



Influence of different fuels on the properties of Solution-Combustion synthesized palladium/ceria catalysts for low-temperature methane combustion

By

Thabiso Perfect Oscar Mkhwanazi

(BSc Honours in Chemistry)

School of Chemistry and Physics

University of KwaZulu-Natal

Durban

South Africa

Masters in Chemistry

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“Learn from yesterday, live for today, and hope for tomorrow. The important thing is not to stop questioning.”.

By Albert Einstein

Abstract

Catalytic combustion of methane is a leading technology in energy production, emission prevention and gas clean-up. Its main advantage over traditional flame combustion is to carry out complete oxidation of fuel at low temperatures. Noble metals supported over high surface area supports are known to combust methane at low-temperatures. However, noble metals supported on oxide supports has been observed to result in high methane combustion activity at low temperatures. In recent studies on methane combustion, it was observed that the use of ceria as a support can significantly improve the catalyst activity. PdO supported on ceria is known to be a very active catalyst for methane combustion. However, this catalyst still suffers from poor activity at low temperature (below 673 K) and deactivation at high temperature (above 973 K) owing to the formation of metallic Pd from PdO particles.

In this study, a comparison between solution combustion synthesis (SCS) and conventional incipient wet-impregnation catalysts was made and discussed for low temperature methane combustion. The PdO/CeO₂ catalysts was prepared by the solution combustion synthesis method (SCS) with different fuels including oxalylhydrazide (ODH), citric acid monohydrate, urea, β -alanine, and tartaric acid were subsequently evaluated for low-temperature methane combustion. Each fuel is known to affects the physical and chemical properties of the catalyst which further influences the catalytic performances. To the best of our knowledge, the effect of fuels on the properties of SCS synthesised PdO/CeO₂ catalysts, for low temperature methane combustion has not been reported. To evaluate these effects, several fuels such as oxalylhydrazide (ODH), citric acid monohydrate, urea, β -alanine, and tartaric acid were used. Furthermore, all prepared catalysts were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive X-ray spectrometer (EDX), laser Raman spectroscopy (LRS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), N₂-physisorption analysis and X-ray photoelectron spectroscopy (XPS). Furthermore, all prepared catalysts were tested for methane combustion activity at 4 vol% methane in air and GHSV of 15 000 h⁻¹.

The N₂-Physisorption analysis revealed that SCS ceria had a high surface area and a smaller crystallite size when compared to the commercial ceria. From Raman spectroscopy, the SCS ceria was established to contain more defects and thus, contained a higher amount of lattice oxygen in

comparison to the commercial ceria. The SCS ceria provided almost 2.5-fold higher methane conversion than the commercial ceria at 600 °C. When the 2 wt.% PdO/CeO₂ catalysts were compared, it was revealed that the SCS synthesized catalysts had a higher surface area and more oxygen vacancies and thus, higher catalytic activity in comparison to the catalysts prepared using wet impregnation.

The study of the effect of fuels revealed, that different fuels result in catalysts with different physical and chemical properties. The surface areas of the prepared catalysts were observed to decrease according to the following trend, Pd_{0.03}Ce_{0.97}O_{2-δ}-urea > Pd_{0.03}Ce_{0.97}O_{2-δ}-tartaric acid > Pd_{0.03}Ce_{0.97}O_{2-δ}-alanine > Pd_{0.03}Ce_{0.97}O_{2-δ}-citric acid > Pd_{0.03}Ce_{0.97}O_{2-δ}-ODH. Raman spectroscopy, revealed that the amount of oxygen vacancies decreased in the order of Pd_{0.03}Ce_{0.97}O_{2-δ}-citric acid > Pd_{0.03}Ce_{0.97}O_{2-δ}-ODH > Pd_{0.03}Ce_{0.97}O_{2-δ}-alanine > Pd_{0.03}Ce_{0.97}O_{2-δ}-tartaric acid > Pd_{0.03}Ce_{0.97}O_{2-δ}-urea. The H₂-TPR and XPS studies, revealed that the citric acid and ODH synthesized catalysts contained supported PdO in comparison to the other SCS synthesized catalysts. The T₅₀ was observed to decrease in the following order Pd_{0.03}Ce_{0.97}O_{2-δ}-citric acid > Pd_{0.03}Ce_{0.97}O_{2-δ}-ODH > Pd_{0.03}Ce_{0.97}O_{2-δ}-urea > Pd_{0.03}Ce_{0.97}O_{2-δ}-alanine > Pd_{0.03}Ce_{0.97}O_{2-δ}-tartaric acid. However, the T₁₀₀ was observed to decrease in following order Pd_{0.03}Ce_{0.97}O_{2-δ}-citric acid > Pd_{0.03}Ce_{0.97}O_{2-δ}-urea > Pd_{0.03}Ce_{0.97}O_{2-δ}-ODH > Pd_{0.03}Ce_{0.97}O_{2-δ}-alanine > Pd_{0.03}Ce_{0.97}O_{2-δ}-tartaric acid.

Preface

The work conducted and described in this thesis was conducted in the Catalysis Research Group, at the School of Chemistry and Physics, University of KwaZulu-Natal, Westville, South Africa. This research was conducted from February 2016 to June 2018 under the supervision of Prof. Holger B. Friedrich and co-supervision of Dr. Sooboo Singh and Dr. Abdul S. Mahomed.

The work presented in this thesis is that of my own and it has not been submitted for any degree to any other tertiary institution. However, when the work of other authors have been cited, due acknowledgement has been provided in the text.

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Nomenclature

Abbreviations

3WV	: Three-way valve
4WV	: Four-way valve
BET	: Brunauer Emmet Teller
BPR	: Back pressure regulator
CO-PROX	: Preferential oxidation of carbon monoxide
DFT	: Density functional state theory
D	: Crystallite size
D _{BET}	: Crystallite size obtained from BET analysis
EDX	: Energy-dispersive X-ray spectroscopy
FWMH	: Full width at half maximum
g	: Grams
GC	: Gas chromatography
GHSV	: Gas hourly space velocity
H ₂ -TPR	: Hydrogen temperature-programmed reduction
HRTEM	: High resolution transmission electron microscopy
MFC	: Mass flow controller
ODH	: Oxalyl hydrazide
OSC	: Oxygen storage capacity
PR	: Pressure regulator
PXRD	: Powder X-ray diffraction
TEM	: Transmission electron microscopy
XPS	: X-ray photoelectron spectroscopy

XRD : X-ray diffraction

Chemical formulas

$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$: Ammonium cerium (IV) oxide

$\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$: Citric acid monohydrate

CeO_2 : Cerium dioxide

CH_4 : Methane

CO : Carbon monoxide

CO_2 : Carbon dioxide

$\text{HO}_2\text{CCH}(\text{OH})\text{CH}(\text{OH})\text{CO}_2\text{H}$: Tartaric acid

H_2 : Molecular hydrogen

H_2O : Water

H_2SO_4 : Sulphuric acid

$\text{NH}_2\text{CH}_2\text{CH}_2\text{COOH}$: β -alanine

NH_2CONH_2 : Urea

$\text{NH}_2\text{NHCOCOONHNH}_2$: Oxalyl hydrazide

N_2 : Molecular nitrogen

O_2 : Molecular oxygen

Pd : Palladium

$\text{Pd}(\text{NO}_3)_2$: Palladium (II) nitrate hydrate

PdO : Palladium oxide

PdO_2 : Palladium(IV) Oxide

SiC : Silicon carbide (Carborundum)

Notations

ΔH	: Enthalpy, in kJ/mol
μm	: Micrometer
A	: Area in chromatogram
d	: Diameter, in nm
ml	: Milliliter
ml.min^{-1}	: Milliliter per minute
mm	: millimeter
mol%	: Mole percentage
nm	: Nanometer
T	: Temperature, in °C or K
T_{10}	: Temperature for a CH_4 conversion of 10%, in °C
T_{50}	: Temperature for a CH_4 conversion of 50%, in °C
T_{100}	: Temperature for a CH_4 conversion of 100%, in °C
TOF	: Turn over frequency, in s^{-1}
X	: Conversion, in %

Greek notations

B	: Beta
ρ	: Density, in g/cm^3
θ	: Diffraction angle, in °
λ	: Wavelength, in Å

Table of Contents

Abstract.....	ii
Preface.....	iv
Declaration 1 - Plagiarism.....	v
Acknowledgements	vi
Conference Contributions	vii
Nomenclature	viii
Abbreviations.....	viii
Chemical formulas	ix
Notations	x
Greek notations	x
Table of Contents	xi
Table of Figures.....	xv
Table of Schemes.....	xviii
Table of Tables	xviii
Chapter 1	1
1.1 Introduction to methane combustion	1
1.2 Literature Review.....	2
1.2.1 Hydrogen production	2
1.2.2 Methane combustion	4
1.2.3 Catalytic combustion of methane.....	5
1.2.4 Light-Off temperature curves	6
1.2.5 The effect of methane (fuel)/oxygen ratio on methane combustion	7
1.2.6 Methane Combustion Catalysts	7
1.2.7 Active metals in methane combustion catalysts.....	8

1.2.8 Variables affecting Pd based catalysts in methane combustion	9
1.2.8.1 Palladium loading.....	10
1.2.8.2 Palladium particle size	11
1.2.8.3 Palladium oxide (PdO) and palladium metal (Pd ⁰) as active phases for methane combustion	12
1.2.8.4 Reduction of PdO to Pd.....	13
1.2.8.5 Methane combustion pathways and inhibition by water over Pd-based catalysts	14
1.2.9 Catalyst Supports	16
1.2.10 Ceria as a catalyst support for oxidation reactions	17
1.2.10.1 Defects in ceria	18
1.2.11 Structure sensitivity in methane combustion over palladium-ceria catalysts.....	19
1.3 Solution combustion synthesis	21
1.3.1 Parameters affecting solution combustion	22
1.3.1.1. Flame type	23
1.3.1.2 Characteristic temperature	24
1.3.1.3 Gases generated	25
1.3.1.4 Fuel-oxidant ratio	25
1.3.1.5 Fuels	27
Motivation and Objective of this study	30
References	32
Chapter 2	37
Experimental.....	37
2.1 Catalysts preparation	37
2.1.1 SCS catalysts preparation.....	37
2.1.2 Preparation of 2wt.% PdO/CeO ₂ using wet impregnation.....	38

2.2 SCS catalysts characterisation	39
2.2.1 Powder X-Ray diffraction.....	39
2.2.2 Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) analysis	40
2.2.3 N ₂ -physisorption	40
2.2.4 Raman Spectroscopy	41
2.2.5 Scanning Electron Microscopy.....	41
2.2.6 Transmission Electron Microscopy	41
2.2.7 High Resolution Transmission Electron Microscopy.....	42
2.2.8 H ₂ Temperature Programmed Reduction.....	42
2.3 Palladium supported catalyst characterisation	42
2.4 Catalytic testing	42
2.4.1 Reactor setup and Reactor tube packing	42
2.5 Methane combustion	46
2.5.1 Catalysts pre-treatment	46
2.5.2 Methane combustion over ceria based catalysts.....	47
2.5.3 Methane combustion via lattice oxygen.....	47
2.5.4 Conversion calculations	47
References	48
Chapter 3	49
Characterisation of Pd _{0.03} Ce _{0.097} O _{2-δ} catalysts synthesized using different fuels	49
3.1 Enthalpy of combustion	49
3.2 Inductive Coupled Plasma-Optical Emission Spectroscopy	50
3.3 X-Ray diffractogram (XRD) studies	50
3.4 N ₂ -Physisorption analysis.....	54
3.5 Raman spectroscopy studies	55

3.6 Scanning electron microscopy	57
3.7 Transmission electron microscopy	58
3.8 High-resolution Transmission electron microscopy	59
3.9 Temperature programmed reduction (TPR) studies	60
3.10 The XPS analysis of $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$	62
References	68
Chapter 4	71
4.1 Methane combustion over ceria-based catalysts	71
4.1.1 Methane combustion over commercial and SCS ceria	71
4.2 Methane combustion over palladium-ceria based catalysts	73
4.2.1 Methane combustion with SCS catalysts	74
4.2.2 Effect of fuels on methane combustion	74
4.2.3 Comparison between the citric acid synthesised catalyst with the urea synthesised catalyst in methane combustion.	77
4.2.4 Reaction mechanisms	78
4.3 Methane combustion over the citric acid catalyst	80
4.3.1 Heating and cooling curves	80
4.3.2 Effect of different GHSV studies	81
4.3.3 Time on stream studies	83
4.3.4 Time on stream at different GHSVS	84
4.3.5 The role of lattice oxygen	85
References	86
Chapter 5	89
Summary and Conclusions	89
Chapter 6	92
Additional remarks and recommendation for future research	92

