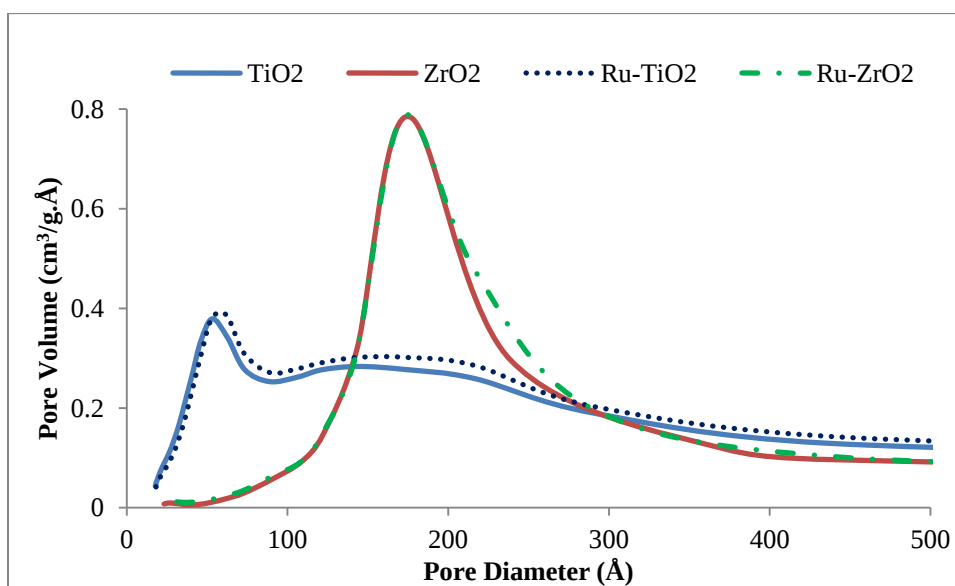


Figure 4.2. Pore size distribution patterns of the supported Ru catalysts

The pore size distribution for the materials is presented in Fig. 4.2, which clearly confirms the mesoporous nature of the samples. No change in the pore structure and pore volumes can be seen following the addition of Ru. These results correlate with the BET surface areas and isotherms obtained for the Ru catalysts.

4.3.1.2 Powder X-ray diffraction

The XRD diffractograms of the supported Ru catalysts are shown in the supplementary information (Fig. S4.1). RuO phases are not observed in the diffractograms suggesting that these RuO particles are highly dispersed on the surfaces of the TiO₂ and ZrO₂. Only characteristic peaks of pure anatase TiO₂ (ICDD File No: 01-089-4921), and monoclinic and tetragonal phases of ZrO₂ (ICDD File Nos: 01-074-1200 and 01-080-255) are seen.

4.3.1.3 X-ray photon spectroscopy

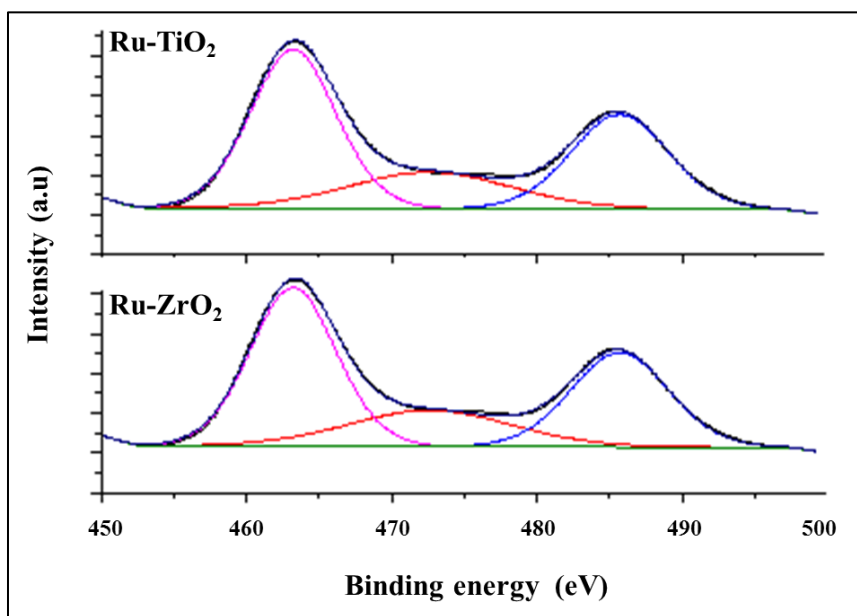


Figure 4.3. XPS curve fittings for the Ru 3p binding energies

XPS analyses of the materials were carried out. The XPS curve fitting for Ru 3p is shown in Fig. 4.3 for both the supported Ru oxide catalysts. The binding energies of Ru 3p_{1/2} and Ru 3p_{3/2} are at 468 and 463-4 eV, respectively. These are attributed to RuO particles present on the supports [22, 23].

The XPS spectra of the Ti 2p_{3/2}, Zr 3d_{5/2} and the O 1s are shown in the supplementary information (Fig. S4.2). The O 1s peak positions, also shown in Table 4.2, shift between 530.8 and 531.3 eV for the supports, which is also characteristic for RuO₂ [22]. The Ti 2p and Zr 3d peaks are sharp, intense and not distorted in any way, indicating that the electronic states of Ti

and Zr are mainly Ti^{4+} or Zr^{4+} at the binding energies presented [22]. Furthermore, the Ru metal content estimated from XPS is in agreement with those of ICP.

Table 4.2. Binding energies of the supported catalysts

Catalyst	Binding Energy (eV)					Ru wt. %
	Ru ($3p_{3/2}$)	Ru ($3p_{1/2}$)	O (1s)	Ti ($2p_{3/2}$)	Zr ($3d_{5/2}$)	
Ru-TiO ₂	463.1	468.2	531.3	459.1	-	0.8
				464.3	-	
Ru-ZrO ₂	464.2	468.1	530.8	-	185.5	0.9
				-	188.1	

4.3.1.4 Temperature programmed studies

The reducibility of the catalysts was investigated by TPR experiments and the results are shown in Fig. 4.4. From the profile it can be seen that there are two early reduction peaks at 114 and 161 °C for the Ru-ZrO₂ catalyst and three peaks at 120, 126 and 172 °C for the Ru-TiO₂ catalyst. The first (early) reductions can be attributed to those of well dispersed RuO_x or RuO₂ particles to metallic Ru⁰, whilst the second (higher temperature) reduction could be of oxidized Ru species that strongly interact with ZrO₂ or TiO₂, possibly located within some of the narrow pores of the supports [24]. Different explanations have been offered for reduction peaks that are observed beyond 200 °C. Firstly, some reports suggest that these could be due to the reduction of very strongly interacting Ru species with the support, which results from strong metal-support interactions when Cl⁻ precursors are used during synthesis [7]. Secondly, these peaks could be due to the reduction of the supports themselves, promoted by the presence of Ru [25]. A study by Li et al. [26] on the TPR profile of Ru supported on TiO₂ proposed that RuO₂ may not only exist on the surface of support but also be embedded completely or partially within the support itself. The surface exposed RuO₂ particles may also become decorated by migration of the support (Ru particles move inwards) under reducing environments. Therefore the differences in these locations and decorations result in RuO₂ particles being reduced at different reduction temperatures, at higher temperature.

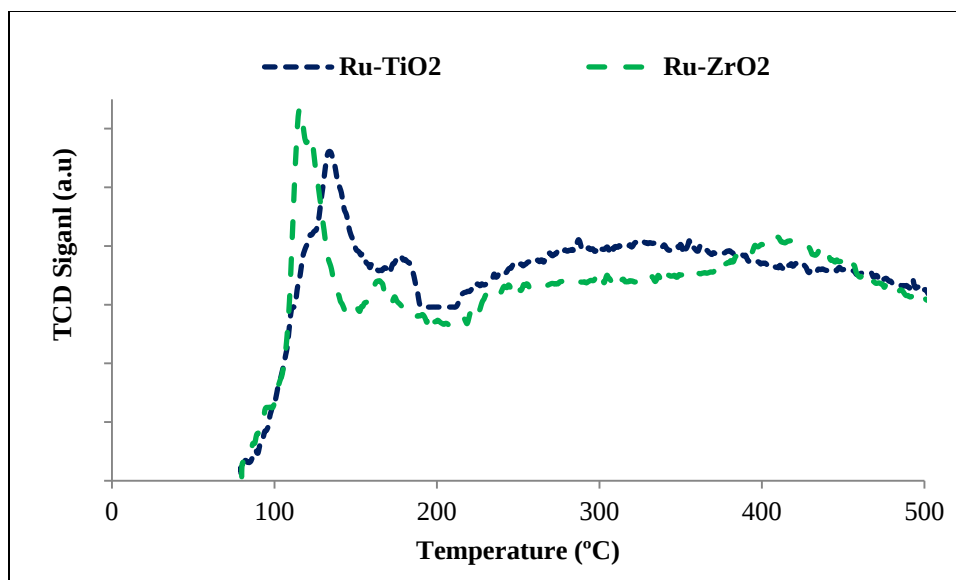


Figure 4.4. H₂-TPR profiles of the supported Ru catalysts

Results from TPO experiments conducted on the reduced Ru catalysts are shown in Fig. 4.5. From the TPO profile of the Ru-TiO₂ catalyst, oxidation occurs at 47 °C, a shoulder is seen at 111 °C and a larger pronounced peak at 135 °C. The Ru-ZrO₂ catalyst, unlike the TiO₂ supported sample, shows one peak at 55 °C. Both these catalysts show signs of oxidation at moderate O₂ consumptions above 200 °C. Kim et al. [13] reported that lower temperature oxidations can be attributed to the oxidation of chemisorbed H₂, whereas the following sharp oxidation peak/s originate from the oxidation of metallic Ru⁰ to RuO₂. The peaks obtained from the catalyst profiles can therefore be attributed to firstly the oxidation of chemisorbed H₂, which in this case is only evident for the Ru-TiO₂ catalyst at 47 °C, since TiO₂ is more reducible than ZrO₂, and also surface capping of O₂ is more prominent on these materials. The peaks observed at 55, 111 and 135 °C are those for the oxidation of metallic Ru⁰ to RuO₂. After 200 °C, the observed oxidations could probably be due to the oxidation of the supports that were partially reduced by H₂ spillover.

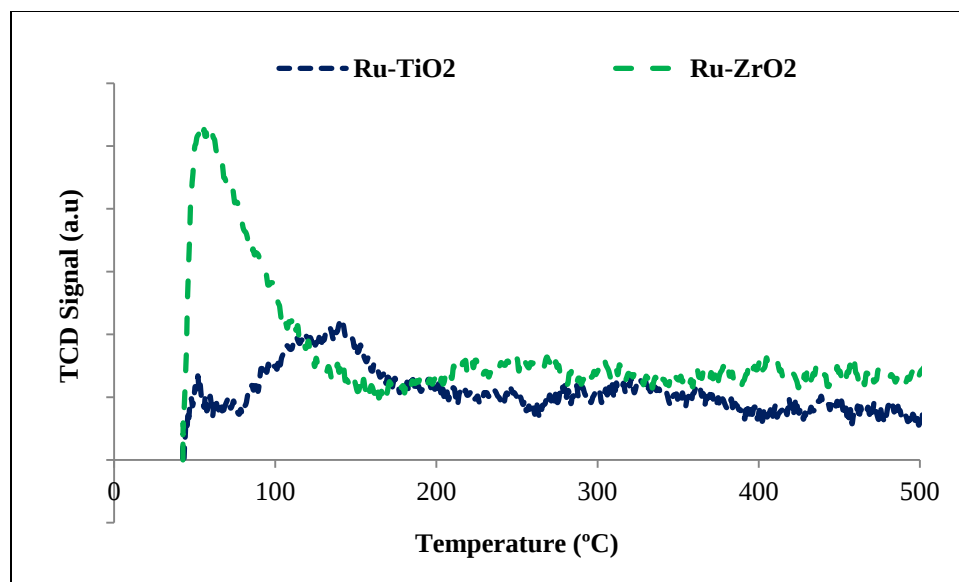


Figure 4.5. O₂-TPO profiles for the supported Ru catalysts

4.3.1.5 FTIR-CO

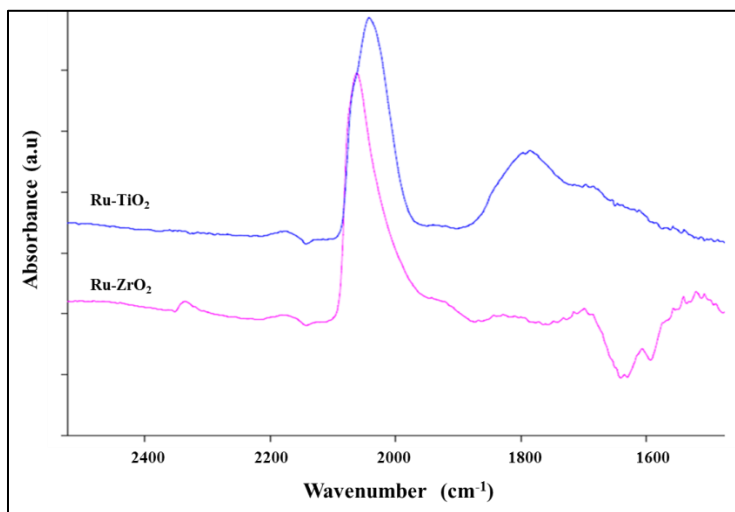


Figure 4.6. FTIR-CO spectra of the supported Ru catalysts

The supported Ru catalysts were analyzed by FTIR using CO as the probe molecule, from RT to 200 °C (Supplementary information Fig. S4.3). CO adsorption bands on these materials are only evident from 150 °C. The intensities of the bands increased gradually with increasing temperature, indicating the enhanced adsorption of CO on the exposed Ru⁰ surfaces. The supports by themselves showed no evidence of CO chemisorption within the temperature range

studied. Fig. 4.6 shows the spectra of CO chemisorbed at 200 °C on the two catalysts. A broad band centred between 2050-2000 cm^{-1} for both the supported catalysts can be assigned to CO linearly adsorbed on Ru^0 sites [3, 27]. Slight peak tailing within the region of 2100-2200 cm^{-1} is also observed and according to Choque et al. [27] these could be assigned to multi-carbonyls on Ru species, produced by either CO chemisorption on small Ru^0 particles, or by direct CO adsorption over partially reduced Ru particles (not in this case). For the Ru-ZrO₂ catalyst tailing of the broad band between 1900-2000 cm^{-1} could be attributed to bridge-bonded carbonyls on Ru^0 crystallites [3] which is absent for the Ru-TiO₂ catalyst. Furthermore, bands on the Ru-TiO₂ catalysts around 1800 cm^{-1} can be attributed to bridged bonding of CO on Ru particles [28].

4.3.1.6 CO chemisorption

CO chemisorption results for the Ru catalysts reduced at different temperatures are shown in Table 4.3. From this it can be seen that with higher reduction temperatures there is a gradual decrease in the amount of CO chemisorbed, metal dispersed and the metallic surface area. These trends relate to an increase in the crystallite size of the Ru metal, which was also seen for Ru on a SiO₂ support [13]. These trends arise since metal dispersion is proportional to the metallic surface area for supported metal catalysts [13]. Ru-ZrO₂ displays better dispersions and surface areas compared to the Ru-TiO₂ catalyst which was also evident from the Pt and Ir supported catalysts (Chapter 2 and 3). Similarly, these support (TiO₂) interactions with Ru create partially reduced surface oxides (in close proximity to Ru) that migrate towards the active metal (embedding it) resulting in a decrease of the metal dispersion and metallic surface area. This in turn hinders the metal dispersion and the metallic surface area, which appear to be lower at higher reduction temperatures. The Ru-TiO₂ catalysts showed lower metal dispersions across the temperature ranges investigated, which correlates with the TPO results where a greater degree of oxidation occurs at higher temperatures. This is due to the reducibility of the support, catalyzed by Ru, which is higher for the TiO₂ support. These results correlate closely to Pt and Ir systems (Chapter 2 and 3), as well as reports on Pt supported on TiO₂ and ZrO₂ [29-31].