Appendix A	93
Test units design and Components	93
Appendix B	95
List of chemicals, reactor conditioning and data analysis using a micro GC	95
List of chemicals.....	95
Reactor conditioning:	95
Appendix C	98
Characterization.....	98

Table of Figures

1.1 The steps for fuel processing of gaseous, liquid and solid fuels for high temperature and low-temperature fuel cell applications.....	2
1.2 Schematic diagram of a fuel processing system.....	4
1.3 Conversion against temperature curve for catalytic combustion of methane.....	5
1.4 Methane conversion over Pd-based catalysts.....	7
1.5 Recent catalysts used in low-temperature methane combustion.....	8
1.6 Monthly average prices of PGMs between September 2012 and September 2017.....	9
1.7 Influence of palladium loading on methane conversion.....	10
1.8 TOF of Pd/Al₂O₃ catalysts versus mean particle diameter.....	11
1.9 The effect of (a) Extent of Pd oxidation and (b) Extent of PdO reduction on methane combustion activity at various temperatures.....	13
1.10 Schematic illustration of proposed mechanisms for PdO decomposition and Pd re-oxidation.....	14
1.11 Effects of O₂, H₂O, and CO₂ on methane oxidation rates.....	15
1.12 Methane dissociation on a surface Pd–PdO site pair.....	15
1.13 The fluorite structure of ceria.....	18
1.14 The crystal structures a) pure ceria and b) doped ceria.....	18
1.15 Top and c) side views of the equilibrium surface Pd-O-Ce superstructure predicted by DFT calculations. O and Ce atoms belonging to the surface superstructure phase are	

displayed in lighter colors. b) Density of electronic states (DOS) and projected DOS (PDOS) for the Ce 4f (red area) and Pd 4d (green area) states.....	20
1.16 The total apparent barrier for CH ₄ activation over the thermodynamically favored Pd ⁿ⁺ state compared to an oxidized Pd ^{(n+m)+} state.....	21
1.17 Schematic diagram of Me ₂ O _n powder synthesized by SCS.....	22
1.18 The evolution of a smoldering flame during the combustion reaction containing Ca(NO ₃) ₂ , Al(NO ₃) ₃ and β-alanine.....	23
1.19 The evolution of a flaming flame during the combustion reaction containing Ca(NO ₃) ₂ , Al(NO ₃) ₃ and Urea.....	24
1.20 The effect of fuel-oxidant ratio on adiabatic temperature and moles of gases produced.....	26
2.1 The schematic diagram of the programmable furnace combustion process.....	37
2.2 Schematic representation of the test unit used in methane combustion.....	45
2.3 The schematic diagram of the reactor tube.....	46
3.1 X-ray diffractograms of Pd _{0.03} Ce _{0.97} O _{2-δ} prepared by solution combustion synthesis.....	51
3.2 Schematic diagram showing incorporation of oxide ion into ceria lattice using Kroger-Vink notation.....	52
3.3 X-ray diffractograms of commercial CeO ₂ and PdO/CeO ₂ -IWI catalysts.....	53
3.4 Raman spectra of Pd _{0.03} Ce _{0.97} O _{2-δ} prepared by solution combustion synthesis.....	55
3.5 SEM images of a) Pd _{0.03} Ce _{0.97} O _{2-δ} Tartaric acid, b) Pd _{0.03} Ce _{0.97} O _{2-δ} Urea, c)Pd _{0.03} Ce _{0.97} O _{2-δ} Alanine, d) Pd _{0.03} Ce _{0.97} O _{2-δ} Citric acid and, e)Pd _{0.03} Ce _{0.97} O _{2-δ} ODH.....	58
3.6 TEM images of a) Pd _{0.03} Ce _{0.97} O _{2-δ} Tartaric acid, b)Pd _{0.03} Ce _{0.97} O _{2-δ} Urea,c) Pd _{0.03} Ce _{0.97} O _{2-δ} Alanine, d) Pd _{0.03} Ce _{0.97} O _{2-δ} Citric acid and, e) Pd _{0.03} Ce _{0.97} O _{2-δ} ODH.....	58

3.7	HRTEM images of a) $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Tartaric acid, b) $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Urea, c) $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Alanine, d) $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Citric acid and, e) $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ ODH.....	59
3.8	HRTEM (line scan images) of a) $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Tartaric acid, b) $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Urea, c) $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Alanine, d) $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Citric acid and, e) $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ ODH.....	60
3.9	TPR of $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ prepared by solution combustion synthesis.....	61
3.10	The XP spectra of Ce3d of catalysts prepared by SC using different fuels.....	63
3.11	The XP spectra of Pd 3d of catalysts prepared by SC using different fuels.....	64
3.12	The XP spectra of O1s of catalysts prepared by SC using different fuels.....	66
4.1	Methane combustion over a) CeO_2 -comm and b) CeO_2 -SCS with 4% CH_4 in air and at a GHSV of $15\,000\text{ h}^{-1}$	72
4.2	Methane combustion over a) PdO/CeO_2 - wet impregnation and b) PdO/CeO_2 -SCS at 4% CH_4 in air and at a GHSV of $15\,000\text{ h}^{-1}$	73
4.3	Methane combustion over $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ prepared by various fuels at 4% CH_4 in air and at a GHSV of $15\,000\text{ h}^{-1}$	75
4.4	The effect of crystallite on methane combustion under $350\text{ }^\circ\text{C}$	76
4.5	Reaction model over the Catalysts.....	80
4.6	Methane combustion heating and cooling curve over $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ citric acid at 4% methane in air, $15\,000\text{ h}^{-1}$ GHSV.....	81
4.7	Methane combustion over $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ citric acid at 4 % methane in air, GHSV of $15\,000\text{ h}^{-1}$ and $30\,000\text{ h}^{-1}$	82
4.8	Time on stream over $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ citric acid using 4 % methane in air, at $500\text{ }^\circ\text{C}$ and a GHSV of $15\,000\text{ h}^{-1}$	83
4.9	Time on stream over $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ citric acid at $600\text{ }^\circ\text{C}$, 4 % methane in air and a GHSV of $15\,000\text{ h}^{-1}$	84

4.10	Time on stream over $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ citric acid at 600 °C, 4 % methane in air and a GHSV of 30 000 h ⁻¹	84
4.11	Methane combustion over $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ citric acid with 4 % methane in nitrogen and 4 % methane in air, at a GHSV of 15 000 h ⁻¹ , and 350 °C.....	85

Table of Schemes

1.1	Methane oxidation reaction pathways.....	16
4.1	Methane combustion via the LH mechanism.....	78
4.2	The MvK mechanism of methane combustion over $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ catalyst synthesised by urea, alanine, ODH, citric acid and tartaric acid as fuels.....	79
4.3	The schematic diagram of the reaction mechanism of methane combustion over $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ citric acid and $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ ODH.....	80

Table of Tables

1.1	Commonly used fuels in solution combustion synthesis.....	28
3.1	The effect of fuels on the nature of combustion.....	41
3.2	The actual loading of the prepared catalysts.....	50
3.3	Crystallite size, d-spacing and lattice strains for $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ prepared by solution combustion synthesis.....	52
3.4	The surface area, pore sizes and pore volume of the $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ prepared by solution combustion synthesis.....	54
3.5	Oxygen vacancies of the synthesised catalysts.....	56
3.6	The hydrogen consumption and release calculated below 250 °C.....	62
3.7	The population of Ce^{3+} on the surfaces of catalysts prepared using SCS with different fuels.....	64
3.8	The population of Pd^{2+} on the surfaces of catalysts prepared using SCS with different fuels from XPS analysis.....	65

5.1 Summary of the physical and chemical properties of the solution combustion synthesised catalysts.....	90
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Chapter 1

1.1 Introduction to methane combustion

Fossil fuels have made a major contribution to the energy demands in South Africa. However, the negative environmental impact of fossil fuel usage, and their imminent expiration date has led to a growing need for cleaner and sustainable alternative fuels. This has driven South Africa's commitment to the exploration of renewable energy sources. Hydrogen (H_2) is regarded as a clean, safe and a reliable alternative source of energy to the diminishing fossil fuel reserves. Hydrogen energy involves the use of fuel cell technology and hydrogen as an energy carrier. This process can directly convert chemical energy into electrical energy with no harmful emissions at the point of use. However, due to the lack of adequate infrastructure for hydrogen production, storage, and transportation, an on-board fuel processor is warranted. Hydrogen South Africa (HySA), a focussed research initiative funded by the Department of Science and Technology (DST), is currently working on the development of a fuel processor as a key focus area. Platinum group metal (PGM) based catalysts are central to this initiative, due to the abundance of PGM's in South Africa.

Currently, on-board fuel processors use the steam reforming process to produce H_2 on site for the polymer electrolyte membrane fuel cells (PEMFC) to compensate for the lack of infrastructure for the supply of adequate hydrogen, as the energy source. However, the use of steam reforming results in the production of carbon monoxide which is detrimental to the catalysts lifetime, since it is poisonous to the platinum anode used in the PEMFC. Additional processes are then needed to clean the hydrogen prior to the PEMFC and these additional steps increase the operational cost of the PEMFC. A major drawback of using steam reforming is the additional external heat needed to drive the process due to the endothermicity of the reaction. To compensate for this, the exothermic methane combustion reaction is seen as a means to supply heat for the reforming process.

Key criteria for methane combustion catalysts are:

- High CH_4 conversion to ensure maximum heat is produced.
- High CO_2 selectivity to obtained efficient combustion.
- Highly active catalysts at various GHSVs

1.2 Literature Review

Research and development for the utilization of alternative energies has become a major focus area to address increasing environmental problems such as air pollution, water pollution, ozone layer depletion, and global warming.^{1, 2} It is well known that hydrogen can serve as a renewable energy source due to its non-polluting nature.^{1, 3} Furthermore, several hydrogen application areas, including ammonia synthesis, catalytic hydrogenation processes, and fuel cells have triggered the development of hydrogen production technologies^{1, 4}, because molecular hydrogen is not naturally available.⁵

1.2.1 Hydrogen production

The fuel processing technology is essential to convert many possible fuel sources such as biomass, hydrocarbons, and alcohols, to hydrogen. Among the various fuels, methane is a promising source for hydrogen as it is the main component in natural gas and renewable biogas. There are many possible reaction routes to generate hydrogen from methane, although there are also other early-stage hydrogen production technologies such as electrolysis and photo-catalytic water splitting. For fuel cell applications, methane is reformed to hydrogen in the reformer as shown in Figure 1.1.

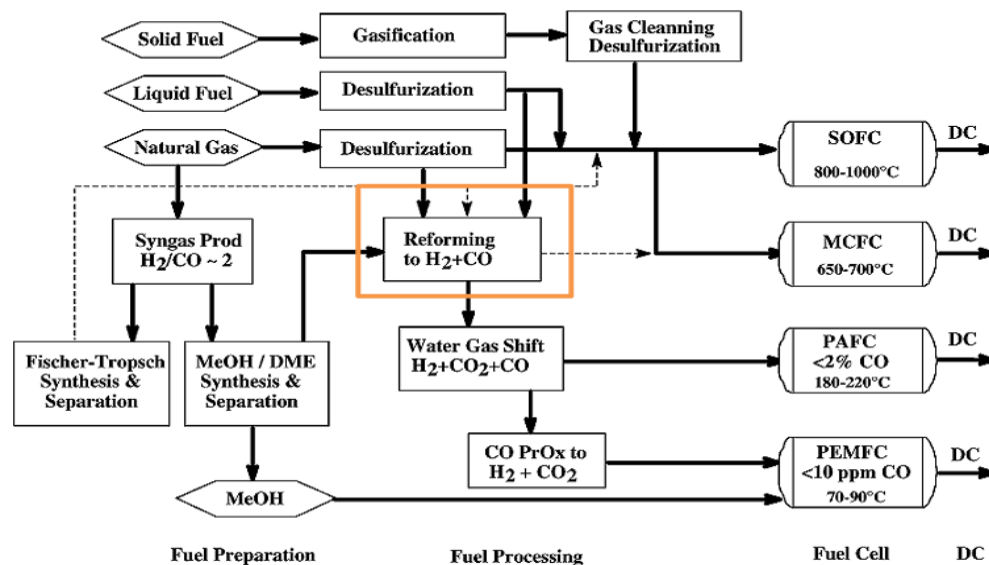
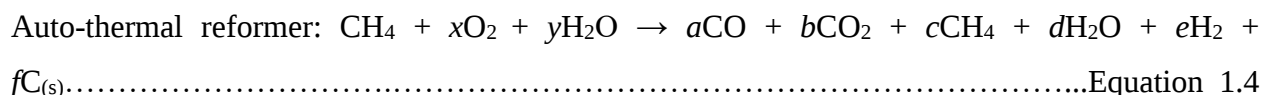
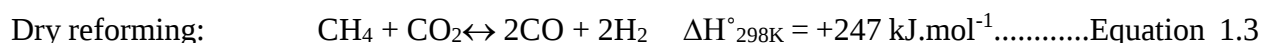
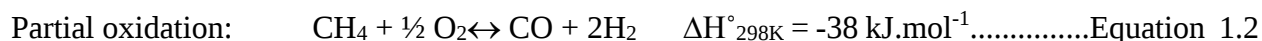
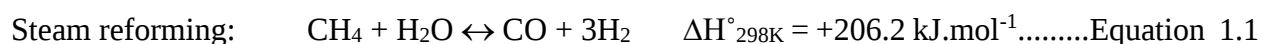


Figure 1.1 The steps for fuel processing of gaseous, liquid and solid fuels for high-temperature and low-temperature fuel cell applications.⁶

There are many possible routes to generate hydrogen from methane as summarized by the reactions shown from Equation 1.1 to 1.4⁵:



Steam reforming (SR) is a catalytic endothermic process in which a hydrocarbon (e.g. methane) reacts with steam to produce hydrogen and carbon monoxide (Equation 1.1)^{7,8}.

Due to the endothermicity of the steam reforming reaction, very high reaction temperatures are required to achieve high methane conversion.⁸ However, to achieve these required high temperatures an external energy source is needed, and despite SR requiring a high energy input, it has been widely employed to large-scale hydrogen production.⁸ Various reforming catalysts such as Rh, Ru, Pd, Pt, Co, and Ni supported on alumina have been extensively investigated.⁷ Among these catalysts, nickel-based catalysts have been widely used for hydrogen production by the steam reforming reaction.⁷ However, it was reported that the use of the nickel based catalysts resulted in the formation of carbon, which deactivates the catalysts.⁹ To avoid this problem, several researchers evaluated other alternative routes for producing hydrogen via methane, such as partial oxidation,⁹ dry reforming and auto-thermal reforming.

The partial oxidation of methane is a mildly exothermic reaction that also saves energy. This reaction is known to occur at low temperatures over transition metals producing H_2 and CO at a mole ratio of two, which is suitable for methanol and Fischer Tropsch synthesis.⁹ However, this reaction is not suitable for fuel cell application since a low amount of H_2 is produced, when compared to steam reforming.⁹ Additionally, this reaction requires the removal of heat generated to avoid total methane oxidation.⁹ In contrast, dry reforming is an endothermic reaction which requires energy to sustain the reaction.¹⁰

Dry reforming employs CO_2 as an oxidant, and is known to partially oxidise methane to carbon monoxide and hydrogen.¹⁰ However, this reaction produces H_2 and CO at a mole ratio of 1, and is not applicable in the production of hydrogen for fuel cells, since a large amount of CH_4 will be needed to achieve the desired amount of H_2 . Furthermore, an increase in the amount of hydrogen

produced results in an increase in the CO content, which is detrimental to the fuel cell electrodes since CO is a known Pt poison.

Auto-thermal reforming (ATR) combines the contribution of steam reforming (SR) and partial oxidation (POX), in which the hydrocarbon reacts both with steam and oxygen, as seen in Equation 1.4.⁸ In principle, ATR may be considered as a thermal self-sustained catalytic process, in which the exothermicity of the hydrocarbon oxidation reaction supplies the system with the heat needed for the SR reaction.^{8, 11} However, this reaction is known to produce a lower yield of hydrogen in comparison to SR. Additionally, this reaction requires a robust control system to switch between POX and SR to achieve the maximum hydrogen production.⁹

In recent literature, catalytic methane combustion has been noted as a source of energy for SR since the heat that is subsequently generated can be used to supply the energy required¹², as shown in Figure 1.2.

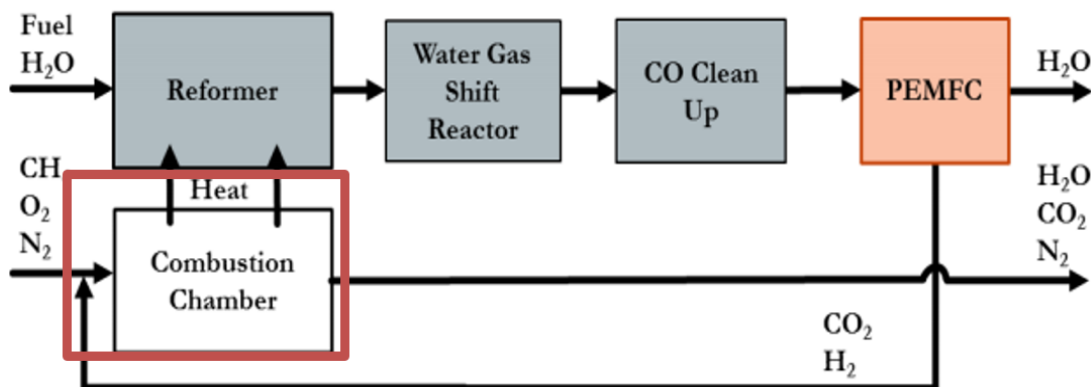


Figure 1.2 Schematic diagram of a fuel processing system.¹³

1.2.2 Methane combustion

Catalytic and non-catalytic methane combustion produces energy which can be used for various applications, including heat generation for remote use, such as for soldiers and space flights, to produce electricity, and supply heat to microscale reactors carrying out endothermic reactions. However, industrial applications of non-catalytic methane combustion are restricted since this combustion process requires an ignition source and must be carried out within given flammability limits and specific concentrations of the fuel in air.¹⁴ The catalytic combustion of methane is known to be unaffected by the limitations that affect the non-catalytic combustion of methane. Additionally, the former uses a catalyst which aids in the total combustion of methane.

1.2.3 Catalytic combustion of methane

Catalytic combustion is known as an oxidation reaction that occurs on the surface of a heterogeneous catalyst and has been a focus area for some time due to efforts to obtain alternative sources of energy. The overall methane combustion reaction may be represented by Equation 1.5,¹⁵ and partial methane oxidation to CO by Equation 1.2.^{15, 16}



The general pattern of conversion against temperature for catalytic combustion of methane (hydrocarbons) is well-established and this relationship is shown in Figure 1.3.

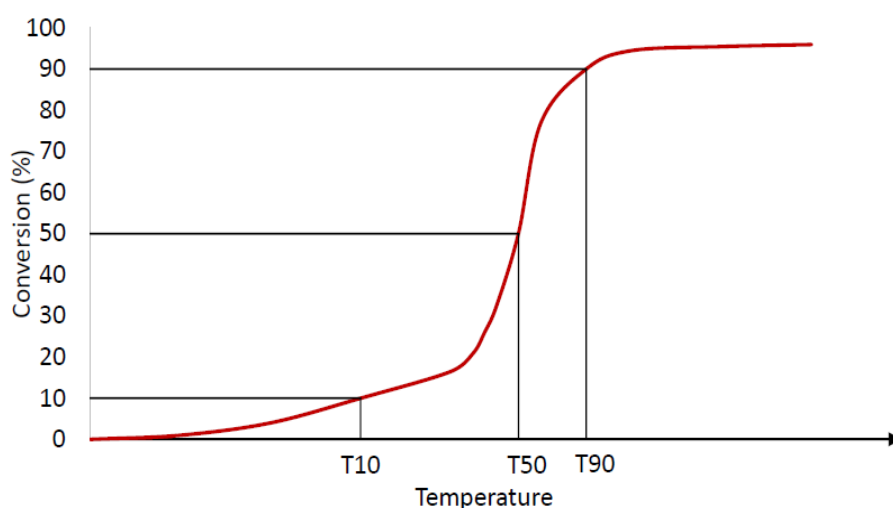


Figure 1.3 Conversion against temperature curve for catalytic combustion of methane.¹⁵

As can be observed from Figure 1.3, the conversion graph generally takes the form of an s-shape, whose regions are very much dependent on the catalyst being used.¹⁵ The T_x in the graph represents the minimum temperature required to achieve a specific methane conversion, for example, at T_{50} , a 50% conversion is obtained at that particular temperature. This temperature will change depending on the catalytic materials being tested. In general, the conversion against temperature curve for the catalytic combustion of methane consists of discrete regions where either kinetic or diffusion limitations are dominant.¹⁵ At temperatures below T_{50} , the rate of the reaction is known to be limited by kinetics, where the number of the active sites and consequently, the active metal particle size have a significant effect on the conversion.^{12, 14} However, at temperatures above T_{50} the rate of the reaction is limited by diffusion factors where the catalyst microstructure, porosity, and the active metal/support morphology have a significant effect in the conversion.^{12, 14} T_{50} is referred to as the light off temperature, a point where the rate of the reaction limitations changes

from kinetic factors to the diffusion factors.¹⁷ At temperatures above T_{50} , the methane conversion rapidly increases and generates heat. Consequently, the heat generated results in a significant increase in the catalyst's surface temperature.^{15, 18} At the region above T_{90} , the catalyst's thermal stability becomes an important factor since this region is associated with high temperatures.^{15, 18}

In essence, it is important to consider the kinetic and diffusion factors at relevant temperatures and conversions when designing the catalytic system for methane combustion. Additionally, other factors such as catalyst thermal stability and light off temperature are to be considered. In general, the s-shaped curve for catalytic combustion of methane can be better achieved at a low reaction gas space velocity (GHSV) and this is due to the fact that the conversion is dependent on the contact time between the reactants and the catalyst.^{15, 18} Therefore, the optimisation of the GHSV is an important consideration as it affects the light off temperature of a given catalyst.

1.2.4 Light-Off temperature curves

The light-off curve is the conversion-temperature plot of a catalytic reaction; it is usually used in catalyst development. Moreover, the catalytic activity can be measured by the conversion of methane at different temperatures using the light off curve. Thus, a low light-off temperature (temperature at which 50% methane conversion is achieved) is desired as this would result in the minimum energy required to start-up the fuel processor. However, there has been controversy on the accuracy of the light off temperature curves due to temperature jumps wherein temperature jump refers to the rapid increase of the temperature on the surface of the catalyst as the conversion increase. Trimm *et al.* observed a jump in methane combustion activity as the temperature increases over a platinum based catalyst,¹⁵ which they attributed to the heat generated on the surface of the catalyst, known to occur during methane combustion since the reaction is exothermic.¹⁵ The heat generated during the reaction then causes the metal particles on the surface of the catalyst to have a higher temperature resulting in the conversion jumps. Kaul *et al.* observed a temperature difference of 190 °C between the supported metal¹⁹ and the support, while Sharma *et al.* observed a minimum temperature difference. However, Sharma *et al.* attributed the minimum temperature difference to the rapid dissipation of heat transferred from the metal particle to the support.²⁰

In a study by Persson *et al.*, aimed at measuring the activity by recording the methane conversion while increasing the temperature stepwise at regular time intervals, it was observed that the conversion jumps were not a true reflection of the catalyst surface temperature increase, since the reaction conditions were not stable before the temperature was increased, as shown in the Figure

1.4,²¹ furthermore, they suggested that the most accurate catalyst surface temperature should be taken as an average temperature obtained at regular time intervals.