Table 4.3. CO chemisorption data of the supported Ru catalysts

Catalysts	Properties	Temperature of reduction (°C)			
		200	240	280	320
Ru-TiO ₂	Metal dispersion (%)	67.0	63.6	54.2	43.3
	Metallic surface area (m ² /g metal)	117.6	111.7	98.5	76.1
	Crystallite size (nm)	5.2	5.7	6.0	6.7
	Chemisorption capacity (CO/Ru)	0.51	0.32	0.29	0.21
Ru-ZrO ₂	Metal dispersion (%)	81.5	77.5	59.4	52.7
	Metallic surface area (m ² /g metal)	143.2	135.9	170.9	92.6
	Crystallite size (nm)	5.0	5.5	5.5	6.4
	Chemisorption capacity (CO/Ru)	0.55	0.35	0.28	0.23

4.3.1.7 High resolution transmission electron microscopy

HR-TEM imaging was used to estimate the particle sizes of the RuO present on the supports. RuO particles measured on both the supports had a similar particle size range, however, slightly smaller particles were always found for the Ru-ZrO₂ catalyst. Typical particle measurements are shown in Fig. 4.7. The average particle size of Ru on TiO₂ is 5.6 nm, while it is 5.1 nm for Ru on ZrO₂. Also, selected area diffraction (inserts) indicates that both the catalysts are crystalline in nature. These results are similar to those of Pt systems using Cl⁻ precursors during the synthesis, which generally give better interactions on ZrO₂ rather than TiO₂ [32]. This gives smaller particles for ZrO₂ supported materials, since ZrO₂ is more electropositive than TiO₂ and thus has a higher affinity for interacting with the RuCl₃ precursor during the synthesis, where the point of zero charge of the supports were controlled at pH 7-7.5 [33]. These differences in the particle sizes can be related to the TPR, FTIR-CO and CO chemisorption results obtained for both catalysts. Similar trends were observed for all of these techniques and the obvious differences observed could be attributed to the effects of the supports themselves, rather than the active metallic Ru available on the catalysts.

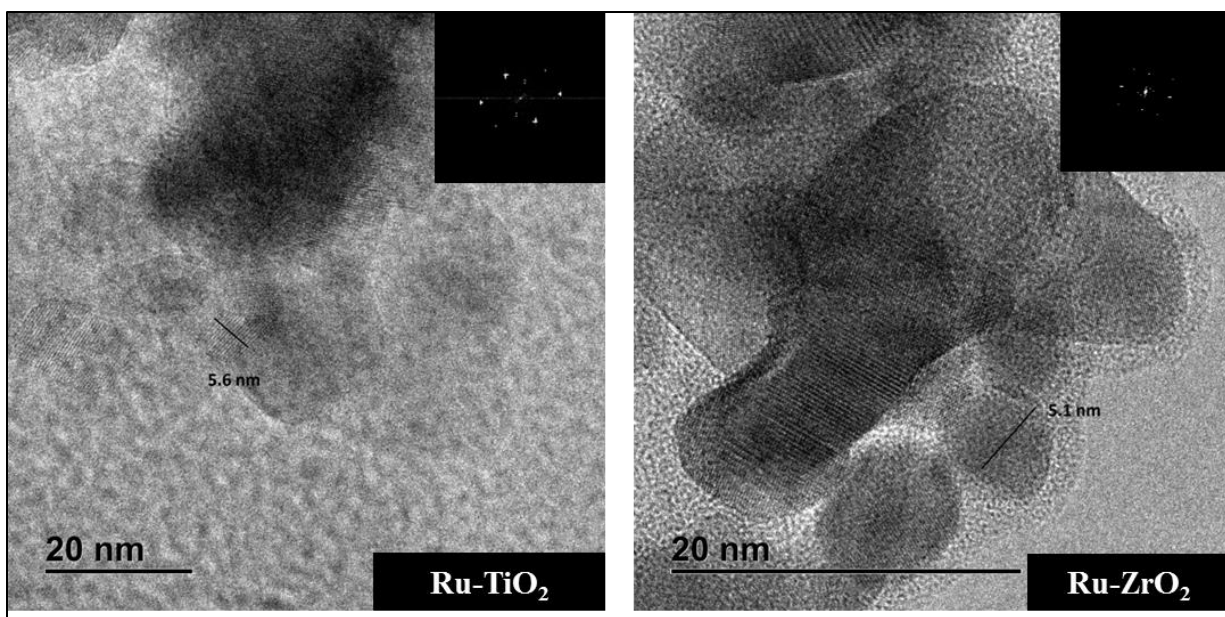


Figure 4.7. HR-TEM imaging of the supported Ru catalysts (Inset: selected diffraction patterns)

4.3.2 Catalytic testing

4.3.2.1 CO oxidation

Total oxidation of CO using the stoichiometric amounts of O₂ (0.5 %) was carried out over the supported Ru catalysts. Fig. 4.8 shows the activity of the catalysts from 80 to 200 °C. Both catalysts display almost identical activity plots within the temperature range screened. Above 80 °C, a significant increase in the oxidation rate is noted and at 100 °C, a CO conversion of ± 83 % is observed. This increases to ± 95 % at 120 °C and remains constant thereafter. The O₂ conversions for these catalysts (supplementary information Fig. S4.4), correlates with the CO conversions, indicating that for CO conversion, molecular O₂ is utilized, rather than lattice O₂ from the support. From these identical activity results, the particle size measurements of the Ru metals, and similar CO chemisorption capacities on the two supports, it is evident that the Ru metal itself is responsible for the activity towards the oxidation of CO and not by the supports.

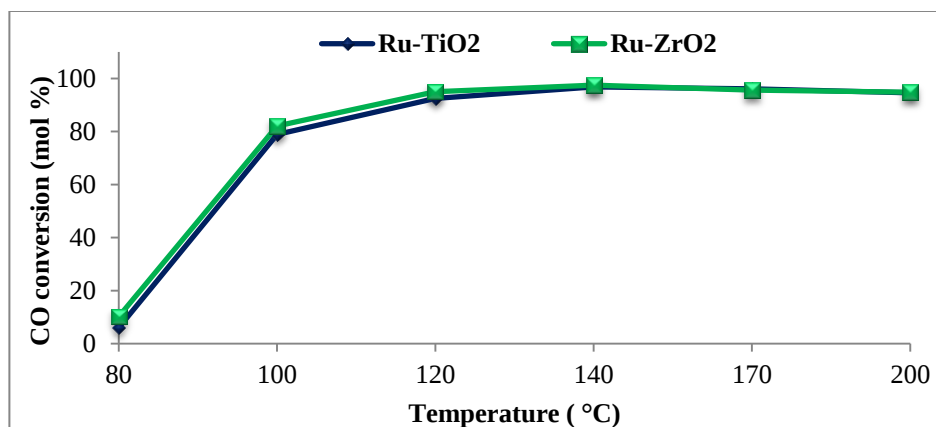


Figure 4.8. Total oxidation over the supported Ru catalysts at a GHSV of 12 000 h⁻¹

4.3.2.2 Preferential oxidation

The trend in the PROX activity over the Ru catalysts with increasing temperature is shown in Fig. 4.9. These results show that both catalysts are active from 80 °C, but the Ru-ZrO₂ catalyst, overall, shows better activity than the Ru-TiO₂ catalyst across the temperature ranges investigated. From 150 °C onwards, both these catalysts show an increase in CO conversion and at 200 °C Ru-ZrO₂ reaches a maximum conversion of ± 22 % and Ru-TiO₂ ± 13 %. Selectivity towards CO₂ (Fig. 4.9) shows that at higher temperatures the Ru catalysts even in the presence of O₂, start methanating CO, whilst simultaneously oxidizing it, which has been observed previously [7]. These reactions also could be taking place on different active sites on the catalysts. The O₂ conversions (shown in the supplementary information Fig. S4.4) for both catalysts are high (120 °C), with low selectivity towards CO₂ formation at low CO conversions.

Unlike the Pt and Ir systems (Chapter 2 and 3), both supported catalysts here for CO₂ formation using lattice O₂ instead of molecular O₂ for the reaction (O₂ conversion, supplementary information Fig. S4.4). H₂ consumptions (supplementary information Fig. S4.5) for the catalysts show that H₂ oxidation is the dominant reaction and is more prominent for the Ru-TiO₂ that has a lower reducibility, lower metal dispersions and higher temperature oxidation profiles than the Ru-ZrO₂ catalyst. Above 120 °C both catalysts show activity towards the methanation of CO, which is evident in Fig. 4.9. Kim et al. [9] reported that increasing CO conversions during the PROX reaction over 5 wt. % Ru-Al₂O₃ catalysts above

170 °C may be due to either the water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$) or CO methanation ($\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}$) taking place. Over these Ru- Al_2O_3 catalysts, CO methanation occurred simultaneously with PROX which was reported to still be beneficial for CO removal, especially at high temperatures. For the ZrO_2 and TiO_2 supported catalysts exceeding 200 °C would not be advisable, since ZrO_2 and TiO_2 supports are more easily reduced compared to Al_2O_3 [29, 34-36]. Also, due to the strong metal-support interactions, H_2 oxidation is favoured. Considering that both CO methanation and PROX takes place simultaneously, H_2 consumption during the reaction would be higher at higher temperatures. If 100 % CO conversion is obtained, 3 mols of H_2 will be used if following the CO methanation pathway [11] at higher temperatures, additionally 1 mol of H_2 would also be consumed using the O_2 that is also present in the feed gas to oxidize CO.

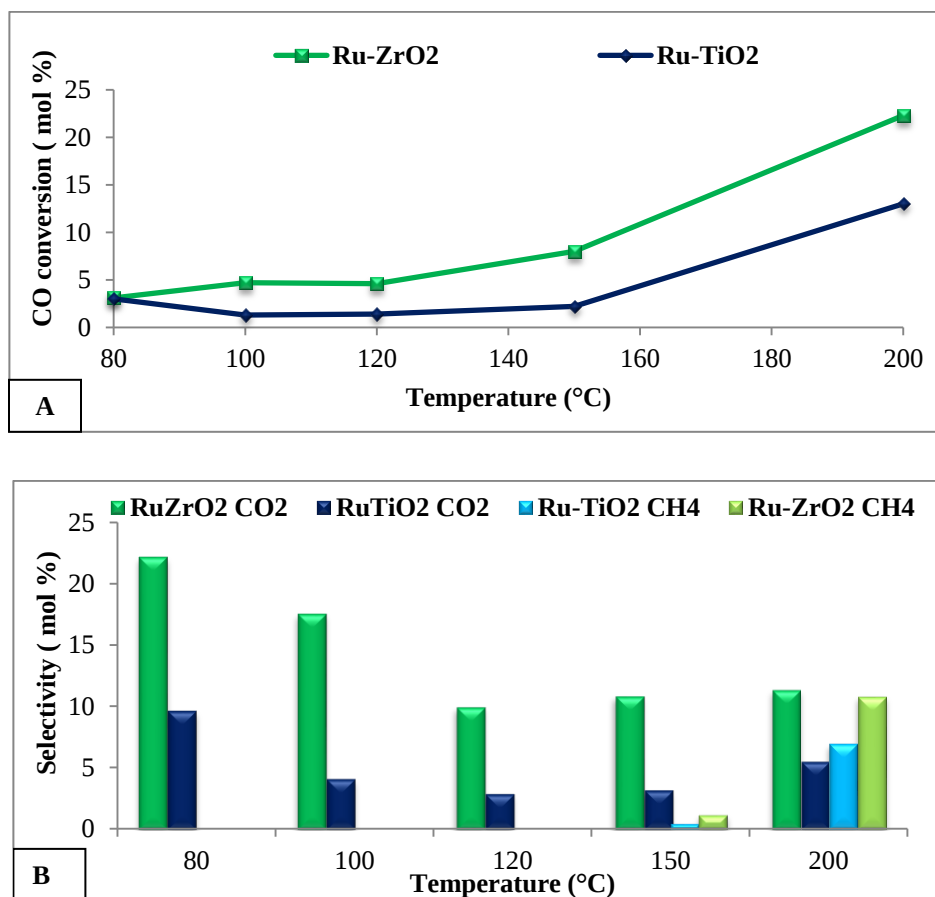
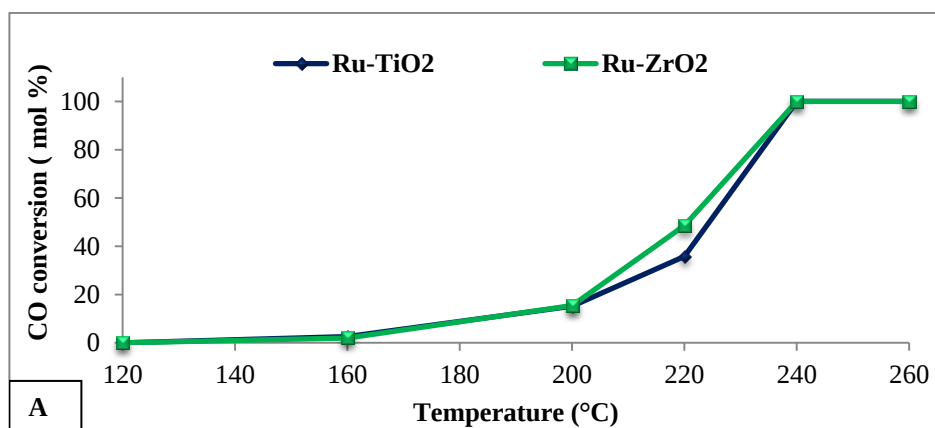


Figure 4.9. PROX over the supported Ru catalysts with increasing temperature using a GHSV of 12 000 h⁻¹ (A: CO conversion and B: Selectivity)

A study by Di et al. [3] showed that using a feed composition of 1% CO, 1% O₂ and 1 % H₂ over a 2 wt. % Ru-TiO₂ catalyst prepared by photo-deposition, 100 % CO conversion at 147 °C could be obtained, but H₂ conversion for this catalyst was 100 % at 87 °C. Also, higher temperatures resulted in a decrease in CO conversion and CO₂ selectivity. This in turn shows that H₂ oxidation was dominant over these materials. In a previous study [1], the effect of varying λ values of O₂ on the activity of Pt-Ni-Al₂O₃ and Pt-Al₂O₃ was shown. Increasing the λ values increased the CO₂ selectivity, but at the same time it could also increase the H₂ selectivity, depending on the catalyst. PROX for on-board applications requires the addition of O₂ to the reformat gas, which is an additional cost and using stoichiometric amounts would be better. Additionally, the catalyst must be preferential in oxidizing CO and not H₂ within the desired reaction temperature ranges.

4.3.2.3 Hydrogenation reactions

The results of the CO hydrogenation reactions over the supported Ru catalysts are shown in Fig. 4.10. Activity for both these catalysts, irrespective of supports, is seen from about 160 °C onwards. From 200 °C there is a rapid increase in the activity and both the catalysts achieve maximum CO conversions at 240 °C of 99.9 % and this remains constant until 260 °C with no evidence of deactivation. This is supported by the high selectivities towards CH₄ formation over both the catalysts within the temperature range investigated. No sign of CO₂ formation is seen over these catalysts. The H₂ conversions indicate minimal usage (~1.7 %) during the conversion of CO to CH₄.