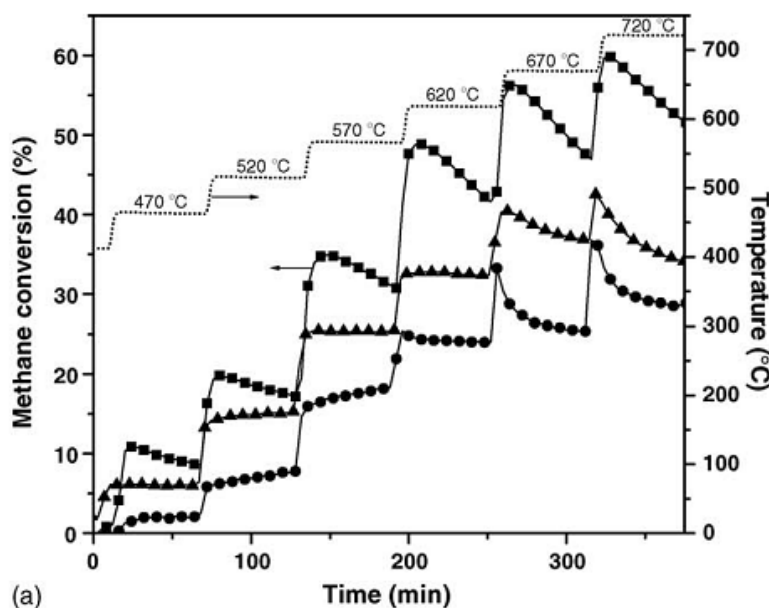


Figure 1.4 Methane conversion over Pd-based catalysts.²¹

1.2.5 The effect of methane (fuel)/oxygen ratio on methane combustion

The fuel/oxygen ratio ($[\text{CH}_4]/[\text{O}_2]$) has a strong effect on the total oxidation of methane to CO_2 .¹⁵ Under oxygen-rich conditions, methane was oxidized to carbon dioxide over Pt and Pd supported on alumina.^{15, 21, 22} However, under oxygen-deficient conditions, the formation of carbon monoxide was observed over $\text{Pt}/\text{Al}_2\text{O}_3$, $\text{Pd}/\text{Al}_2\text{O}_3$ and $\text{Rh}/\text{Al}_2\text{O}_3$ catalysts.²¹ Furthermore, Pd based catalyst was observed to be highly selective to formation of CO_2 in comparison to the $\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{Rh}/\text{Al}_2\text{O}_3$ under lean oxygen conditions.²¹ The conversion of methane to CO_2 and water increased with increasing temperature until complete consumption of oxygen occurred, and thereafter the formation of CO was observed, while the partial pressure of CO_2 remained almost constant.¹⁵

1.2.6 Methane Combustion Catalysts

The catalysts used in methane combustion generally include an active metal on a support.²³ The nature of the active metal and the support can vary as shown in Figure 1.5.

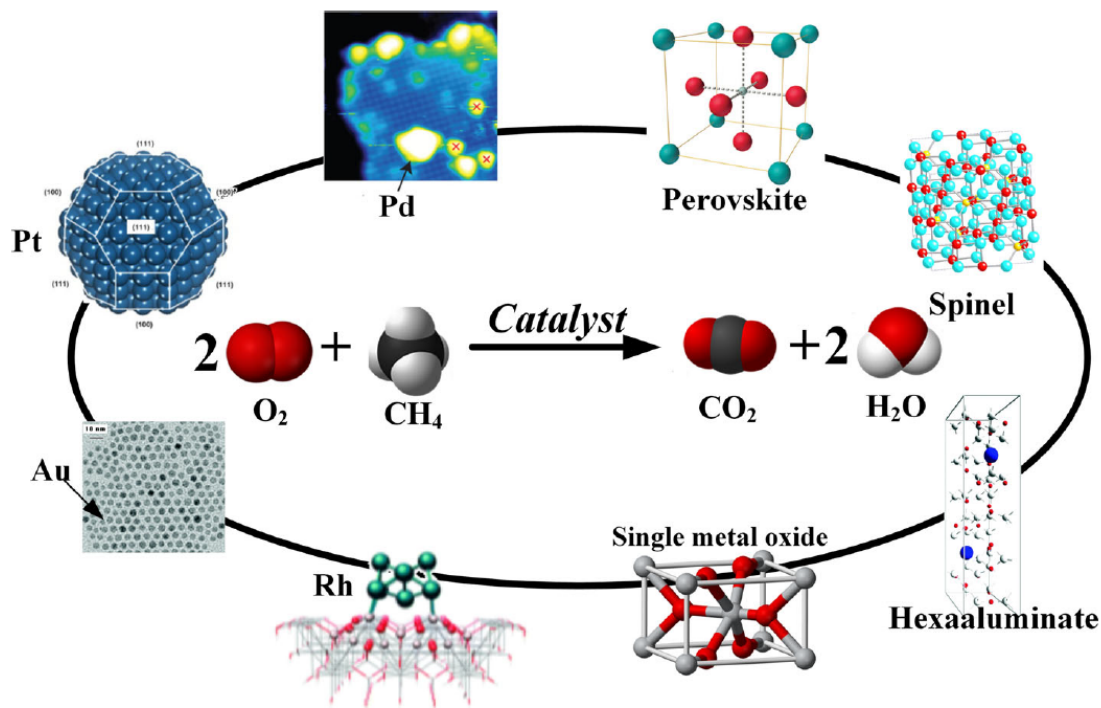


Figure 1.5 Recent catalysts used in low-temperature methane combustion.²³

As shown in Figure 1.5, there are several choices when it comes to choosing an appropriate support and an active metal.²³ The factors leading to the proper choices are important to consider when designing an optimum catalyst for methane combustion²⁴. These include:

- The catalyst being able to achieve total methane combustion at low temperatures and high GHSVs.
- The catalysts must be thermally stable at high temperatures to avoid deactivation
- The catalyst's properties such as surface area, elemental composition and microstructure must be maintained at optimum conditions as these factors affect the catalyst activity.

1.2.7 Active metals in methane combustion catalysts

In recent history, platinum group metal (PGM) based catalysts and other transition metal based catalysts have been widely used in methane combustion studies, and it has been observed by Choudhary *et al.*^{23,25} that PGM based catalysts exhibited higher catalytic activity per active site when compared to the non PGM based catalysts. To that effect, palladium and platinum are the most studied PGMs due to their high resistance to sulphur poisoning and ease of complete methane combustion at low temperatures.²⁵ However, Pd based catalysts showed a higher methane conversion at low temperature compare to the Pt based catalysts. The study carried out herein was

focused on the use of palladium as the PGM, since it is widely available in South Africa and is relatively cheaper than Pt, and Rh (Figure 1.6) and also serves to empower South African-based catalyst manufacture.²⁶

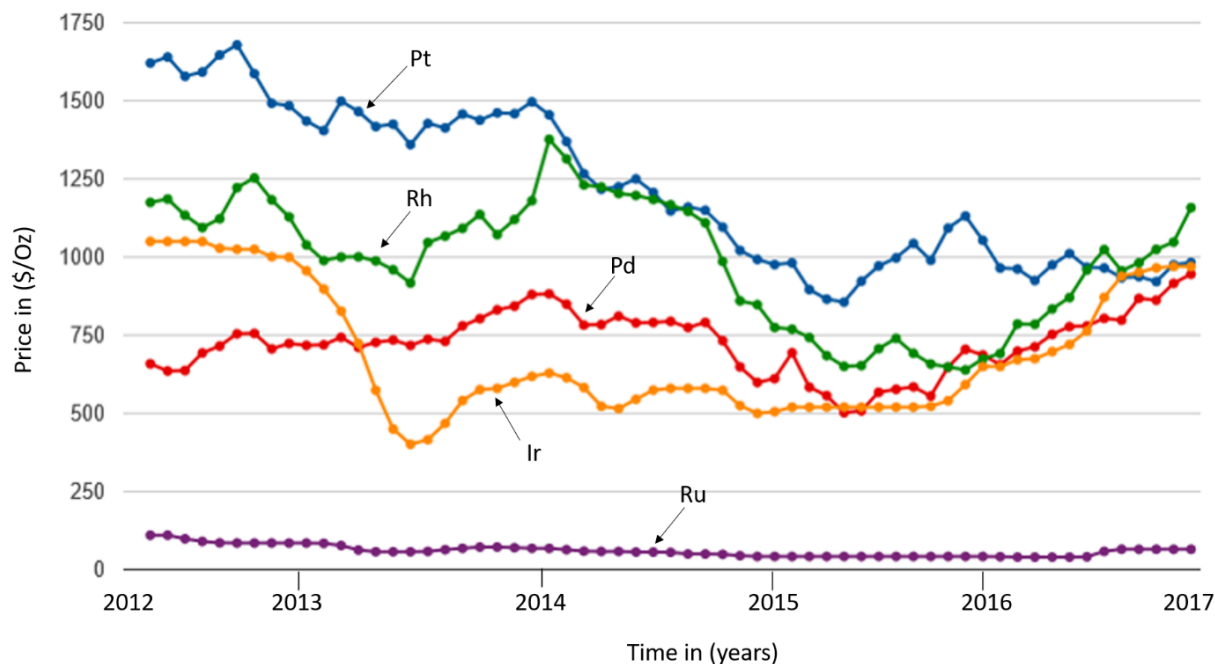


Figure 1.6 Monthly average prices of PGMs between September 2012 and September 2017.²⁷

From Figure 1.6, it can be observed that ruthenium is least expensive when compared to the other PGM's, because it is most available. Ruthenium is known to oxidize various organic compounds, however, Machida *et al.*, reported that methane combustion over ruthenium catalysts is dependent on the ruthenium phase present in the catalyst.²⁸ They observed that supported Ru catalysts exhibited similar conversions of methane as supported Pt catalysts.²⁸ In the comparative study of methane combustion over Pt, Pd and Rh supported on Al_2O_3 ; the catalytic activity ranking was given by $\text{Pd} > \text{Rh} > \text{Pt}$.²⁸⁻³¹ Kinnunen *et al.*, reported a methane conversion rate (at 300 °C) of $7 \mu\text{mol}_{\text{Pt}}^{-1}\text{s}^{-1}$ for a catalyst containing 2.3% Pt supported on Al_2O_3 . While the rate over the 2.3% Pd/ Al_2O_3 was observed to vary between 566 and 426 $\mu\text{mol}_{\text{Pd}}^{-1}\text{s}^{-1}$.³² Persson *et al.* reported that the monometallic Pd catalyst showed a high catalytic activity when compared to the bimetallic Pt-Pd catalysts.²²

1.2.8 Variables affecting Pd based catalysts in methane combustion

The activity of Pd based catalysts for methane combustion has been reported to be affected by several factors such as the metal loading, particle size of palladium, its oxidation state and dispersion, as described further in the following sections.^{21, 33-35}

1.2.8.1 Palladium loading

The effects of palladium loading on methane combustion have been studied by several researchers, although there is still some confusion with regard to this.^{16, 18, 25} In experiments conducted by Escandón *et al.* in a fixed bed reactor, over three samples of Pd supported on alumina, with metal loadings of 0.4, 0.84, and 2.12 wt.%,³⁶ they observed that the specific catalyst performance decreased with an increase in palladium loading.³⁶ Moreover, Ge'lin and Primet stated that the effect of palladium loading can be explained based on the palladium crystallite size and dispersion.¹⁸ Thus, the decrease in the catalytic activity when the palladium loading was increased was attributed to a lower metal dispersion when a higher loading of palladium was used.¹⁸ It was also reported that commercial catalysts prepared with 0.5 wt.% palladium were optimum for high catalytic yields, compared to loadings higher than 0.5 wt.%.¹⁸ These findings, however, were in contrast to those of Euzen *et al.*³⁷, who observed that an increase in palladium loading led to an increase in the catalytic performance, as shown in Figure 1.7. Moreover, the increase in the loading led to an increase in the specific active sites.³⁷ Euzen *et al.* further observed the fast deactivation of the 3 wt.% Pd catalyst in comparison to the 10 wt.% Pd and 1 wt.% Pd catalyst in time on stream studies. This deactivation was attributed to the transformation of PdO to Pd.³⁷

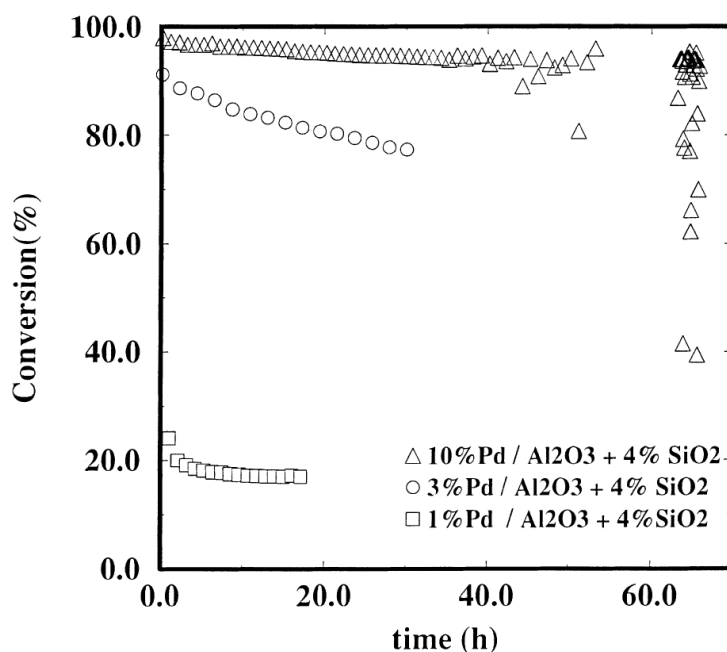


Figure 1.7 Influence of palladium loading on methane conversion³⁷

1.2.8.2 Palladium particle size

The palladium particle size can be characterised by the ratio of linear/bridged adsorption modes of carbon monoxide, as determined by infrared spectroscopy.³⁸ The linear/bridged peak ratio decreases as the Pd particle size increases.³⁸ The linearly bonded carbon monoxide band is attributed to the adsorption on all types of sites, while the bridged bonded band is attributed to adsorption on the faces of Pd crystals.^{38,39} Small crystallites of Pd with more corner and edge sites gave a higher linear to bridge peak ratio and the ratio of linearly bonded to bridge bonded sites on the large crystallites was lower.³⁸ The effect of palladium particle size on the turnover frequency (TOF) for methane combustion has also been widely investigated by several researchers.³² Hicks *et al.* observed that under oxidizing conditions, the order of Pd oxidation increases with a decrease in the Pd particle size and the increasing number of the crystal imperfections.^{38,39} The larger Pd particle size is known to be partially oxidized, and breaks to form small crystallites covered with adsorbed oxygen.

Roth *et al.* observed a linear relationship between the turnover frequency and mean particle size for the particles smaller than 12 nm as shown in Figure 1.8.⁴⁰

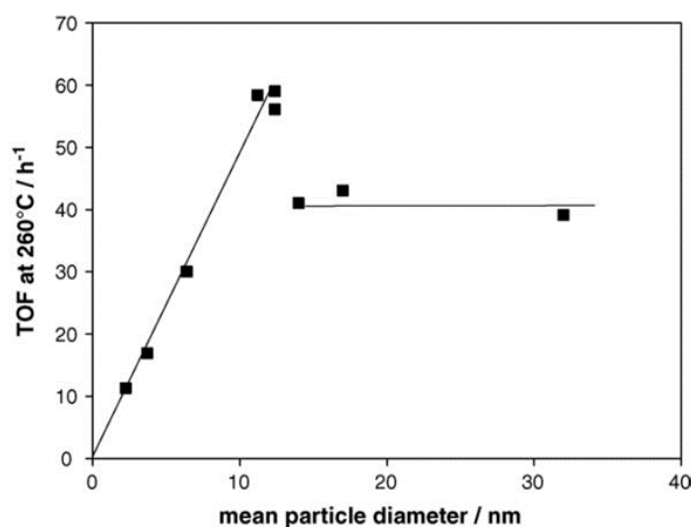


Figure 1.8 TOF of Pd/Al₂O₃ catalysts versus mean particle diameter.⁴⁰

From Figure 1.8, it is observed that the maximum TOF at 260 °C/h was achieved over a Pd mean particle size of 12 nm. Thereafter, the TOF dropped to 40/h when the size increased beyond 12 nm, and remained constant with a further increase in the mean Pd particle size. Consequently, these results suggest that large and small palladium particles have different catalytic properties. For larger particles, the catalytic activity mostly depends on the geometric surface area of the Pd

particle and the Pd phase.⁴⁰ Roth *et al.* also stated that the surface PdO film layer is highly reactive for methane combustion and, thus, this can be used to explain the constant TOF obtained at Pd particle sizes above 12 nm, as larger Pd particles are more easily reducible, resulting in the formation of Pd⁰, which is less active for methane combustion.^{40, 41} However, for the small particles, the increase in the TOF was observed to be linear as a consequence of methane oxidation turnover rates being dependent on the density of the oxygen vacancies.^{40, 41} The size of the palladium crystallites is quite dependent on the support composition and method of preparation.^{40,41}

1.2.8.3 Palladium oxide (PdO) and palladium metal (Pd⁰) as active phases for methane combustion

Several studies have attempted to determine the nature of the active site and establish the mechanistic details for methane combustion over Pd-based catalysts.⁴²⁻⁴⁶ There is, however, still a lot of confusion regarding the nature of the Pd species involved in combustion. Findings of an experiment conducted by Hicks *et al.* at 573 K using 50 Torr methane, 110 Torr oxygen, and 900 Torr He over Pd/alumina catalysts reported that PdO dispersed on Pd crystallites was more active for methane oxidation than PdO dispersed over alumina.⁴² Additionally, Oh and Mitchell reported the thin layer of PdO supported on metallic Pd as the active form, compared to bulk PdO.⁴⁷

In general, most researchers agree that the PdO phase supported on metallic Pd is the most active phase of palladium for methane combustion.⁴⁸ However, the activity of the Pd based catalysts is not controlled by only the concentration of the PdO, but also by the position of the PdO in the partially reduced/oxidized catalyst.²⁵ Choudhary *et al.* further reported that PdO supported on metallic Pd is more active than Pd supported on PdO and the activity increased by increasing the degree of oxidation of the fully reduced catalyst Pd⁰/Al₂O₃ as shown in Figure 1.9.²⁵ Conversely, Figure 1.9 shows a decrease in methane conversion with the increase of the extent of PdO reduction.

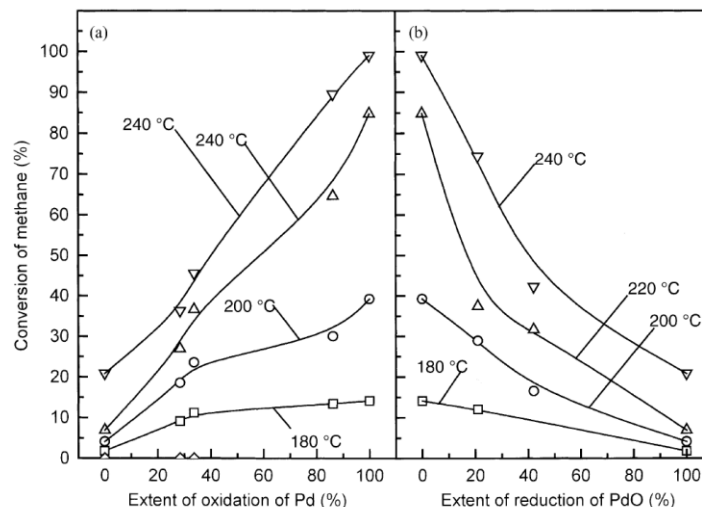


Figure 1.9 The effect of (a) Extent of Pd oxidation and (b) Extent of PdO reduction on methane combustion activity at various temperatures.²⁵

1.2.8.4 Reduction of PdO to Pd

The transformation of PdO into Pd is reported to negatively affect the catalytic activity of PdO-based catalysts for methane combustion by lowering the conversion.^{49, 50} However, CH₄ combustion activity has been reversibly restored upon re-oxidation of Pd⁰ to PdO.^{48, 51} Several attempts had been made to understand this problem using H₂-temperature programming operando spectroscopy, and surface science techniques. Matam *et al.* investigated the nature of the active sites for methane combustion on Pd/Al₂O₃ under reaction conditions.⁵² In this study, the behaviour of Pd on Pd/Al₂O₃ during a methane combustion cycle (heating and cooling) between 127 and 857 °C was monitored under genuine reaction conditions by X-ray absorption spectroscopy in a lab-scale fixed-bed reactor coupled to a mass spectrometer.^{21, 30} Based on the findings of these authors, they concluded that the nature of the active Pd species for the combustion of methane reaction is temperature-dependent, as shown in the Figure 1.10.

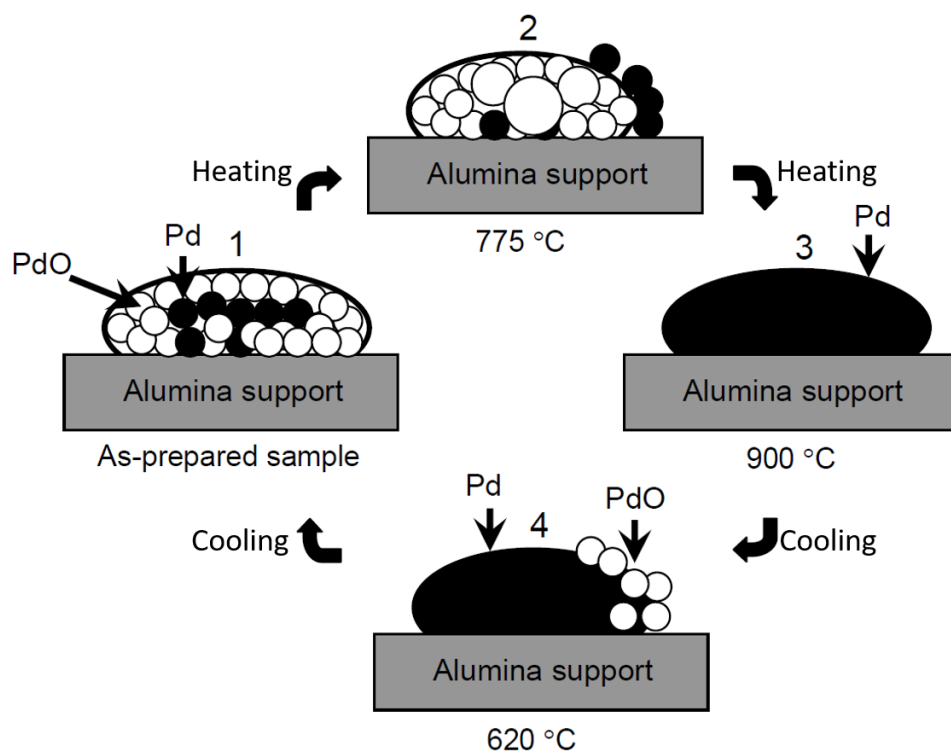


Figure 1.10 Schematic illustration of proposed mechanisms for PdO decomposition and Pd re-oxidation.⁵¹

From Figure 1.10, it is observed that the reduction of PdO to Pd results in the formation of Pd clusters which are known to be less active.⁵¹ The reoxidation of Pd to PdO was observed to occur at temperatures around 620 °C upon the cooling cycle and, consequently, resulted in an increase in activity. At temperatures above 700 °C, the reduced Pd could also catalyse the reaction since the reaction is driven by the heat produced and the catalyst surface temperature.⁵³ However, the presence of water and carbon dioxide on the surface of the catalyst leads to further deactivation.

1.2.8.5 Methane combustion pathways and inhibition by water over Pd-based catalysts

The methane combustion product, water, is known to have a negative effect on the reaction as it results in a loss of conversion due to catalyst poisoning.^{44, 48} Figure 1.11, illustrates the effect of CH₄, O₂, CO₂, and H₂O concentrations on the rate of the reaction.⁴⁴ Methane combustion activity is shown to be directly proportional to the CH₄ concentration with minimum dependence on the O₂ concentration.⁴⁴ Carbon dioxide was observed to have no impact on the conversion of methane while water inhibits the reaction significantly.⁴⁴ Ribeiro *et al.* developed a rate law Equation for methane combustion using Pd-based catalysts⁵⁴ (Equation 1.5) and it was observed to be consistent with the results shown in Figure 1.11.