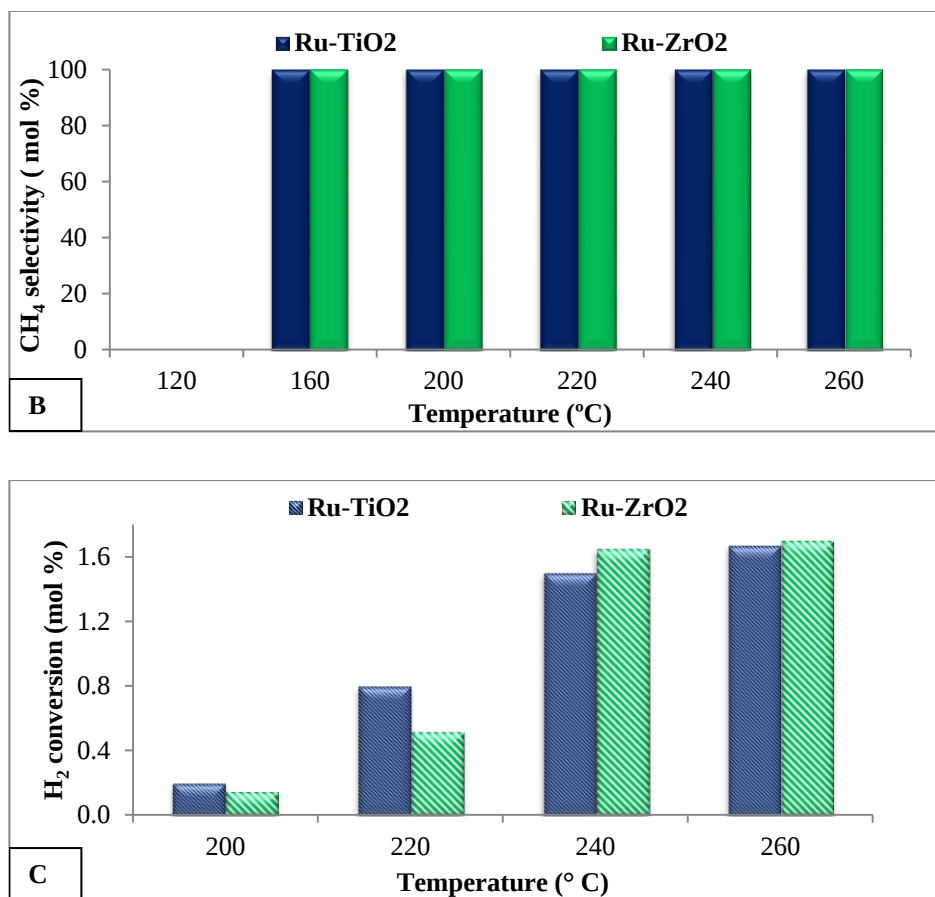


Figure 4.10. CO hydrogenation over the supported Ru catalysts using a GHSV of 12 000 h⁻¹ (A: CO conversion, B: CH₄ selectivity and C: H₂ conversion)

Similarities in CO and H₂ conversion and CH₄ selectivity between the catalysts for this reaction are attributed to the characteristic properties of the active metal and not the effects of the support, which clearly show a difference in the PROX reaction. The TPR, FTIR-CO and TEM results of these supported catalysts are very similar, as are the crystallite sizes and CO chemisorption capacities. However, the Ru metal dispersions and metallic surface areas are not. As mentioned in previous chapters, these are also crucial parameters for the CO hydrogenation reaction, but a study by Panagiotopoulou et al. [6] on supported Al₂O₃ and TiO₂ catalysts showed that higher weight percentage of Ru were more active than lower loaded catalysts. The metal dispersions were higher for the lower loaded catalysts, but showed lower activities for CO conversion. The crystallite sizes of these catalysts were of importance, since 5 wt. % Ru-Al₂O₃ and Ru-TiO₂ catalysts with crystallite sizes of 2.2 and 4.5 nm, respectively, and corresponding metal dispersions of 43 and 21 %, showed optimum activity and higher

rates compared to the 0.5 wt. % Ru-Al₂O₃ and Ru-TiO₂ catalysts that had crystallite sizes of 1.3 and 2.1 nm, with metal dispersions of 70 and 46 %. These authors noted that Ru catalysts are more active towards CH₄ formation and avoid the unwanted RWGS reaction unlike their Pt and Pd counterparts. The selectivity towards CH₄ in the present study clearly supports this, since no traces of CO₂ were detected over these Ru catalysts within the temperature ranges investigated.

A study by Erdöhelyi et al. [37] shows that the dissociation of CO adsorbed on Ru metallic sites is the rate determining step for the CO hydrogenation reaction, explaining the electronic interaction between the metal and the support determines its activity for the specific reaction. These results could suggest that the electronic interactions of Ru with TiO₂ and ZrO₂ in the present study are similar, therefore resulting in similar activity profiles.

Comparing the CO hydrogenation activity of the supported Ru catalysts, maximum CO conversions were obtained at a temperature 100 °C lower than that required for the best performing Pt and Ir catalysts (Chapters 2 and 3). This, according to Panagiotopoulou et al. and Vannice [17, 38], can be attributed to the lower affinity of Ru towards CO adsorption but higher CO dissociation energy than other noble metals. CO strongly chemisorbs on Pt and Ir catalysts which displaces H₂, thus limiting its dissociation and thus requires higher temperatures to weaken the CO-M (M = Pt/Ir) bond for the reaction to proceed. Volcano plots for the CO methanation pathway of metals with respective CO heats of adsorption [17] are in agreement to this explanation.

4.4 Conclusion

Both the supported Ru catalysts showed high activity for the oxidation of CO at lower temperatures compared to the Pt and Ir samples. However, in the presence of H₂, PROX activity is suppressed for these catalysts and the oxidation of H₂ is favored. At higher temperatures both the catalysts start showing methanation activity, despite the presence of O₂, which results in higher CO conversions. CO hydrogenation reactions, on the other hand, with simulated reformat gas feeds for on-board fuel reformers over both the Ru catalysts were shown to be suitable for the removal of trace CO in H₂ rich streams. The catalysts showed excellent results for lowering the CO content in the feed (< 10 ppm) from 240 °C onwards. No

deactivation and decreases in selectivities were observed throughout the temperatures studied. Similarities in the catalytic behavior of these catalysts were attributed to the actual metal Ru on the supports and the interaction with adsorbates (CO and H₂). Ru, having low affinities in adsorbing CO, has high CO dissociation rates and promotes CO methanation with adsorbed H₂. These catalysts show promising results and could be subjected to further testing using ideal exit water-gas shift reformat feeds evaluating their performances and stabilities.

Acknowledgements

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Supplementary information

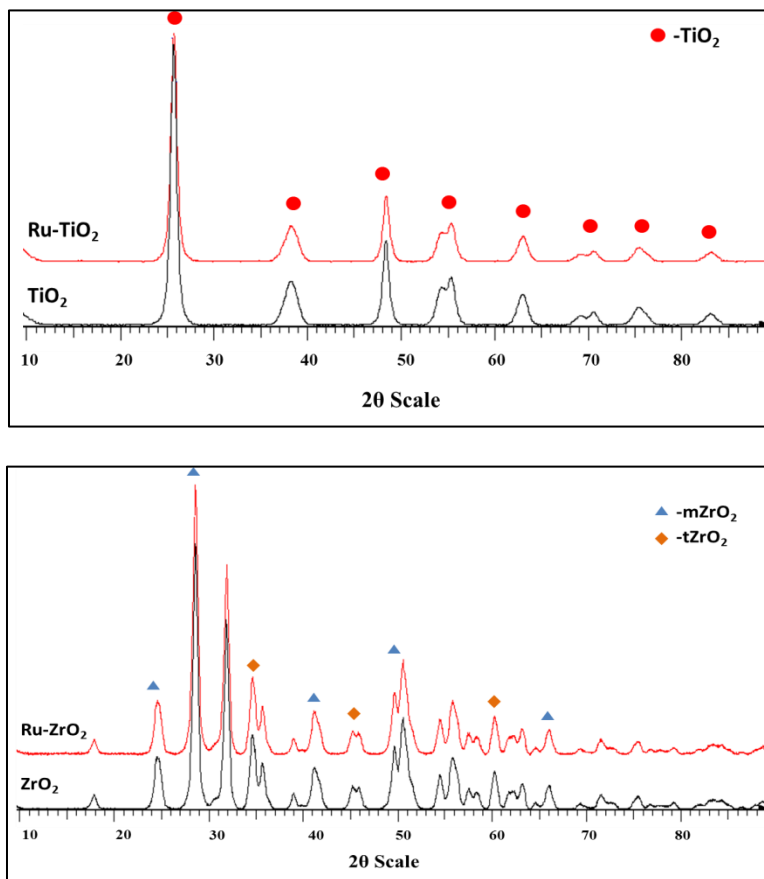


Figure S4.1. XRD diffractograms of the Ru supported materials

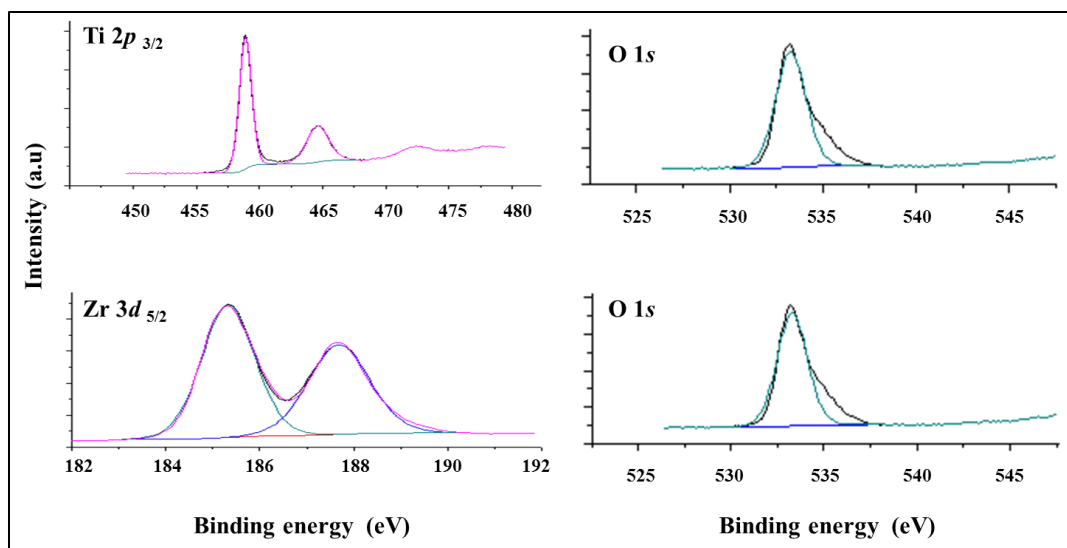


Figure S4.2. XPS spectra of Ti $2p_{3/2}$, Zr $3d_{5/2}$ and the O $1s$ levels of the catalysts

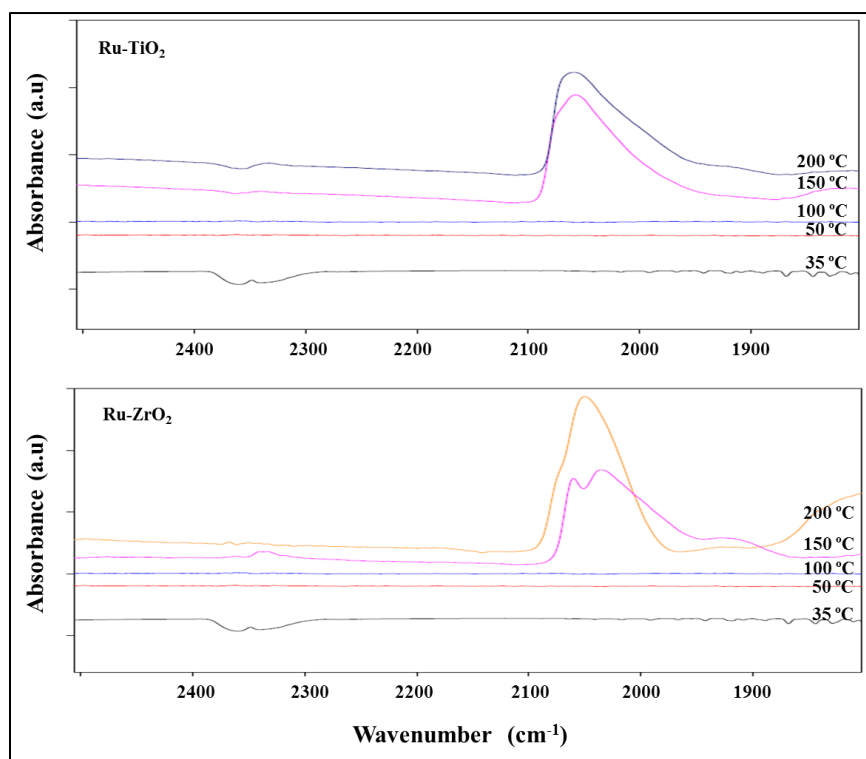


Figure S4.3. FTIR-CO of the supported Ru catalysts with increasing temperatures

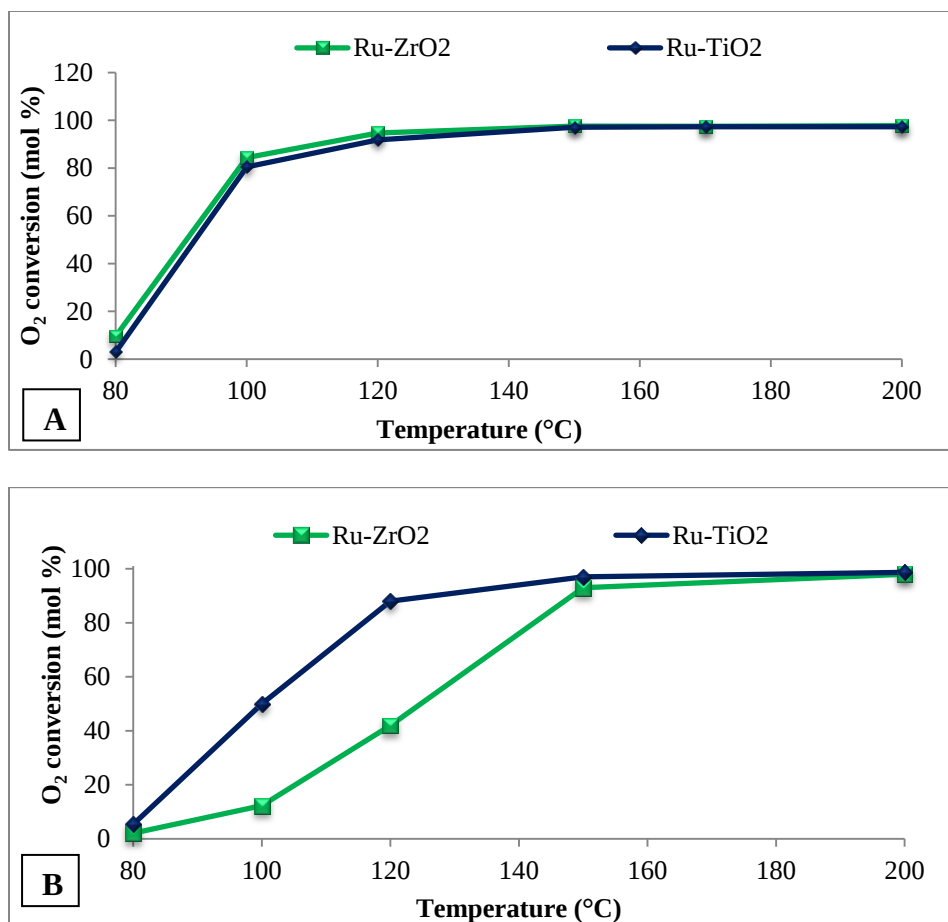


Figure S4.4. O₂ conversion of the supported Ru catalysts for A: Total oxidation and B: PROX

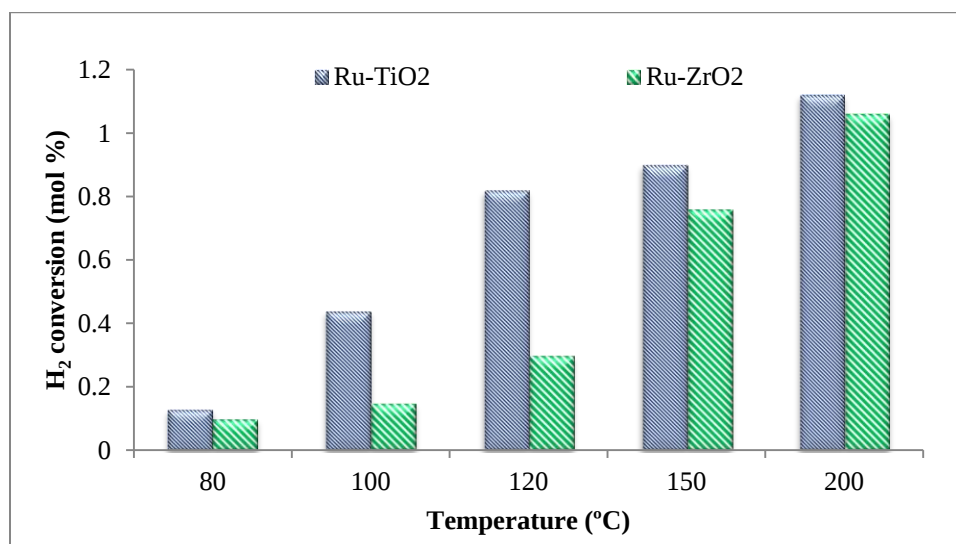


Figure S4.5. H₂ conversion over the supported Ru catalysts for the PROX reaction

Chapter 5

The effects of a realistic water-gas shift reformat feed over the TiO₂ and ZrO₂ supported catalysts.

Ziyaad Mohamed, Sooboo Singh and Holger B. Friedrich*

Catalysis Research Group, School of Chemistry and Physics, University of KwaZulu-Natal,
Durban 4000, South Africa

Abstract

Pt, Ir and Ru (1 wt. %) supported on TiO₂ and ZrO₂ were tested for selective methanation of CO in the presence of H₂, CO₂ and H₂O. Pt supported catalysts showed very little activity towards CO methanation in both the presence and absence of H₂O and favoured the CO₂ methanation and reverse water-gas shift reactions, producing additional CO at 280 and 320 °C. The Ir catalysts were slightly more active than the Pt catalysts but still not selective for only CO methanation. Adding H₂O to the feed over the Ir-ZrO₂ catalysts gave better CO methanation activity, but also methanated CO₂, which altered selectivity. The Ru-TiO₂ and Ru-ZrO₂ catalysts showed the best activity towards CO methanation at temperatures 100 °C lower than the Pt and Ir systems. These catalysts gave 99.9% CO conversions and high selectivity towards CH₄ only (99.9 %) above 220 °C. The CO₂ methanation reaction over these catalysts was totally suppressed until all the CO in the feed was converted, after which active sites became available for CO₂ adsorption and hence its dissociation. The Ru catalysts thus, were effective in removing trace amounts of CO that were present following the water-gas shift reaction to less than 10 ppm. Thus, the Ru catalysts with low weight loadings, show considerable potential for CO clean-up of reformer based hydrogen feeds.

Keywords: Pt, Ir, Ru, CO₂, H₂O, SMET and RWGS

* Corresponding author: Tel.: +27 31 2603107, Fax.: +27 31 260 3091,

E-mail: friedric@ukzn.ac.za

5.1 Introduction

Exit water-gas shift (WGS) feeds that contain trace amounts of CO are detrimental to the Pt anode present in proton exchange membrane fuels cells (PEMFC) [1]. From the many catalytic processes reported for removing the CO impurities, selective methanation (SMET) of CO is a promising method for on-board fuel cell applications and requires no additional cost for setup or reactants [2-5]. The CO methanation reaction was previously used for gas purification, typically H₂, in NH₃ plants for removing CO catalyst poisons and is a reversible, highly exothermic reaction (Eq.1) [2, 6].



However, WGS reformat streams contain significant amounts of CO₂ (15–20%), therefore the reaction must be very selective for CO methanation, avoid CO₂ methanation (Eq. 2), and also avoid the reverse water-gas shift (RWGS) reaction (Eq. 3). These latter reactions lead to the undesired consumption of H₂ and, hence, runaway in the reactor may occur [7, 8].

Previous catalytic studies towards increasing the activity and selectivity for the CO methanation reaction have been conducted in various ways, which included investigating; the effects of active metals such as Ru, Rh, Pt, Pd and Ni, different supports including SiO₂, Al₂O₃, TiO₂, zeolites and carbon nanofibers, the addition of metals as dopants, the nature of the metallic phase as well as the effects of CO₂ and H₂O in these systems [2, 7-14]. From these studies, Ru was found to be the best metal, compared to Rh, Pd and Pt, for the CO methanation reaction. However, the activity of the metal depends on its dispersion and interaction with its support.

Literature reports [6, 15] showed that electronic modification of the metal affects the activation energy of H₂ adsorption due to the metal-support interaction. Also, metals on easily reduced oxides (TiO₂) showed higher activity for methanation than metals on conventional supports (Al₂O₃ and SiO₂), since reducible oxides can create structural defects at the metal support

interface originating from support migrations to the active metal sites, termed as “metal-oxide pair sites”.

The effect of H₂O on the catalysts activity has been studied and been reported to either promote the undesired RWGS reaction over some PGMs, or, in some cases, have negligible or no effects at all with regard to the catalytic activity and selectivity. H₂O concentrations previously reported range between 0 and 30 %, depending on the application that requires the H₂ [3, 6, 16].

Developing a catalyst for effective CO methanation at lower temperatures, whilst avoiding the RWGS and CO₂ methanation reactions, that generally occur at higher temperatures, is of utmost importance. The catalysts for this low temperature CO methanation enhancement should also utilize lower amounts of metal loadings, which should reduce costs, and the catalyst should also be stable for long periods of time.

This work presents the study of 1 wt. % Pt, Ir and Ru supported on TiO₂ and ZrO₂ for the removal of CO in a realistic WGS reformat feed. TiO₂ as support has been previously investigated, but only seems effective when metal contents are $\pm$ 5 wt. % [16]. ZrO₂ is also a well-known reducible support that promotes strong metal-support interaction, however, reports on ZrO₂ supported PGM, remain scarce. The effects of CO₂ (15 %) and H₂O (15 %) in realistic feeds was investigated.

5.2 Experimental

5.2.1 Catalyst synthesis and characterization

All the catalysts used in this section were discussed previously in Chapters 2, 3 and 4. This included the synthesis methods, characterization and dry hydrogenation reactions.

5.2.2 Catalytic testing

Catalytic testing was performed at atmospheric pressure in a stainless steel fixed bed reactor using 0.75 mL of catalyst diluted with 24 gritt carborundum (1:1) similar to the reactions explained previously (Chapters 2, 3 and 4). Prior to catalytic testing the catalysts were pre-treated under a flow of H₂ at 200 °C for 2 h.

5.2.2.1 The effect of CO₂ addition to the reformat gas over the catalysts

Activity measurements were recorded with the addition of 15 % CO₂ and the reactant flow mixture was as follows; 1 % CO, 15 % CO₂, 75 % H₂ and N₂ balance. A GHSV of 12 000 h⁻¹ was employed and the temperatures screened depended on the hydrogenation activity of the catalysts (Chapters 2, 3 and 4). For the Pt and Ir systems temperatures of 280 and 320 °C were used, whilst the temperature of reaction for the Ru samples ranged from 220 to 260 °C. The moles of product/s (CO and CH₄) formed are defined as the difference in moles of product concentration in the effluent gas and moles of product concentration in initial feed gas.

5.2.2.2 The effect of H₂O vapor in the reformat gas over the catalysts

Using the CO₂ mixture containing gas (Section 5.2.2.1), 15 % H₂O was added to obtain an ideal exit water-gas reformat feed. Similar temperatures were used as for the experiments investigating the effect of CO₂ addition only. Time on stream (TOS) experiments was also carried out under these conditions. Water vapor was introduced into the system using a LabAlliance Series I HPLC pump. The outlet stainless steel 1/16" H₂O line feeding the reactors was split using a VICI three way valve and a FS deactivated silica glass capillary column (Agilent technologies) to the reactors. This allowed for the use of very low water flow rates in order to obtain the required amount of H₂O in the reactor. Additionally, this avoided pulsing of H₂O from the pump, thus keeping a constant flow without any pressure drops. The effluent gaseous products were analyzed online using an Agilent Micro-GC CP-4900 TCD with 3 channels. The results were recorded in duplicate and the O₂, C and H₂ balances ranged between 95-105 % for all the reactions. No products other than CO₂, H₂O and CH₄ were observed under conditions tested. The moles of product/s (CO, CH₄ and H₂) formed are defined as the difference in moles of product concentration in the effluent gas and moles of product concentration in initial feed gas.

5.3 Results and discussion

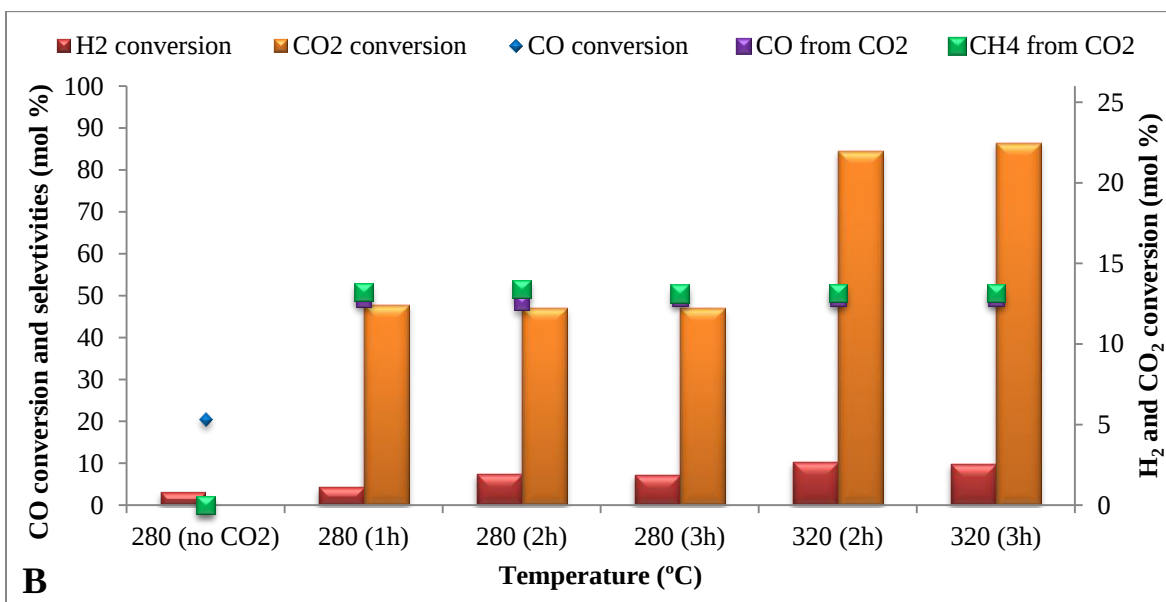
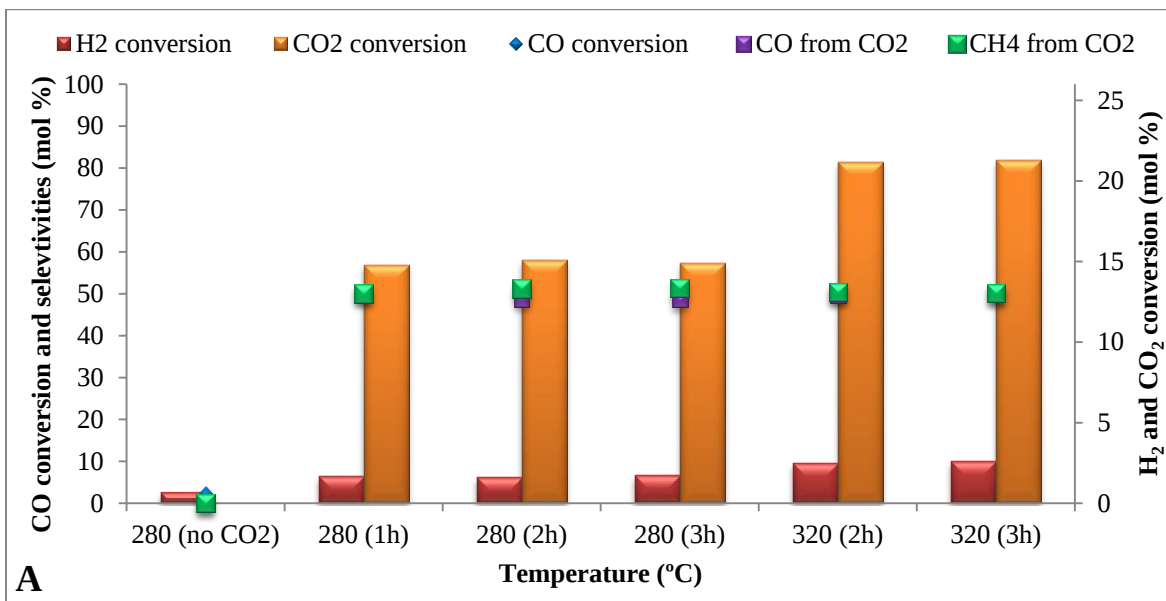
5.3.1 Pt systems

5.3.1.1 The effect of CO₂ addition to the reformat gas over the Pt catalysts

The catalytic results, for the Pt samples in the gaseous feed containing CO₂ are shown in Fig. 5.1. Comparing the activity of the TiO₂ supported catalysts (Fig 5.1. A and B), the PtIMP-TiO₂ catalyst shows very low CO conversion (~2.3 % of the feed without CO₂) at 280 °C, whereas the PtDP-TiO₂ gave ± 20 % conversion at the same temperature. Upon CO₂ addition to the feed, CO conversion over these catalysts is not observed, however, H₂ and CO₂ conversion take place over both the catalysts which remains constant for the duration of the experiment (3 h). Increasing the temperature to 320 °C results in higher H₂ and CO₂ conversions. After CO₂ is added, the selectivities towards CO and CH₄ at both the temperatures investigated remain constant at ± 50 %, implying that CO₂ is likely converted to either CO and/or CH₄. Fig. 5.2 shows the moles of product formed during the reaction, and from this an increase in the CO concentration is observed (more than the initial 1%) and very little CH₄ is over PtIMP-TiO₂, which shows higher CO formation than the PtDP-TiO₂ across the reaction temperature range examined. This indicates that apart from CO methanation, CO₂ is also adsorbed on the active sites and dissociated, forming additional CO via the RWGS reaction as also reported [3, 9]. This correlates to the H₂ conversions at 280 °C (no CO₂) which were very low with low mol % CH₄ formed (Fig. 5.2B), but upon CO₂ addition, the H₂ conversions increase and the quantity of CH₄ formed is much lower.

The results of the PtIMP-ZrO₂ and PtDP-ZrO₂ catalysts (Fig. 5.1 C and D) showed initial CO conversions of ± 30 and 23 %, respectively, in the absence of CO₂. After CO₂ was added to the reaction mixture, the catalysts behaved similarly to the Pt-TiO₂ catalysts, with no CO conversion observed (Fig. 5.2A). The H₂ conversions were lower and slightly higher CO₂ conversions were obtained across the temperature ranges investigated. However, the moles of CH₄ formed over the Pt-ZrO₂ catalysts are higher than those over the Pt-TiO₂ catalysts (Fig. 5.2B), which indicates that the rate of CO₂ methanation over ZrO₂ catalysts are higher. These are attributed to the smaller particles, the higher metal dispersions and higher metallic surface areas of the ZrO₂ catalysts (Chapter 2). Hence, the Pt-ZrO₂ catalysts show higher activities for

the RWGS and CO₂ methanation reactions when compared to the Pt-TiO₂ catalysts. These correlate to the lower H₂ conversions, where the ZrO₂ catalysts produce more CH₄ (Fig. 5.2B) and, hence, more H₂O is formed.