Rate of the reaction = r , calculated based on partial pressure of the reagents

Rate constant = k

$$r = k (\text{CH}_4)^{1.0} (\text{O}_2)^0 (\text{H}_2\text{O})^{-1.0} \dots\dots\dots \text{Equation 1.6}$$

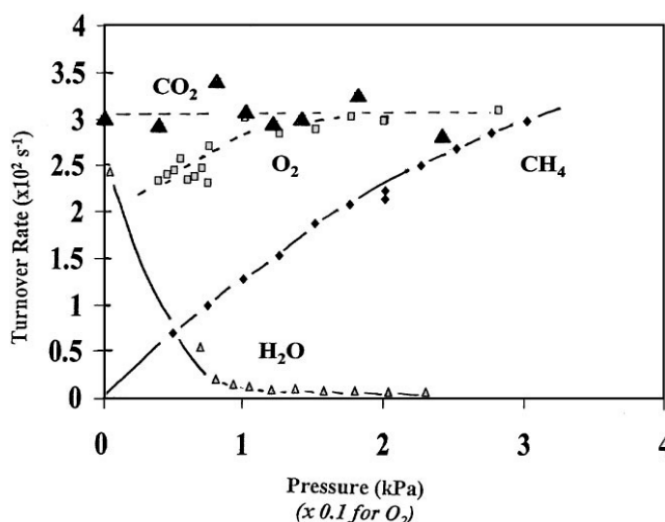


Figure 1.11 Effects of O_2 , H_2O , and CO_2 on methane oxidation rates.⁴⁴

From Figure 1.11 and Equation 1.5, there is no clear indication of how water inhibits methane conversion.⁴⁴ Chen and Ruckenstein outlined that methane combustion occurs over Pd-based catalysts via the dissociative chemisorption of methane on a site pair consisting of adjacent Pd surface vacancies and surface Pd-O species, as shown in Figure 1.12.⁵⁵ In this mechanism the dissociation of the adsorbed methane occurred via C-H bond cleavage by molecular oxygen.⁵⁵ Additionally, this mechanism gave an insight into the rate law expression and, furthermore, predicted the zero-order oxygen rate dependence as observed in Figure 1.11. The proposed mechanism avoids the coexistence of PdO_x in contact with the Pd metallic phase since under these reaction conditions the coexistence of this phase is unstable.

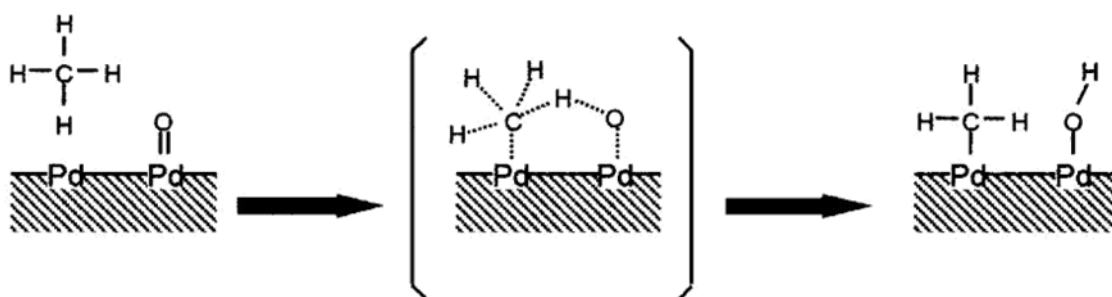
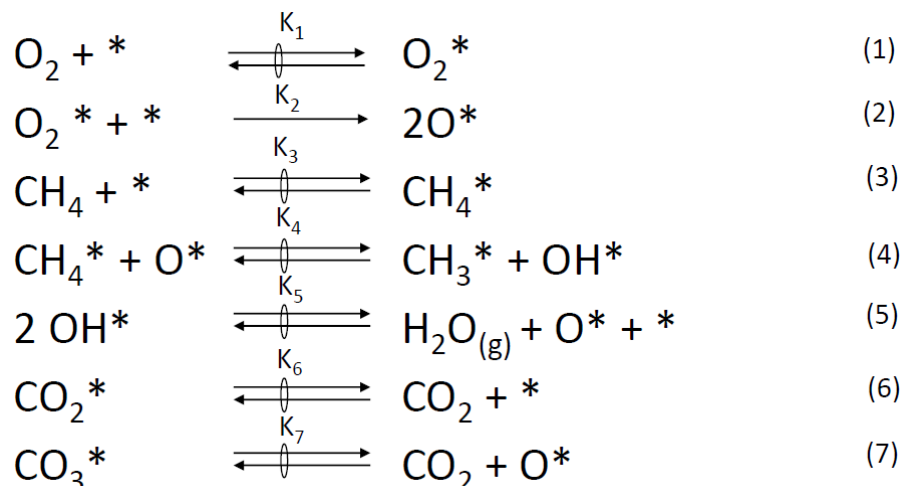


Figure 1.12 Methane dissociation on a surface Pd-PdO site pair.

The mechanism by Chen and Ruckenstein was deemed essential in understanding methane conversion over Pd-base catalysts and, consequently, served as a basis for the understanding of water inhibition.⁵⁵



Scheme 1.1 Methane oxidation reaction pathways.

Figure 1.12 shows a schematic representation of step 3 and step 4 shown in Scheme 1.1, where dissociative chemisorption of methane occurs. Step 3 is known as the rate determining step since the physisorbed CH_4 molecule interacts with coordinatively unsaturated Pd sites (*) before hydrogen abstraction from the CH_4 by the Pd-O surface species, forming surface hydroxyl groups (Pd-OH). Chen and Ruckenstein stated that this process is heavily dependent on the concentrations of CH_4^* , O^* and OH^* , where higher concentrations of CH_4^* and O^* species on the catalyst surface result in an increase in the reaction rate.⁵⁵ This results in the formation of OH^* species which decreases the reaction rate. The OH^* species are then converted into water via a quasi-equilibrated condensation (step 5) which results in an increase in conversion and regeneration of oxygen vacancies. The presence of water molecules results in an inhibition of water formation, resulting in the catalyst surface being heavily populated by OH^* species with no oxygen vacancies.⁵⁴ Consequently, water inhibition occurs via the poisoning of the oxygen vacancy which activates the rate determining step.⁵⁴ Chen and Ruckenstein further observed that water inhibition is very dependent on the quasi-equilibrated desorption of H_2O ; where a high concentration of water results in less available oxygen vacancies for the reaction.⁵⁵

1.2.9 Catalyst Supports

In combustion applications, PGM's have been generally supported over metal oxide supports to improve the thermal stability of the catalyst, to increase the metal dispersion and consequently

increase cost efficiency.¹⁵ Cullis and Willatt studied the effect of Pt and Pd catalysts on various metal oxide supports, namely γ -alumina (γ -Al₂O₃), titania (TiO₂), and thoria (ThO₂) for methane combustion.⁵⁶ The authors reported that blank supports were not active, while the supported metal catalysts showed a higher methane combustion activity than unsupported metal oxides.^{25, 56} They attributed the increase in activity to the increase of an active surface area and dispersion.⁵⁶ Furthermore, they observed that the catalyst activity for both Pd and Pt decreased in the following order of supports: γ -Al₂O₃ > TiO₂ > ThO₂, with a higher catalyst activity seen for Pd-based catalysts compared to Pt.²⁵ This difference in catalytic behaviour was attributed to the support affecting the extent of oxidation of the metal catalysts (to PtO or PdO), with a greater effect seen for Pd. The γ -Al₂O₃ further gave the highest number of oxidized Pd sites. However, γ -Al₂O₃ is not completely stable at higher temperatures (< 800 °C) and it decomposes to δ -Al₂O₃, resulting in the loss of surface area.⁵⁶

In recent studies, it was observed that other metal oxide supports such as zirconia and ceria are very good for methane combustion.^{57,58} Furthermore, Satsuma *et al.* successfully demonstrated that these reducible supports, which have a greater oxygen storage capacity (OSC), are more efficient in the oxidation of CO in comparison to other reducible and non-reducible supports such as Al₂O₃ and SiO₂.⁵⁹ In past decades, several studies have been conducted on ceria as a support for the oxidation of various hydrocarbons and carbon monoxide.⁶⁰

1.2.10 Ceria as a catalyst support for oxidation reactions

Ceria has been used in several oxidation reactions since it possesses OSC as an important characteristic.^{60, 61} This allows ceria to store oxygen in oxygen rich conditions and then provide oxygen to the active components during oxygen lean conditions.^{62, 63} Additionally, this characteristic is vital when ceria is employed as a catalyst support in methane combustion, as the fuel/air ratio is not always constant in a working fuel cell.⁶² Another characteristic of note is the excellent redox ability of ceria as it can switch between Ce³⁺ and Ce⁴⁺, thus creating oxygen vacancies which are important in various oxidation reactions.⁶³

Ceria crystallizes in a fluorite-type structure and possesses a face-centered cubic (FCC) unit cell consisting of tetrahedral sites occupied by oxide ions and vacant octahedral sites.^{53, 64} The structure of the unit cell of pure ceria can be seen in Figure 1.13.

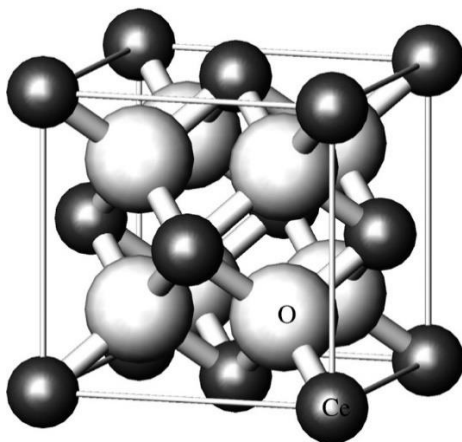


Figure 1.13 The fluorite structure of ceria.^{65, 66}

1.2.10.1 Defects in ceria

The crystal structure of ceria is known to contain defects which affect the redox properties, reducibility, and thermal stability of the support.⁶⁷ Ceria is known to contain point defects as a dominant defect which can be in the form of vacant sites, interstitials and the substitution of ceria atoms by foreign atoms.⁶⁷ Point defects can be further grouped into two types; intrinsic and extrinsic defects.⁶⁷ Intrinsic defects are known to arise from thermal treatment, while extrinsic defects arise from an introduction of various foreign ions into the lattice structure of ceria.⁶⁷ Thus, most doped ceria contains extrinsic defects in the form of oxygen vacancies as shown in Figure 1.14.⁶⁷

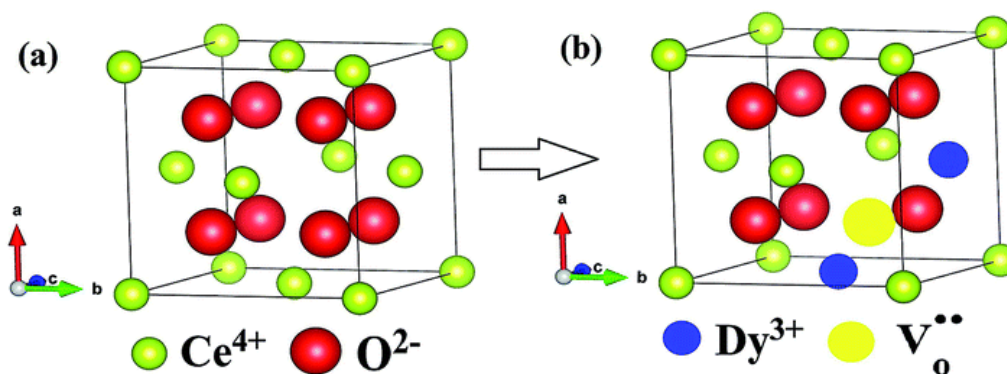


Figure 1.14 The crystal structures a) pure ceria and b) doped ceria.⁶⁸

As observed in Figure 1.14 b, two Ce^{4+} sites (here face-centered sites) are occupied by a dopant, in this case Dy^{3+} ions, which results in the formation of the oxygen vacancy ($\text{V}_\text{o}^{\bullet\bullet}$).⁶⁸ Here, the occupancy of Ce^{4+} ions in the 4a site and O^{2-} ions in the 8c site of un-doped ceria are 0.9989 and