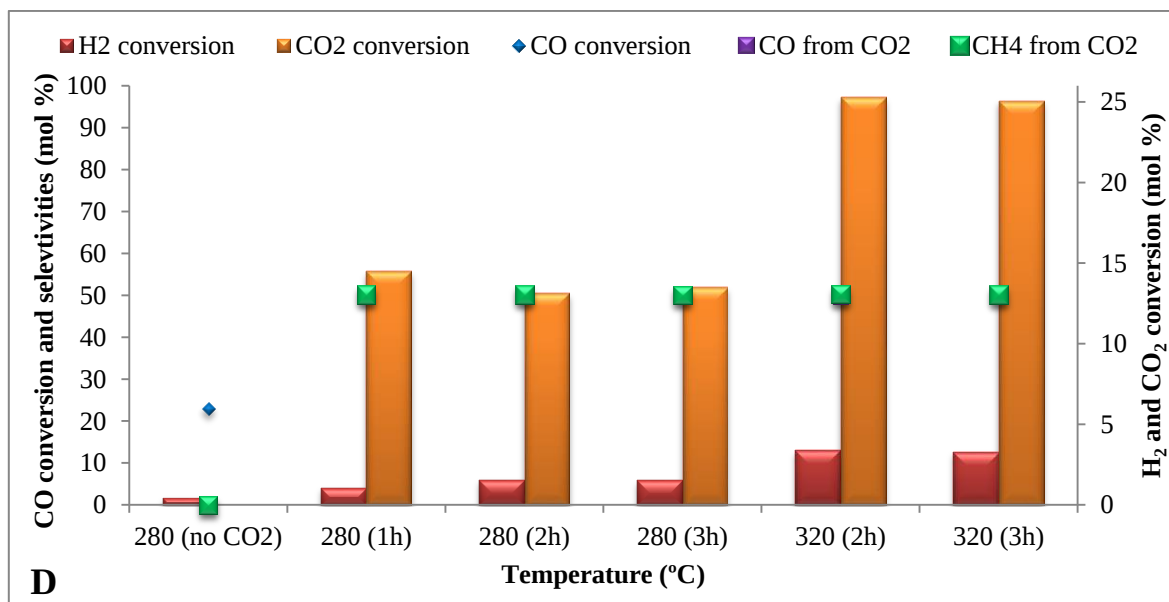
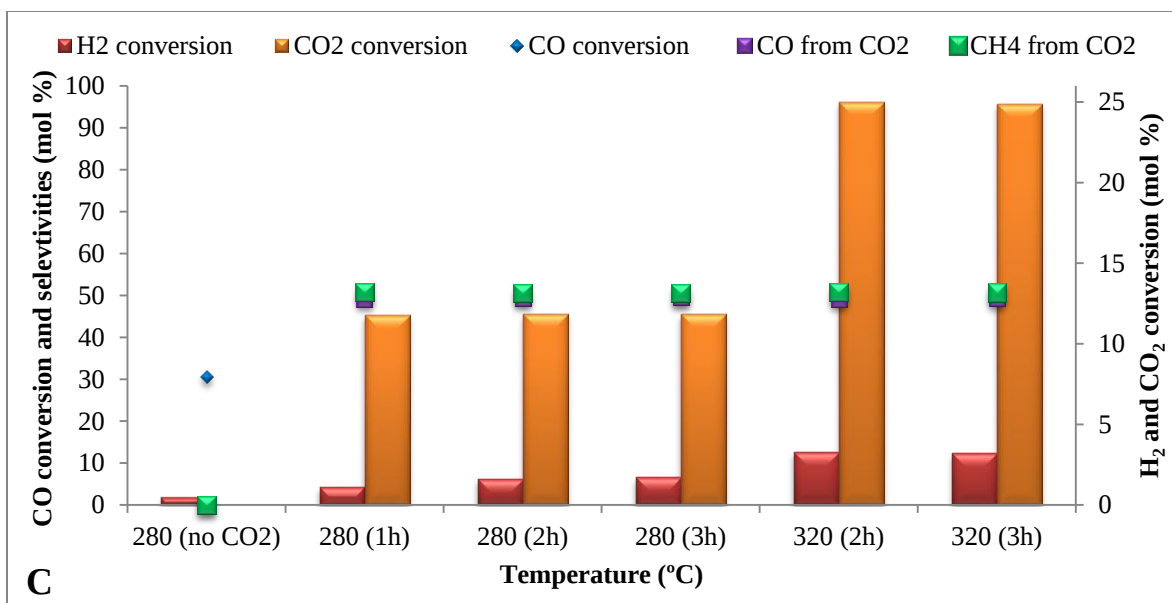


Figure 5.1. The effect of CO₂ addition in the reformate gas on the CO conversion and selectivity to products as well as the H₂ and CO₂ conversion over the supported Pt catalysts (A: PtIMP-TiO₂, B: PtDP-TiO₂, C: PtIMP-ZrO₂ and D: PtDP-ZrO₂)

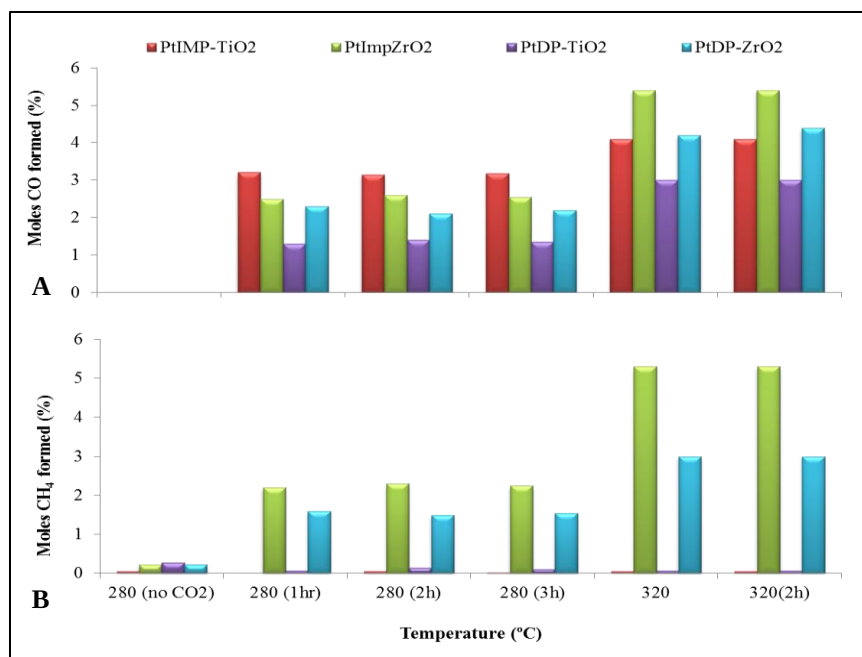
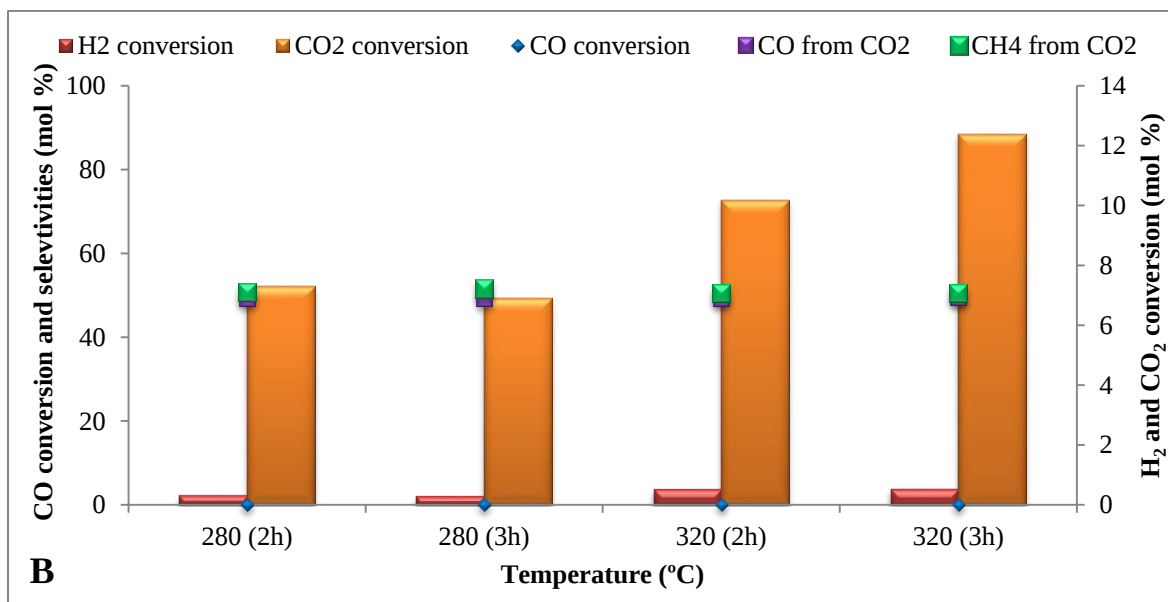
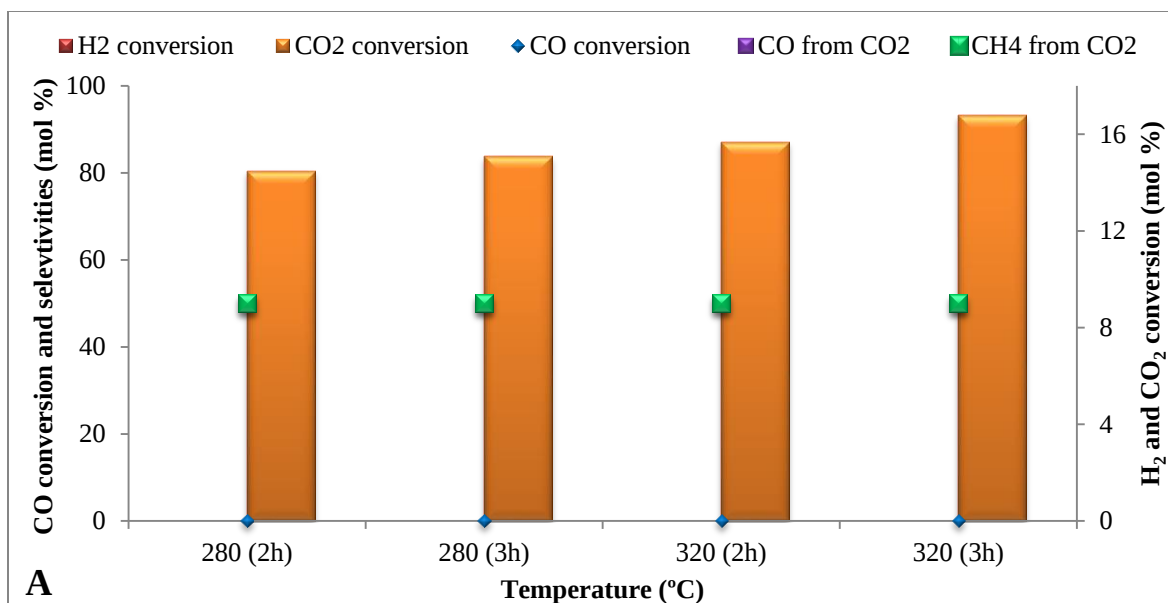


Figure 5.2. Moles of product formed following the addition of CO₂ to the reformate gas mixture over the supported Pt catalysts (A: Moles of CO formed and B: Moles of CH₄ formed)

5.3.1.2 The effect of H₂O vapor in the reformate stream over the Pt catalysts

The activity of the catalysts in the presence of CO₂ and H₂O is shown in Fig. 5.3. Water vapour causes noticeable effects on the catalytic activity with regards to the CO₂ and H₂ conversions, but the selectivities (CO and CH₄) still remain at $\pm 50\%$. The product formation presented in Fig. 5.4, however, also shows noticeable differences compared to the dry reactions (Fig.5.1).

Firstly, comparing the PtIMP-TiO₂ and the PtDP-TiO₂ catalysts (Fig. 5.3 A and B), the CO₂ conversion over PtIMP-TiO₂ only reaches a maximum of $\pm 16\%$ and that over PtDP-TiO₂ $\pm 12\%$, with little evidence of H₂ conversions. The moles of CO formed over the PtIMP-TiO₂ at both temperatures investigated were higher than those over PtDP-TiO₂, and lower CH₄ formation is also seen (Fig. 5.4B). H₂ is additionally formed over these catalysts (Fig. 5.4C). This indicates that H₂O vapour presented in the feed stream is used for the WGS reaction, while CO₂ and/or CO are being methanated (Fig. 5.4B). These trends are also reported in literature [9]. H₂ formed (Fig. 5.4C) over the PtIMP-TiO₂ catalysts was higher than that over PtDP-TiO₂ catalysts and hence showed lower or no H₂ conversions (Fig. 5.3A) compared to the PtDP-TiO₂ catalyst.



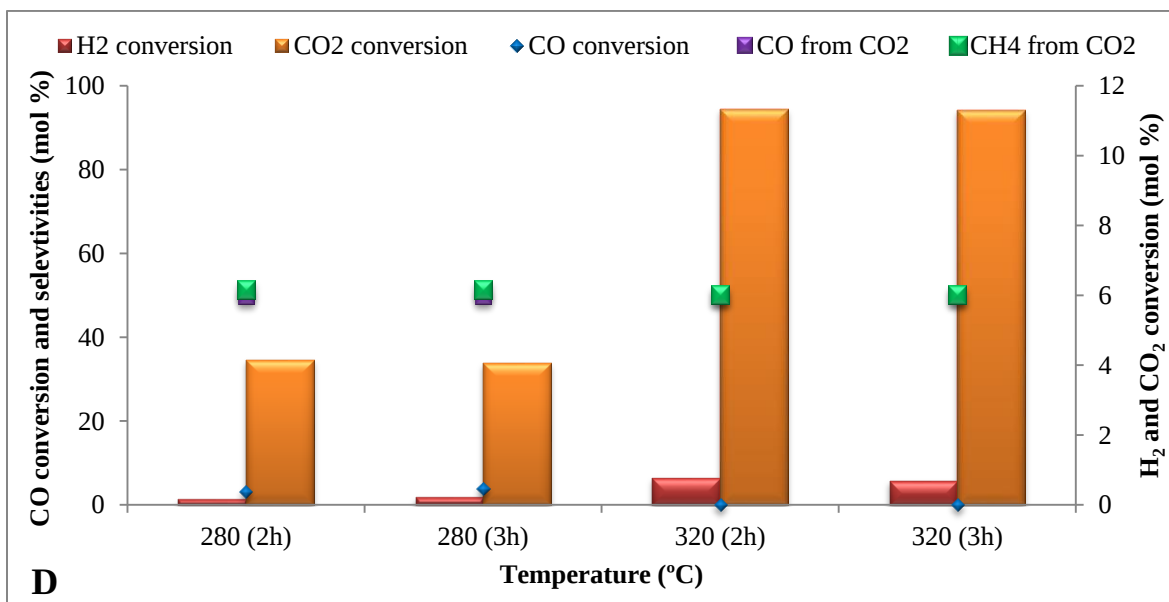
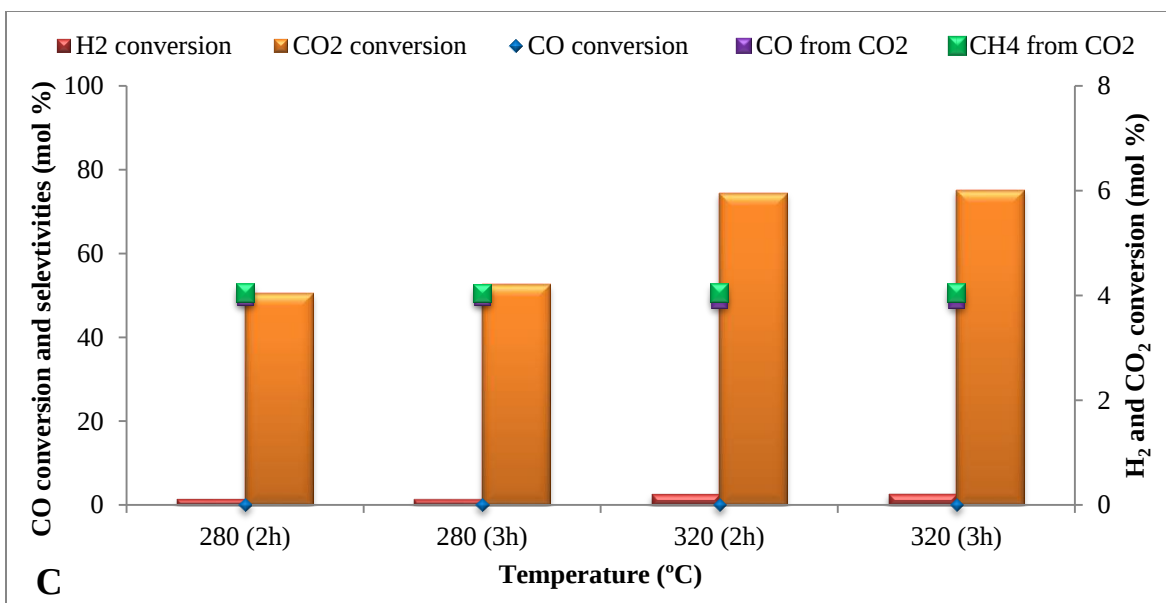


Figure 5.3. The effect of a real water-gas shift feed on the CO conversion and selectivity to products over the supported Pt catalysts, as well as the H₂ and CO₂ conversion (A: PtIMP-TiO₂, B: PtDP-TiO₂, C: PtIMP-ZrO₂ and D: PtDP-ZrO₂)

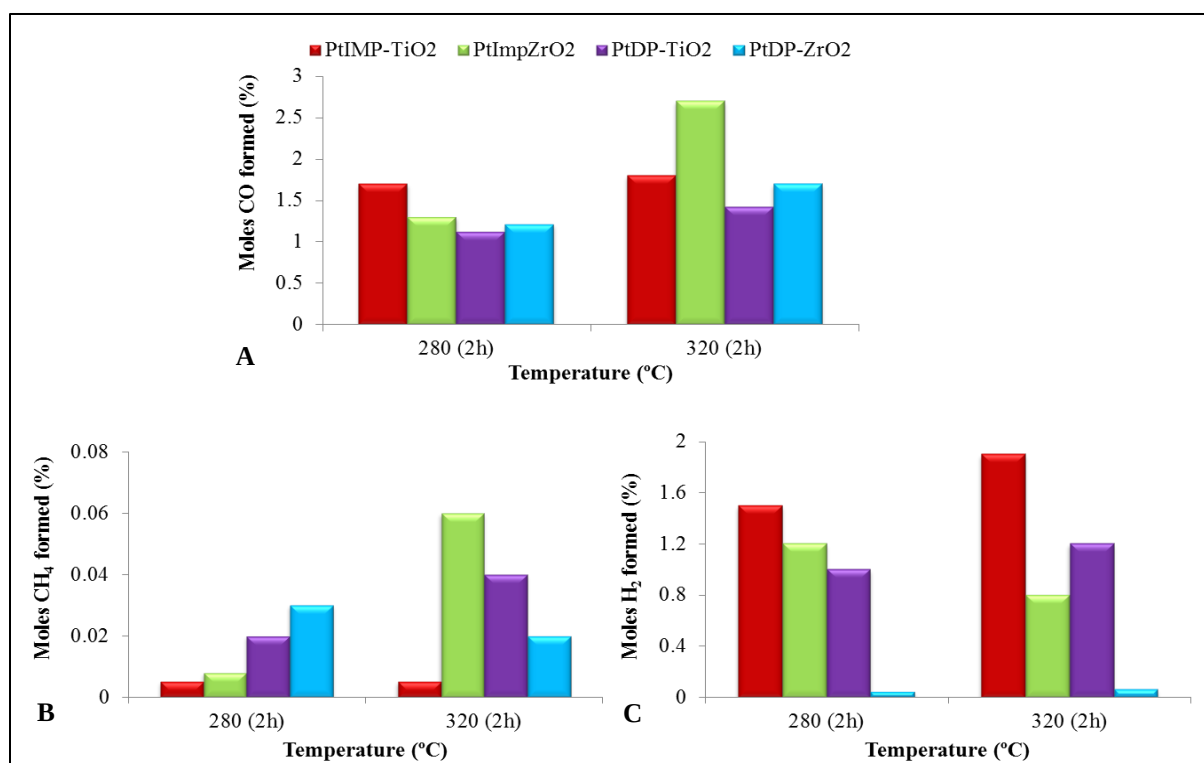


Figure 5.4. Moles of product formed using real water gas-shift feeds over the supported Pt catalysts (A: Moles of CO formed, B: Moles of CH₄ formed and C: Moles of H₂ formed)

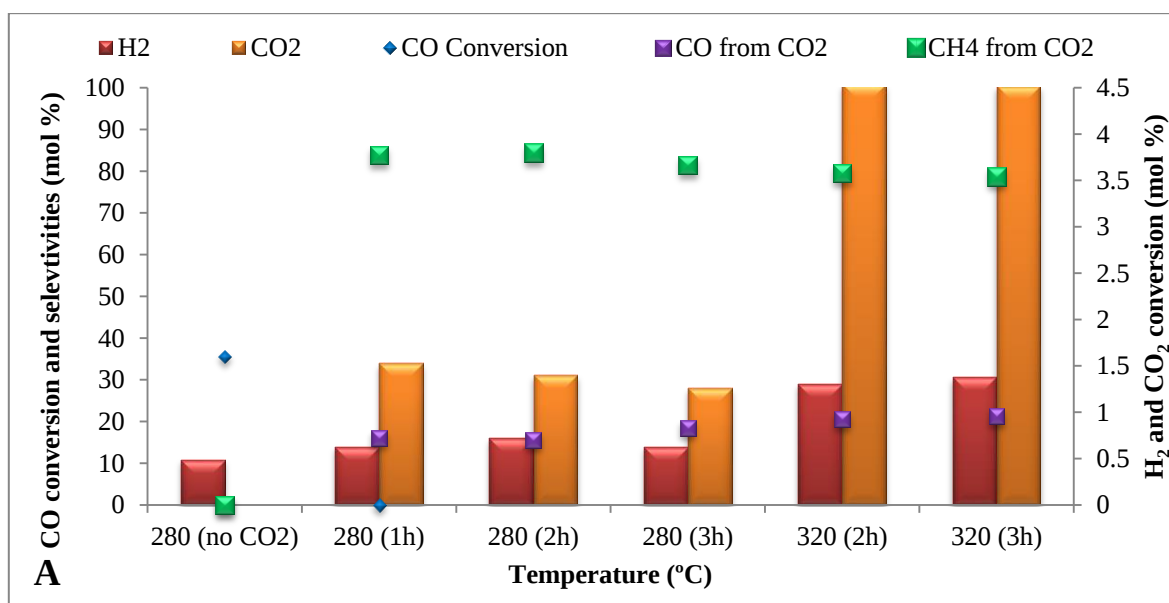
PtIMP-ZrO₂ and PtDP-ZrO₂ catalysts, on the other hand, show lower CO₂ and H₂ conversions compared to the Pt-TiO₂ systems (Fig. 5.3 C and D). The PtIMP-ZrO₂ catalyst shows a lower CO₂ conversion (± 6 %) with more CO and CH₄ formed (Fig. 5.4A and B), but less H₂ at 320 °C compared to the PtDP-ZrO₂ catalyst. Furthermore, the PtDP-ZrO₂ catalyst, upon addition of H₂O at 280 °C, shows evidence of CO conversion (feed CO) to CH₄ but at 320 °C, CO produced via CO₂ hydrogenation or RWGS exceeds CO conversions. These catalysts, regardless of changes or differences in activity, still favour the RWGS reaction and CO₂ methanation more than the Pt-TiO₂ catalysts. According to Kim et al. [17], although Pt adsorbs CO strongly, in the presence of CO₂ the RWGS reaction is favoured and the variations observed in the activity are mainly due to the nature of these Pt particles on the support. In this case the variations in activity are attributed to the differences obtained in the particle sizes, and the effects of the different supports (metal dispersions and metallic surface areas). Panagiotopoulou et al. [9] found similar activities for Pt and suggested that CO strongly chemisorbs to the metal and does not dissociate rapidly, and with larger particles H₂ and CO₂ interact on different active sites favouring CO₂ methanation via the RWGS reaction.

Panagiotopoulou et al. [16] later explained that the RWGS reaction and CO hydrogenation reaction proceed in parallel at higher temperatures, and eventually the rate of CO formed by the RWGS could become higher than the rate of CO hydrogenation, resulting in higher CO concentration in the effluent gas. Comparing results presented for the Pt catalysts in Figs. 5.3 and 5.4, Pt-ZrO₂ showed better activity, although low, which is attributed to the higher metal dispersions and smaller particle size of Pt on ZrO₂.

5.3.2 Ir systems

5.3.2.1 The effect of CO₂ addition to the reformat gas over the Ir catalysts

CO conversion data for the supported Ir catalysts in the presence of CO₂ are shown in Fig. 5.5. Initial CO conversion at 280 °C (no CO₂) for the Ir-TiO₂ catalyst is $\pm$ 35 % (Fig. 5.5A) and when CO₂ is added, similar to the Pt systems, no CO conversions are seen. The Ir-TiO₂ catalyst at 280 °C shows a CO₂ conversion of $\pm$ 1.4 % that increases to $\pm$ 4.5 % at 320 °C which is much lower than that obtained over the Pt catalysts. The selectivity towards CH₄ from CO₂ ($\pm$ 81 %) is higher over the selectivity of CO from CO₂ ($\pm$ 18.5 %), with a slight decrease (CH₄ from CO₂) or increase (CO from CO₂) across the temperature range. H₂ conversion for this catalyst reaches a maximum of $\pm$ 1.38 % at 320 °C. The moles of product formed for this catalyst (Fig. 5.6) show lower CO formation (via RWGS) than the Pt systems, with higher CH₄ formation.



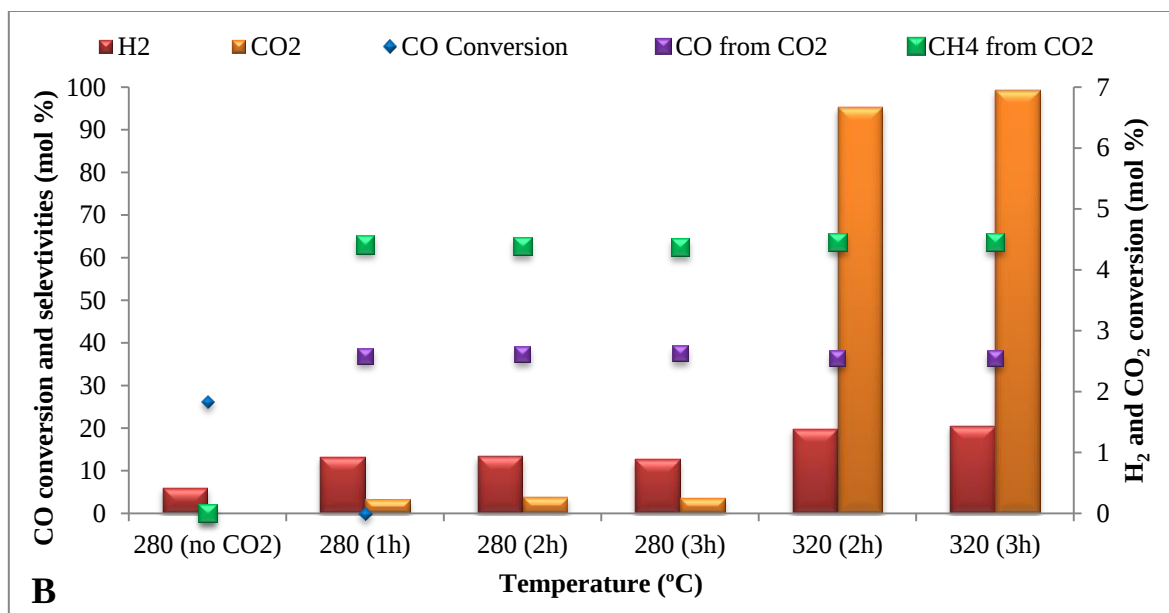


Figure 5.5. The effect of CO₂ addition in the reformat gas on the CO conversion and product selectivity as well as the H₂ and CO₂ conversion over the supported Ir catalysts (A: Ir-TiO₂ and B: Ir-ZrO₂)

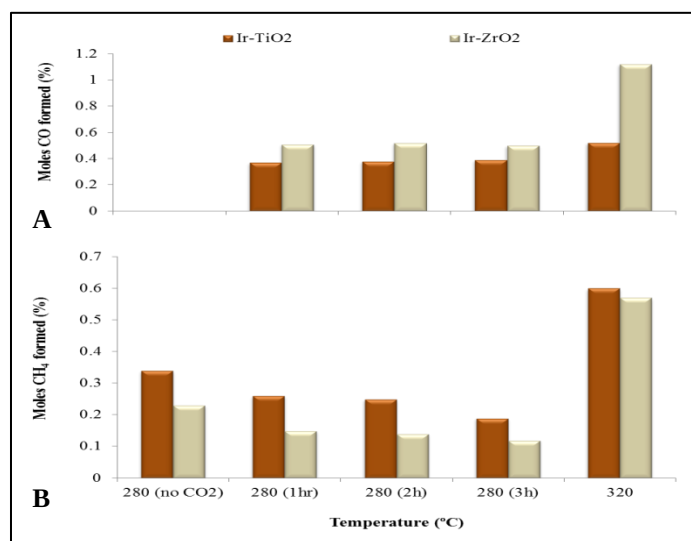


Figure 5.6. Moles of product formed following the addition of CO₂ to the reformat gas mixture over the supported Ir catalysts (A: Moles of CO formed and B: Moles of CH₄ formed)

The Ir-ZrO₂ catalyst shows a CO conversion of ± 26 % (Fig. 5.5B) in the absence of CO₂ and when CO₂ is introduced no CO conversions is seen. Ir-ZrO₂, compared to the Ir-TiO₂, shows higher CO₂ conversion at 320 °C with similar H₂ conversion. Selectivities towards the

products, however, unlike the Ir-TiO₂ catalyst, show ± 62 % selectivity towards CH₄ and ± 37 % towards CO. The moles of products formed for this catalyst show greater CO formation (Fig. 5.6A) with lower CH₄ formation (Fig. 5.6B) compared to the Ir-TiO₂ catalyst. This catalyst hydrogenates CO₂, but at a lower rate than the Ir-TiO₂, and also forms additional CO which is not desired.

5.3.2.2 The effect of H₂O vapor in the reformat stream over the Ir catalysts

The effect of H₂O vapour in the feed stream over the Ir catalysts is shown in Fig. 5.7. Ir-TiO₂ at 280 °C shows a CO₂ conversion of ± 2 % which remains relatively unchanged at 320 °C. H₂ conversion for this catalyst is low, as seen also in the absence of water (Fig. 5.5A), and reaches a maximum of ± 0.9 % at 320 °C. The selectivity towards CH₄ from CO₂ is ± 61 % at 280 °C and decreases to ± 50 % at 320 °C. Analyses of the moles of product formed over this catalyst (Fig. 5.8) shows that the amount of CO and CH₄ formed is lower than that formed in the absence of H₂O (Fig. 5.6) indicating that H₂O reduces the CO₂ methanation reaction over on the catalyst, but the amount of CO₂ (2 %) converted still exceeds that of CO (1 %) in the feed.