0.9859 respectively.⁶⁸ In doped ceria, the occupancy of Ce^{4+} ions decreases with the increased dopant concentration, and the occupancy of dopant ions (Dy^{3+}) in the 4a site increases due to the replacement of the Ce^{4+} ions with the Dy^{3+} ions. Consequently, increasing the Dy^{3+} ions concentration results in the decrease in an occupancy of O^{2-} ions at the 8c site since there are less dopant-oxygen bonds compared to the Ce^{4+} ions-oxygen bonds. The formation of these oxygen vacancies has been confirmed in earlier studies.^{69, 70} From recent studies, the lattice parameter increases with dopant concentration, which is because the ionic radius of Dy^{3+} (1.027 Å) is greater than the ionic radius of Ce^{4+} (0.97 Å).⁶⁸ From Figure 1.14, the $\text{Ce}_{1-x}\text{Dy}_x\text{O}_{2-\delta}$ system, the lattice parameter increases linearly with increasing Dy^{3+} concentration up to $x = 0.25$, following Vegard's law.⁶⁸ Beyond $x = 0.25$, the lattice parameter of the $\text{Ce}_{1-x}\text{Dy}_x\text{O}_{2-\delta}$ system increases linearly, but the rate of increase is different. Using a least-squares fitting algorithm, a linear relationship was obtained between the lattice parameter a and dopant concentration x . These can be represented as:⁶⁸

$$a(x, 0 \leq x \leq 0.25) = 5.39771 + 0.04369 x \dots \dots \dots \text{Equation 1.7}$$

$$a(x, 0.3 \leq x \leq 0.5) = 5.40451 + 0.01847x \dots \dots \dots \text{Equation 1.8}$$

1.2.11 Structure sensitivity in methane combustion over palladium-ceria catalysts

Methane combustion over platinum-based catalysts is a structure-sensitive reaction. Hicks *et al.* explained that this structure sensitivity was caused by the varying reactivity of adsorbed oxygen on the surfaces of palladium.^{42, 43} Methods of catalyst synthesis influence structure and catalytic activity of catalysts. There are several catalyst preparation methods reported, which include wet impregnation, co-precipitation, hydrothermal treatment, core-shell and solution combustion. Cargnello *et al.* reported that the synthesis of core-shell style catalysts, in which a Pd cluster is encapsulated by a ceria shell (Pd@CeO_2), demonstrated high methane combustion rates below 400° C.⁷¹ Using kinetic data taken between 220° to 270° C, the authors demonstrated that the activation barrier over Pd@CeO_2 catalysts is similar in magnitude to barriers over traditional Pd/ceria catalysts with metallic clusters adsorbed on the ceria surface.⁷¹

Colussi *et al.* observed a significant increase in methane combustion rates with no deactivation using solution combustion synthesis (SCS) catalysts compared to the impregnated system.^{53, 72} Furthermore, they noted that this was due to a peculiar Pd-O-Ce supercell structure in which

alternate Ce^{4+} atoms were substituted by Pd^{2+} atoms (see Figure 1.15).^{53, 72} They also noted that this superstructure was extremely active for methane combustion.^{53, 60}

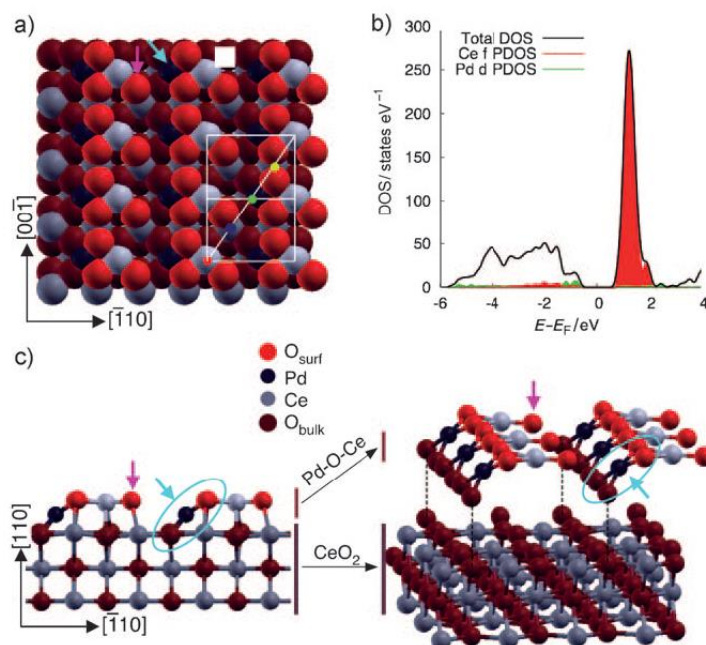


Figure 1.15 a) Top and c) side views of the equilibrium surface Pd-O-Ce superstructure predicted by DFT calculations. O and Ce atoms belonging to the surface superstructure phase are displayed in lighter colors. b) Density of electronic states (DOS) and projected DOS (PDOS) for the Ce 4f (red area) and Pd 4d (green area) states.⁷²

From Figure 1.15 c) it can be observed that this catalyst contained a peculiar Pd-O-Ce which was further supported by Figure 1.15 b), where the band gap is between the occupied Pd 4d and Ce 4f states, while there is no filled Ce 4f gaps which are the characteristic of reduced ceria.⁵³ In studies of PdO/CeO₂, it was observed that Pd can be incorporated into the lattice structure of ceria forming Pd_xCe_{1-x}O_δ mixed oxides with different physical, chemical and catalytic properties than supported PdO_x clusters.⁷³ Moreover, the SCS Pd_xCe_{1-x}O_{2-δ} catalyst showed no deactivation under reaction conditions, while presenting a unique PdO_x phase which could be attributed to the stable Pd⁴⁺ which is formed by over oxidation of Pd²⁺ by ceria, which occurs during the incorporation of Pd in the lattice structure of ceria.^{53, 62, 73} Pd⁴⁺ is known to be the most active phase of Pd in low-temperature methane combustion since it is highly oxidised.^{74, 75} Senftle *et al.* outlined that in the Pd_xCe_{1-x}O_{2-δ} catalyst, the activity is increased by the presence of PdO₂ which results from the formation of Pd⁴⁺.⁷⁶ The stable Pd⁴⁺ was in an octahedral state compared to the square planar Pd²⁺

and furthermore, methane combustion over Pd^{4+} occurs at a lower temperature due to the oxidation state of the Pd species.⁷⁶

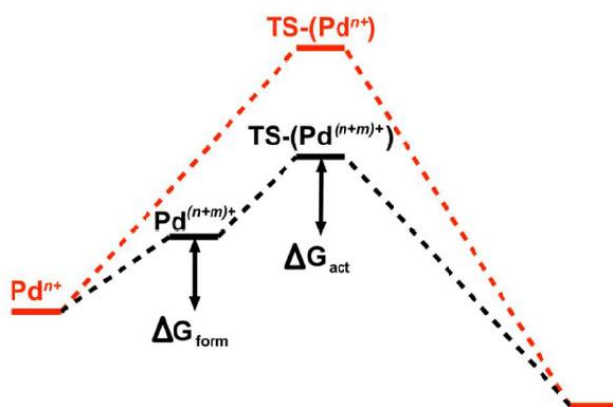


Figure 1.16 The total apparent barrier for CH_4 activation over the thermodynamically favored Pd^{n+} state compared to an oxidized $\text{Pd}^{(n+m)+}$ state.⁷⁶

Senftle *et al.* further outlined that Pd atoms incorporated in the CeO_2 (111) surface underwent a facile $\text{Pd}^{4+} \rightarrow \text{Pd}^{2+}$ transition upon methane activation, leading to a combustion rate many orders of magnitude higher than Pd or PdO surfaces.⁷⁶ This is shown in Figure 1.16, showing the total apparent barrier for CH_4 activation for different Pd oxidation states. The energy barrier over Pd^{4+} is smaller than the activation barrier in Pd^{2+} . This suggests that the oxidation of methane over Pd^{4+} requires less energy resulting in a faster reaction rate.⁷⁶

The previous studies reported herein have shown that solution combustion synthesized palladium-ceria catalysts can be significantly better for methane combustion in comparison to the palladium-ceria catalysts synthesized by other methods. However, there are several parameters in the solution combustion synthesis routes that affect the physical and chemical properties of the synthesized material and, consequently, the catalyst activity. A more detailed discussion in this regard is presented in the chapter that follows.

1.3 Solution combustion synthesis

Solution combustion involves a self-sustained reaction in solutions of metal precursors and different fuels. These fuels can be classified based on their chemical structure, the type of reactive groups such as amino, hydroxyl, and carboxyl bonded to the hydrocarbon chain.⁷⁷⁻⁷⁹ The reaction between the fuel and oxygen-containing species, formed during the decomposition of the nitrate

species, provides high-temperature rapid interactions.^{77, 79} A typical schematic flow diagram of the solution combustion synthesis method is outlined in Figure 1.17.

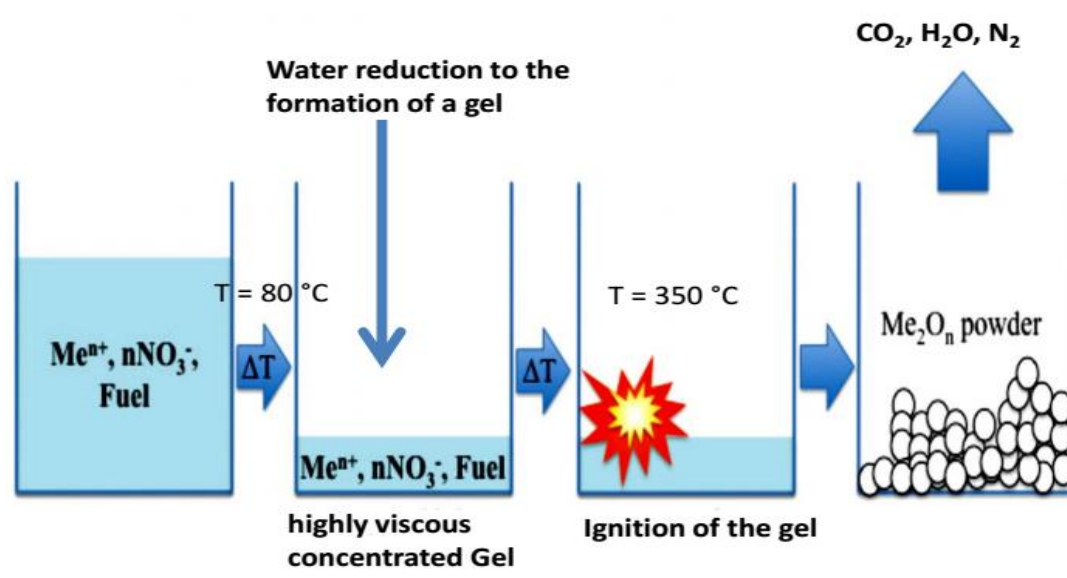


Figure 1.17 Schematic diagram of Me_2O_n powder synthesized by SCS.

Several features of SC contribute to the unique properties of the synthesized products.⁷⁷ Firstly, the initial reaction media, being in the liquid state, allows for the mixing of the reactants at the molecular level, thus allowing precise and uniform formulation of the desired composition on the nano scale.⁸⁰ Second, after gel ignition, the reaction self-propagates reaching a high temperature, sometimes above 1200 K, which ensures high product purity and crystallinity.⁸⁰ This feature allows one to skip an additional step, high-temperature product calcination which normally follows the conventional sol-gel approach, to achieve the desired phase composition.⁷⁷ However, this trend is not always followed, since some catalysts prepared by SCS are calcined to achieve desired phase composition and catalyst stability that may not have been achieved during the propagation step.^{77, 80} Thirdly, the short process duration and the formation of various gases during SC inhibit particle size growth and favour synthesis of nano-size powders with high specific surface area.⁸⁰ Mukasyan *et al.* concluded that SC is an effective method for synthesis of nanoscale materials and it has been used for the production of various metal oxide powders for different advanced applications including catalysts, fuel cells, and in biotechnology.⁷⁷ However, there is minimum information on how the combustion parameters affect the final powder.⁸¹

1.3.1 Parameters affecting solution combustion

Solution combustion parameters play a significant role in the nature of the resulting powder.⁸² The main parameters of combustion, that have been investigated in the literature, include type of flame,

temperature of combustion, generated gases, air-fuel-oxidant ratio and chemical composition of the precursor reagents.⁸² However, there is no adequate information on how different fuels affect solution combustion synthesized powders.