Unlike the Ir-TiO₂ catalyst, upon the addition of H₂O to the reformat gaseous mixture over the Ir-ZrO₂ catalyst, CO conversion (1% from feed) is observed at 280 °C which reaches a maximum of 4.8 % at 320 °C (Fig. 5.7B). This also correlates to no additional CO formation found in the effluent gaseous mixture (Fig. 5.8A). A CO₂ conversion of ± 4.4 % at 280 °C is seen and this decreases to ± 3.7 % at 320 °C with a maximum H₂ conversion of ± 0.5 %. The selectivities over the catalyst remain fairly constant at both temperatures tested at ± 50 % towards CO and CH₄. This catalyst methanates CO in the presence of CO₂, but at the same time also methanates CO₂ and some RWGS activity occurs, since H₂ is also being formed (Fig 5.8C). These findings of decreases in the CO₂ conversion, low H₂ formations and an increase in CH₄ formation were explained by Panagiotopoulou et al. [9], where at higher temperatures the CO methanation reaction is kinetically favoured compared to the WGS reaction. Also, considering the product concentration profiles (Fig. 5.8) and according to similar findings by Tada et al. [7] on a supported Ru catalyst, CH₄ is produced by both CO and CO₂ methanation. CH₄ formed from CO₂ was explained by firstly following the RWGS forming CO and then subsequently CO methanation. Comparing these two catalysts, the Ir-ZrO₂ catalyst shows better activity than the Ir-TiO₂, since the metal-support interactions (Chapter 3) reveal better

metals dispersions, particle sizes and hence activity of the Ir-ZrO₂ catalyst. These all reflect the method of synthesis (controlled pH favouring the zeta potential of ZrO₂) resulting in these catalytic profiles.

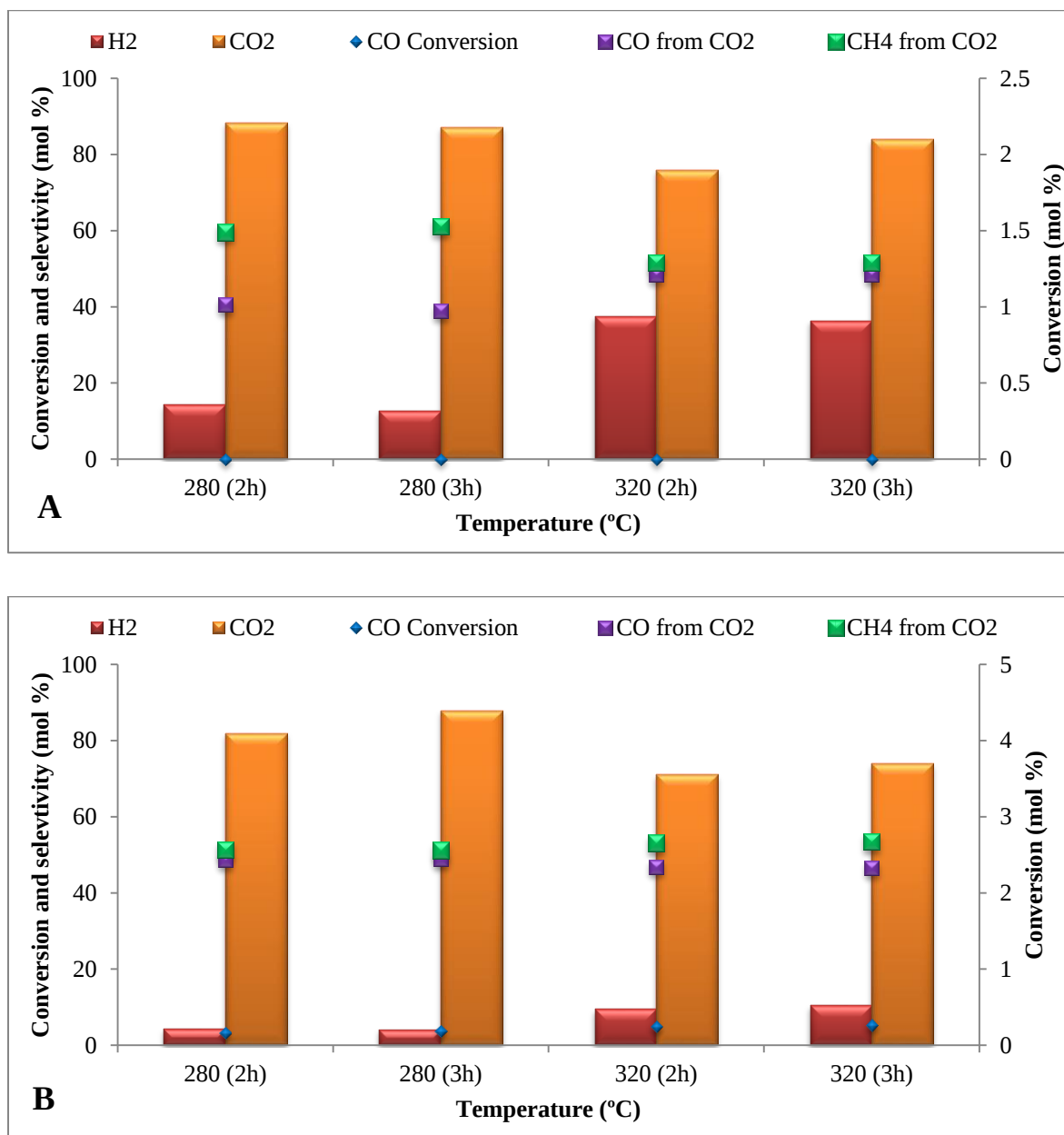


Figure 5.7. The effect of a real water-gas shift feed on the CO conversion and selectivity to products over the supported Ir catalysts, as well as the H₂ and CO₂ conversion (A: Ir-TiO₂ and B: Ir-ZrO₂)

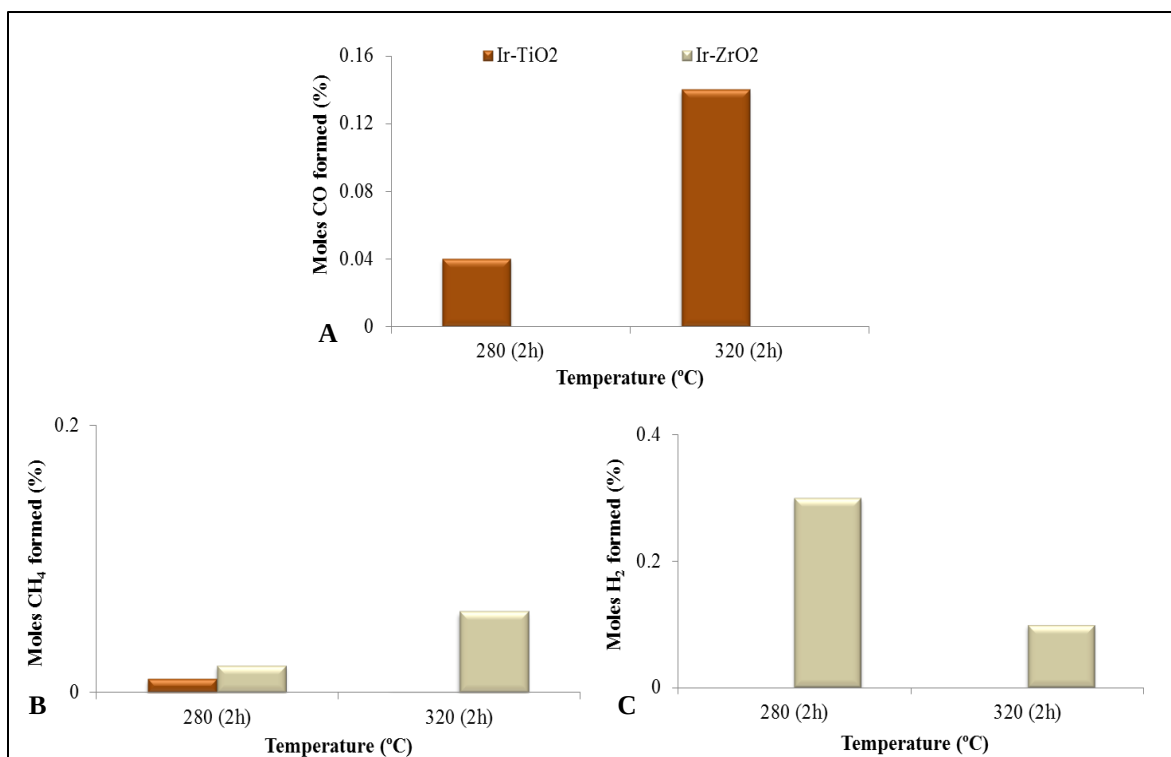


Figure 5.8. Moles of product formed using real water gas-shift feeds over the supported Ir catalysts (A: Moles of CO formed, B: Moles of CH₄ formed and C: Moles of H₂ formed)

5.3.3 Ru systems

5.3.3.1 The effect of CO₂ addition to the reformat gas over the Ru catalysts

The activity of the Ru catalysts using a reformat gaseous mixture containing CO₂ is shown in Fig. 5.9. Unlike the Pt and Ir systems, both these catalysts show activity for only the methanation reaction/s. In the absence of CO₂ at 220 °C (Fig. 5.9), the Ru-TiO₂ catalyst gave a CO conversion of ± 35.8 % and H₂ conversion of ± 0.58 %, whereas the Ru-ZrO₂ catalyst gave a CO conversion of ± 47.2 % and H₂ conversion of ± 0.7 % at 220 °C.

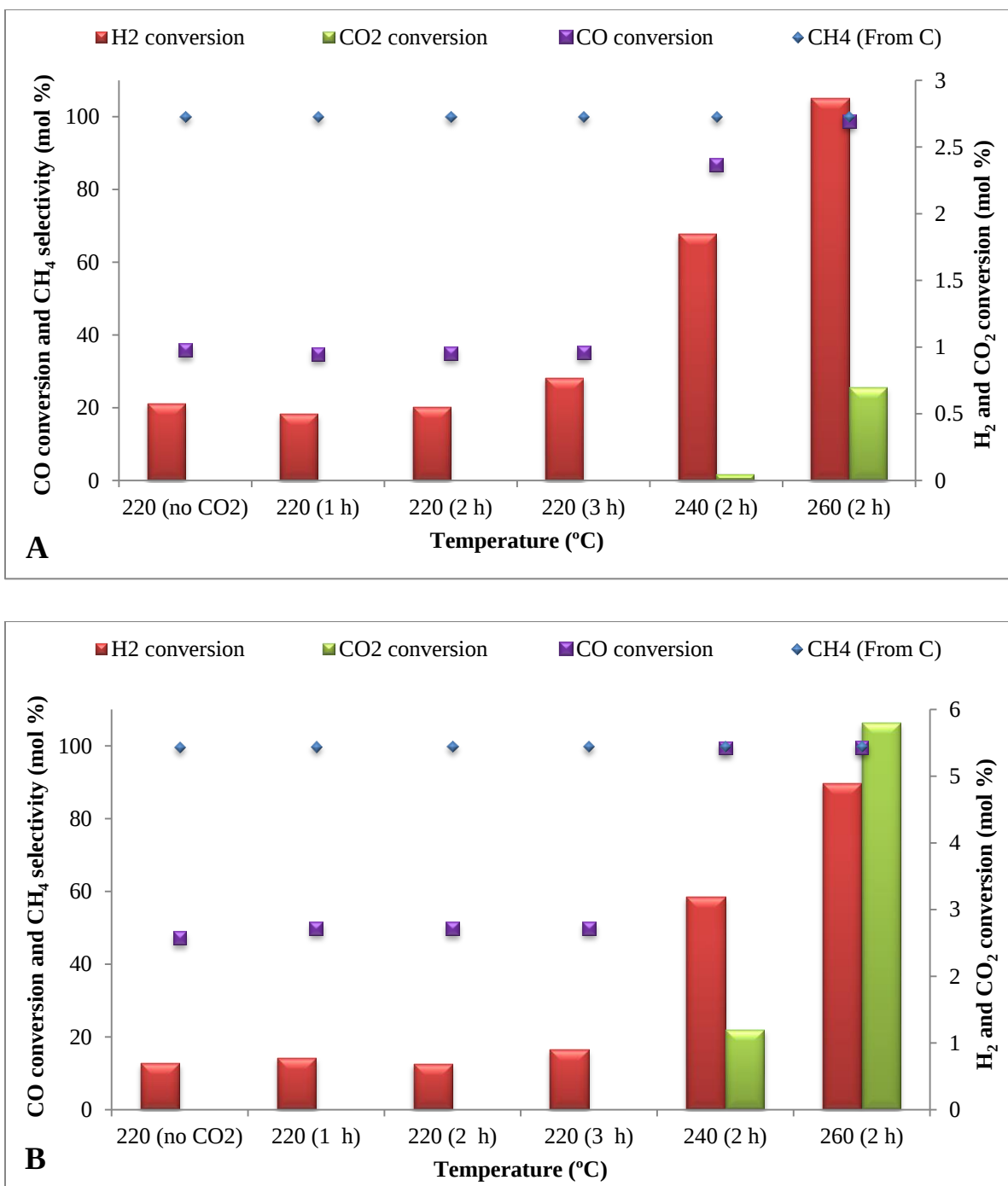


Figure 5.9. The effect of CO₂ addition in the reformate gas on the CO conversion and product selectivity as well as the H₂ and CO₂ conversion over the supported Ru catalysts (A: Ru-TiO₂ and B: Ru-ZrO₂)

Upon CO₂ addition, CO and H₂ conversions remain unaffected and the selectivity to CH₄ for both the catalysts was 99.9 %. Increasing the temperature resulted in higher CO conversions with corresponding H₂ consumptions, where Ru-TiO₂ reaches a maximum CO conversion of 99.9 % at 260 °C and Ru-ZrO₂ 99.9 % at 240 °C. CO₂ conversions over both these catalysts are only observed when CO conversions exceed 95 % and explain the higher H₂ conversions obtained.

Firstly, these catalysts are selective for CO methanation in the presence of CO₂, and only methanate CO₂ when all or most of the CO in the feed is consumed leaving available sites for CO₂ adsorption and methanation. Secondly, although Ru-TiO₂ shows lower CO₂ conversions this does not indicate superiority over the Ru-ZrO₂ catalyst, since this latter catalyst is more active (reaches maximum CO conversion at 240 °C) and methanates more CO₂ than the Ru-TiO₂, due to the availability of active sites and hence giving higher CO₂ conversions. This correlates to the moles of CH₄ formed (Fig. 5.10), once all CO is almost or completely consumed, CO₂ methanation proceeds. Additionally, unlike the Pt and Ir systems, the rate at which CO is methanated over Ru leaves no traces of CO in the product stream.

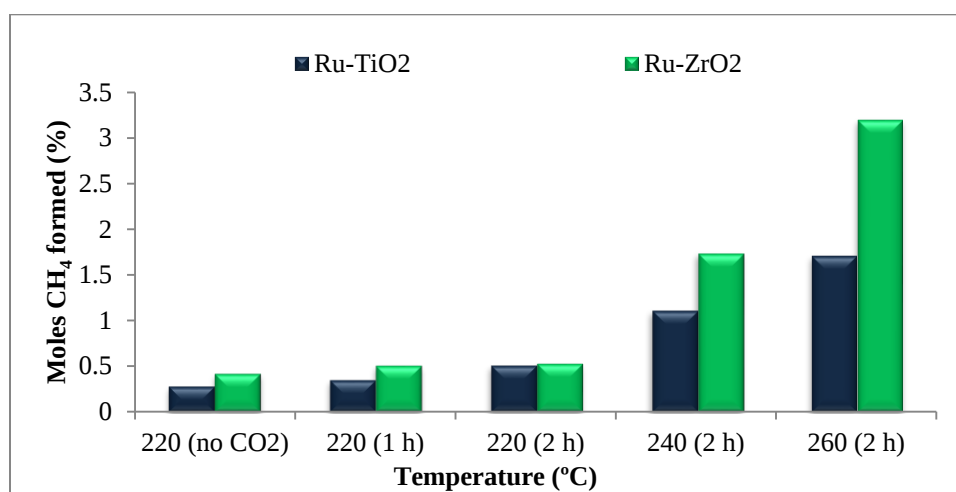


Figure 5.10. Moles of CH₄ formed following the addition of CO₂ to the reformat gaseous mixture over the supported Ru catalysts

5.3.3.2 The effect of H₂O vapor in the reformat stream over the Ru catalysts during SMET

The addition of H₂O vapour to the feed stream over both the Ru catalysts (Fig. 5.11) shows slight decreases (likely negligible) with regards to the CO conversions compared to those in the absence of H₂O (Fig. 5.9). Maximum CO conversions for the catalysts are still obtained following 240 °C. Selectivity towards CH₄ remains constant across the temperature range tested at 100 %. CO₂ and H₂ conversions trends remain similar to those shown as in the absence of H₂O (Fig. 5.9). The moles of CH₄ formed also remains unaffected, with no indication of any additional CO and H₂ production, showing good stability of these catalysts.

The catalysts thus selectively methanate CO in the presence of CO₂ and H₂O vapour which are present in the reformat stream following the WGS reaction. Time on stream data of the Ru catalysts shows excellent stability over 24 h with no decrease in conversion and selectivity (Fig. 5.11). Also, the activities of the supported Ru catalysts are attributed to the metal (Ru) itself which is not greatly influenced by the supports, since activities shown for both catalysts are almost identical, and the characterization of these catalysts (Chapter 4) shows that the particle sizes are very similar and, hence, the crystallite sizes. However, the metal dispersions resulting from ruthenium's interaction with the supports are lower for the Ru-TiO₂ catalyst (67 %) and higher for the Ru-ZrO₂ catalyst (81 %). These interactions are attributed to controlling the isoelectric points during synthesis at a pH more favourable for ZrO₂ and the Ru, compared to Ru and TiO₂ (Chapter 4). These overall explanations are in agreement to reports, where the strong metal-support interaction of supported catalysts could play significant roles in the catalyst activity [16]. In this case, the interaction of Ru-TiO₂ was not as strong as that obtained for Ru-ZrO₂, but still gave similar particle sizes, allowing similar trends in the catalytic activity. Furthermore, the slightly higher activity profiles obtained for the Ru-ZrO₂ catalyst could be attributed to the higher metal dispersions obtained which resulted from a stronger interaction with the support. This was also evident for PtDP and Ir supported on ZrO₂, which showed better activity than the TiO₂ supported Pt and Ir catalysts. Ru catalysts are also reported to having lower affinity for CO₂ adsorption and dissociation, due to a site blocking mechanism by a adsorbed CO layer over the Ru particles. This in turn blocks CO₂ adsorption and hence its dissociation on the surface, hindering, CO₂ methanation, unlike Pt and Ir [4, 8, 9].

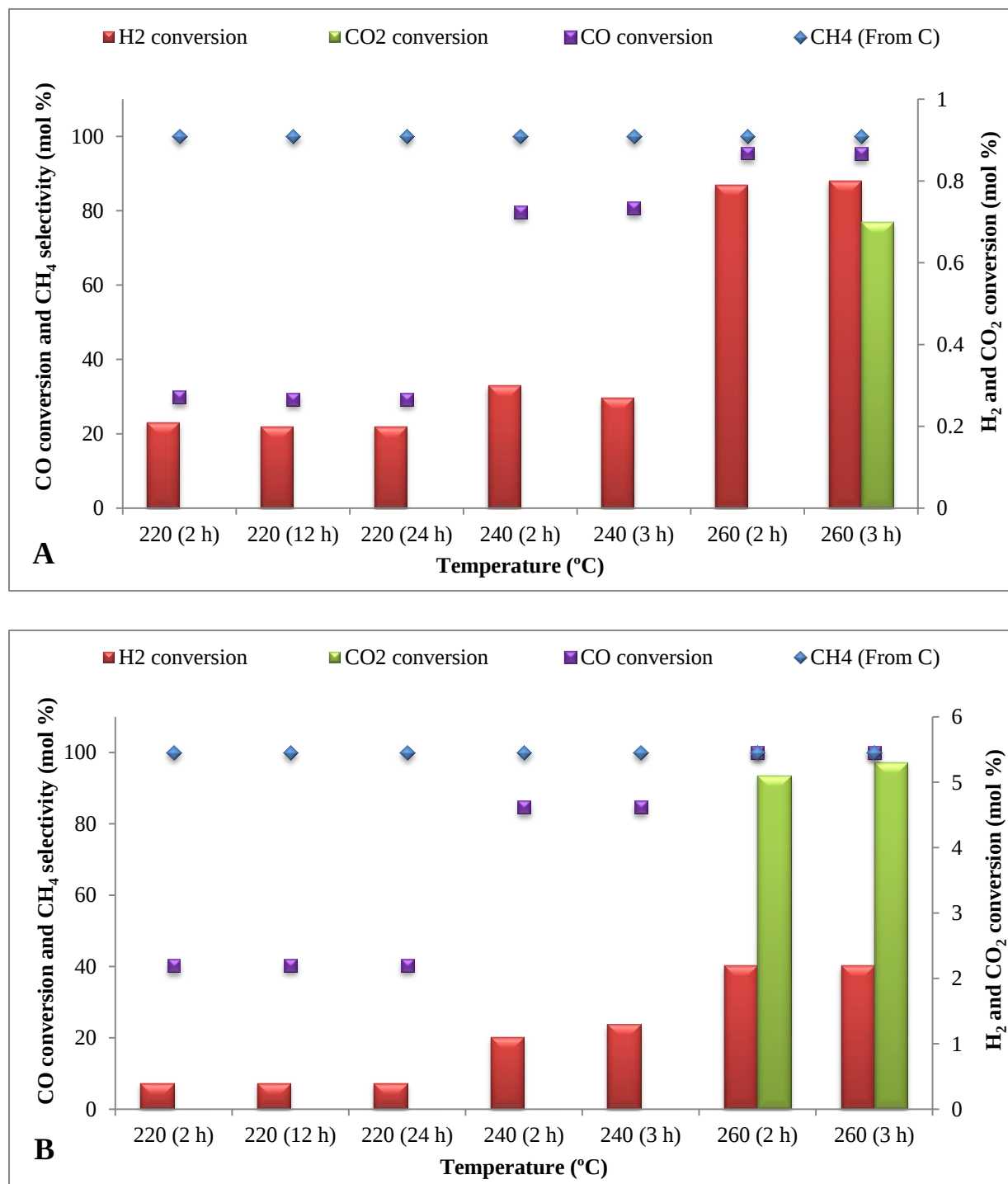


Figure 5.11. The effect of a real water-gas shift feed on the CO conversion and selectivity to product over the supported Ru catalysts, as well as the H₂ and CO₂ conversion (A: Ru-TiO₂ and B: Ru-ZrO₂)

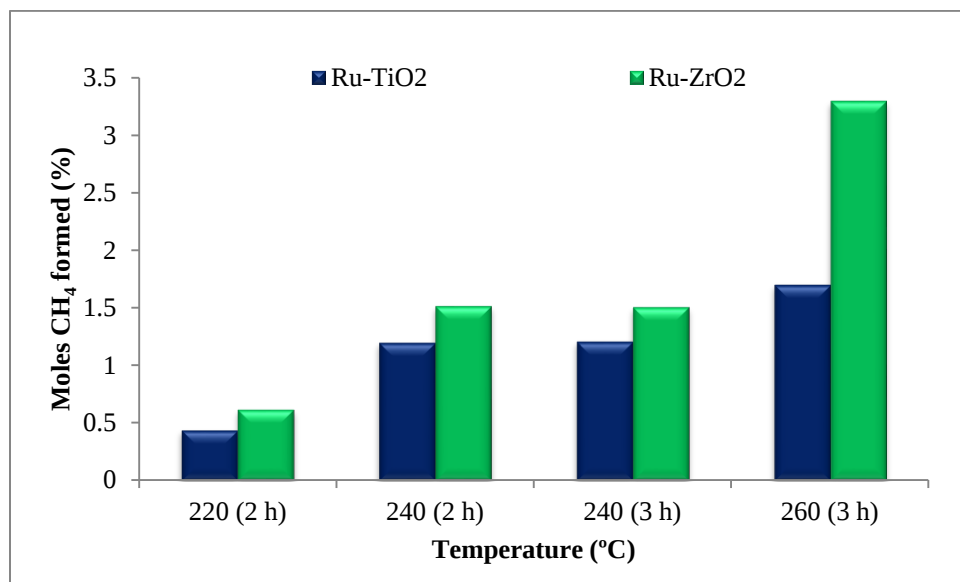


Figure 5.12. Moles CH₄ formed in the SMET reaction over the supported Ru catalysts

In contrast to the Ru systems, CO is strongly chemisorbed to Pt and Ir and does not allow sufficient adsorption of H₂ and its dissociation to allow CO methanation [9]. This is in agreement with a report by Vannice [18], showing CO hydrogenation activity of these metals with the respective heats of adsorption (CO), where Ru has lower values than Pt and Ir. Furthermore, Bligaard et al. [19] reported that another important parameter, apart from the heat of CO adsorption, is the CO dissociative adsorption energy on the specific metal. They showed that Ru achieved highest activity over other PGMs due to it having higher CO dissociative adsorption energies corresponding to their volcano type curve.

A study by Pangiotopoulou et al. [16], using a feed composition of 1% CO, 50% H₂, 15% CO₂ and 0-30% H₂O over a 5 wt. % Ru-TiO₂ catalyst found that maximum CO conversions were obtained at 230 °C, with CO₂ methanation being suppressed until all CO was converted. Also, using lower Ru loadings (0.5 %) the catalyst only achieves a maximum conversion of 50 % at 320 °C. Additionally, the Pt and Pd counterparts favoured the RWGS reaction and were not effective in removing CO. These results relate closely to the ones obtained in this study, but considering the amount of active metal used (1 wt. %) and the H₂ concentration in the feed (above 50 %), the catalysts here are promising, since higher H₂ concentrations were used

which more realistically models the WGS reformat stream and, additionally, the cost efficiency for using lower amounts of precious metals is always favoured.

5.4 Conclusion

Using a realistic water-gas shift reformat feed (containing CO, CO₂ and H₂O) over the catalysts showed different catalytic activity depending on the active metal used. Pt catalysts synthesized by the wet impregnation and deposition precipitation methods favoured the forward and reverse water-gas shift reactions, and also the methanation of CO₂, rendering them poor at CO removal. However, the PtDP-ZrO₂ catalyst, although showing very little/no selective CO methanation, was the best of the Pt systems. Ir-TiO₂ showed lower activity towards the water-gas shift reaction, but still promoted unselective CO₂ methantation, whereas the Ir-ZrO₂ catalyst showed better activity than its TiO₂ counterpart, but was still not selective for CO methanation. Ru supported on both TiO₂ and ZrO₂ showed the best activity and selectively for CO methanation in the presence of CO₂ at temperatures almost 100 °C lower than over the Pt and Ir catalysts. Maximum CO conversions obtained were 99.9 % with 99.9 % selectivity towards CH₄ above 220 °C. The methanation of CO₂ over both the Ru catalysts only progresses once all CO in the feed is converted (99 % conversion), when available active sites are left for CO₂ adsorption. This resulted from CO blocking surface sites and having high dissociation rates that prevented CO₂ adsorption and its dissociation.

H₂O vapour in the feed had little/no effect with regards to the CO conversion and selectivity of these catalysts. Time on stream results showed that these catalysts were stable for 24 h with no deactivation. Slightly higher catalytic activity profiles over the Ru-ZrO₂ catalyst were attributed to the Ru and ZrO₂ interaction, which was achieved in a controlled pH system favouring the zeta potential of ZrO₂. Both these Ru catalysts are promising in terms of cost efficiency and in removing trace CO impurities to less than 10 ppm, which is ultimately needed in proton exchange membrane fuel cells.

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Chapter 6

Summary

The Pt catalysts synthesized by the deposition precipitation method showed higher metal dispersions, metallic surface areas, smaller particle sizes and higher CO chemisorption capacities. These were attributed to controlling the pH to match the isoelectric points of the supports during the synthesis, however, which was more effective over the TiO₂ supported materials since the ZrO₂ support by both preparation techniques used similar pH media and, hence, had similar characteristic properties for both the catalysts. Due to the success of the deposition precipitation method mainly for TiO₂ supported Pt catalysts, the deposition precipitation method was used for Ir and Ru catalyst synthesis.

These ~1 wt. % Pt, Ir and Ru supported on TiO₂ and ZrO₂ catalysts are not suitable for the removal of CO impurities in the reformat gas post water-gas shift using the “dry” PROX reaction. As a result of maintaining the isoelectric points during the synthesis, the ZrO₂ supported materials were always better than the TiO₂, due to the stronger metal-support interactions which were more favourable on ZrO₂ with the Cl⁻ precursors used during the synthesis. Therefore, during the catalytic reactions of the supported catalysts, TiO₂ catalysts mostly showed lower activity, due to their lower reducibility and lower electropositivity compared to ZrO₂. The active metals on both the supports, however, promoted support reduction in close proximity to the active metals, due to the strong metal-support interactions. As a result, H₂ spillover from the active metals onto the supports leads to the creation of O₂ vacancies. These vacancies, during the PROX reaction, utilized molecular O₂ in the feed to re-oxidize the vacancies instead of interacting with CO to produce CO₂. Hence, H₂O formation was more dominant over these catalysts. Additionally, the Ru catalysts, simultaneously methanated CO in competition to the PROX reaction, and thus increase the H₂ consumption. Exceeding 200 °C, also considering that O₂ is additionally supplied for this reaction, is not viable, since at higher temperatures H₂ oxidation and usage will be higher still.

All these catalysts showed exceptional activity for CO hydrogenation in the “dry” feeds, with Pt and Ir giving maximum CO conversions, higher than 95 % above 350 °C, and high selectivity towards CH₄ (>90 %). Ru however, was the best with regards to activity and gave maximum CO conversions of 99.9 % and 99.9 % selectivity towards CH₄ at 260 °C.

After introducing CO₂ and H₂O to the feed, to simulate a realistic model water-gas shift reformat gas, both Pt and Ir systems showed very low activity for selective CO methanation. These catalysts were unselective and simultaneously methanated CO₂ and also showed activity towards the reverse water-gas shift reaction, thus using additional H₂ in the feed. However, both Ru catalysts showed almost no decrease in activity when CO₂ and H₂O were introduced to the feed and gave maximum CO conversions higher than 95 % with 99.9% selectivity towards CH₄ above 240 °C. Evidence of CO₂ methanation is only evident once all CO in the feed is converted, leaving available active sites for CO₂ adsorption and hence methanation. Time on stream experiments showed that these catalysts are stable over 24 h with no decrease in activity and selectivity.

The superior performance of the Ru catalysts over the Pt and Ir counterparts was attributed to the active metals themselves, where Ru has a lower CO heat of adsorption and a higher CO dissociation energy compared to Pt and Ir. Also, during the reaction CO completely occupies the active sites and CO₂ adsorption and dissociation is hindered. The 1 wt. % Ru supported on TiO₂ and/or ZrO₂ catalysts prepared by the deposition precipitation method are effective in removing trace CO from water-gas shift reformat feeds to levels less than 10 ppm. These Ru catalysts are cost efficient, show high stability, require no additional reactant in the reformat gas and thus can be used in proton exchange membrane fuel cell applications.