1.3.1.1. Flame type

The formation of the combustion flame arises through the chemical burning of the transformed substances when heat is generated. Mimani outlined that during the combustion reaction, different types of flames are generated and these depend on the fuel employed and oxidizer-fuel ratio, as shown in Figure 1.18 and Figure 1.19.⁸³ The type of flame in SCS plays an important role in controlling the particle size of the as-synthesized powders.⁸² In general, under controlled conditions, SCS generates a flaming or smoldering type flame which can endure for seconds or even minutes.⁸³ The flame type is dependant mainly on the fuel used.

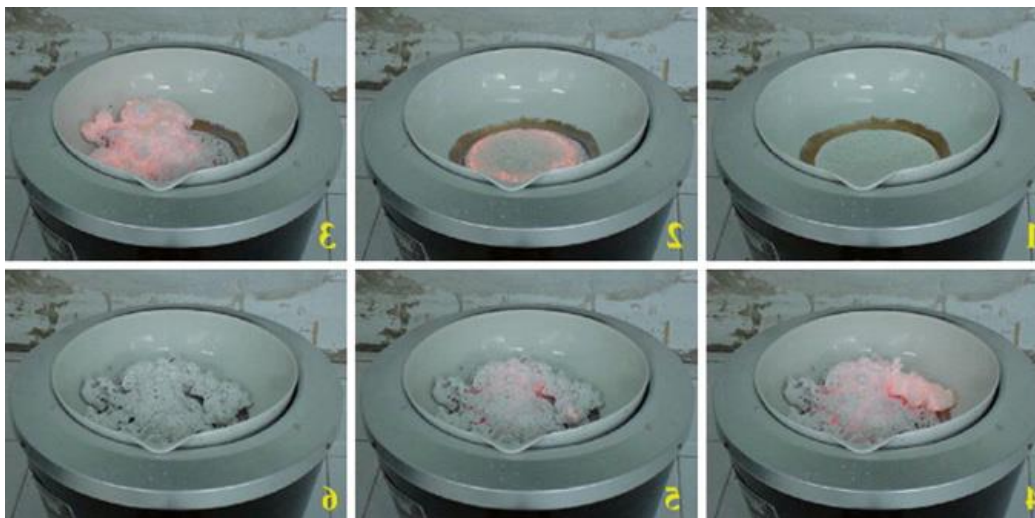


Figure 1.18 The evolution of a smoldering flame during the combustion reaction containing $\text{Ca}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$ and β -alanine.^{84, 85}

Ianos *et al.* observed that when β -alanine was used as a fuel in the combustion of $\text{Ca}(\text{NO}_3)_2$, and $\text{Al}(\text{NO}_3)_3$; a smoldering flame was observed (Figure 1.18). However, when the fuel was changed to urea, a flaming flame was observed, as shown in Figure 1.19.⁸⁵

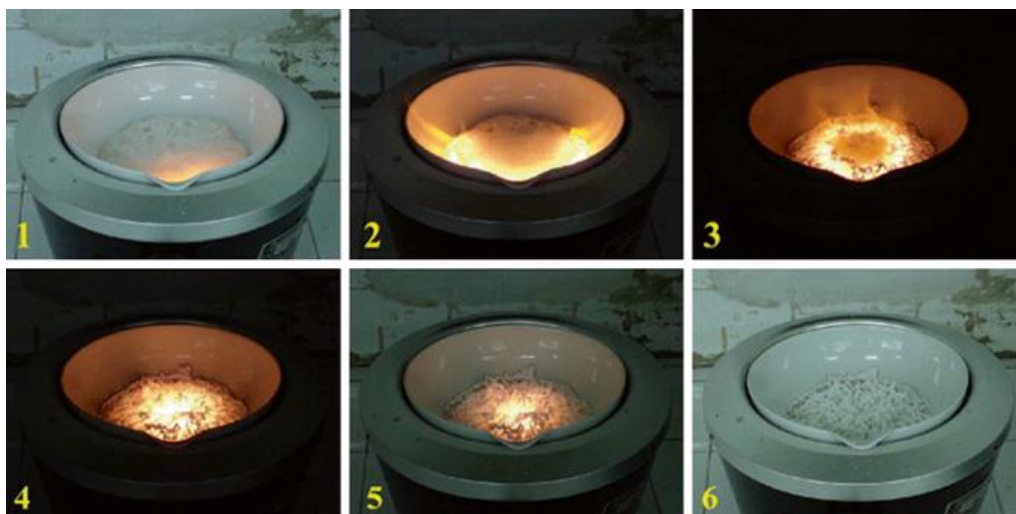


Figure 1.19 The evolution of a flaming flame during the combustion reaction containing $\text{Ca}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$ and urea.⁸⁴

Ianos *et al.* concluded that different fuels results in defferent flames wherein smoldering flame is associated with the formation of small particle size of the synthesised material while the flaming flame is associated with bigger particle size of the synthesised material. Urea was more reactive and thus resulted in the formation of the flaming flame, while β -alanine was less reactive and was observed to form a smoldering flame.⁸⁵ Furthermore, the reactivity of the combustion reaction is dependent on the ligand groups of the molecules of the fuel and the compositional ratio of fuel and oxidant. In addition, Ianos *et al.* stated that the combustion reaction process between the mixture of the reactants (fuel and oxidizer) may be hypergolic (ignition by contact) or the ignition may be initiated by an external source.⁸⁵ These conditions are crucial for generating the flame.

1.3.1.2 Characteristic temperature

There are four important temperature regimes that are known to affect the combustion process and thus the resulting powder; these include,⁸²

- Initial temperature, (T_o), which is the average temperature of the reagent solution before the reaction is ignited.
- Ignition temperature, (T_{ig}); represents the point at which the combustion reaction is dynamically activated without an additional supply of external heat.
- Adiabatic flame temperature, (T_{ad}), is the maximum combustion temperature achieved under adiabatic conditions and
- Maximum flame temperature, (T_m), which is the maximum temperature reached in the actual configuration, i.e. under conditions that are not adiabatic.

In general, most of these temperatures are very difficult to measure, however, the ignition process is known to occur with a minimum amount of the reactants.⁸⁰ When this solution is rapidly heated above the temperature where the chemical reaction rate is high enough; the rate of heat release is greater than the rate of heat dissipation. The adiabatic temperature (T_{ad}) can be calculated from the Equation below⁸⁴:

$$Q = \int_{T_0}^{T_{ad}} \sum_j n_j C_{p,j} dT ,$$

where Q and $C_{p,j}$ represent the heat of the reaction and the specific heat of the j^{th} product as a function of temperature, respectively. T_0 represent temperature at 300 K, while n_j represent the amount of each compound. From studies by Vita *et al.*, the adiabatic temperature (T_{ad}) was again shown to depend on the type of fuel used, since each fuel has a different enthalpy of combustion.⁸¹ Moreover, the resulting powder synthesized from a high enthalpy fuel was observed to have a lower surface area and larger particle size.

1.3.1.3 Gases generated

It is well-established that in combustion synthesis, the powder morphology, particle size, and surface area are directly related to the number of moles of gases that escape during combustion. The gases break large clusters and create pores.^{81, 82} The clusters disintegrate under conditions of increased production of combustion gases and under these conditions more heat is released from the system, hindering particle growth.⁸⁰ The difference in particle size, using different fuels, depends on the number of moles of gaseous products released during combustion. However, in recent studies by Vita *et al.* and Morfin *et al.* this phenomenon was not observed, rather they found that the physical and chemical properties of the final powder depended on the enthalpy of combustion which affected the nature of combustion.^{81, 86}

1.3.1.4 Fuel-oxidant ratio

A fuel is a substance capable of breaking the CH bonds (electron acceptor).⁸² An oxidant is a substance that helps in burning and provides oxygen (electron donor).^{82, 84} Only when the oxidizer and fuel are intimately mixed in an appropriate proportion can an exothermic chemical reaction be initiated that then generates substantial heat.^{84, 87} The temperature reached when the reaction starts in the oxidizer and fuel solution is called the ignition temperature. The ratio of fuel and oxidizer is considered as a significant parameter in determining the properties of synthesized powders obtained by combustion.^{82, 86} Product properties such as crystallite size, surface area, morphology,

phase, degree and nature of agglomeration, are generally controlled by adjusting the fuel-oxidant ratio. The fuel-oxidant ratio determines the influence of gases on the morphology of the particles. The pore size also depends on the fuel-oxidant ratio, since the greater the amount of fuel, the greater the heat of enthalpy and thus the greater pore size and particle size.⁸¹

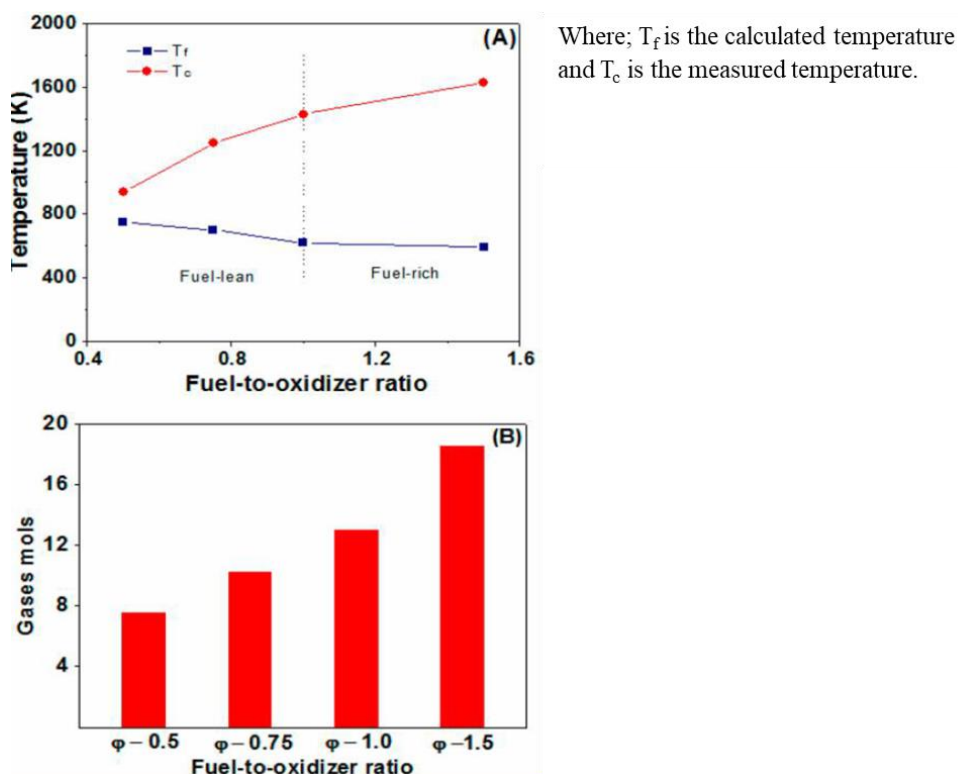


Figure 1.20 The effect of fuel-oxidant ratio on adiabatic temperature and moles of gases produced.^{84, 87}

In recent studies, Zhou *et al.* observed that an increase in the fuel-oxidant ratio resulted in an increase in the adiabatic temperature and number of moles of produced gases as shown in Figure 1.20.⁸⁷ The fuel-oxidant ratio affects the nature of combustion and thus results in powders with different properties.⁸⁷ In a study conducted on the effect of adiabatic temperature with respect to the nature of combustion; it was observed that the higher the adiabatic temperature, a more voluminous and rapid combustion occurred.⁸¹ Furthermore, the prepared powder was observed to have a larger particle size and larger pore size. The formation of a larger particle size was attributed to the agglomeration of the smaller particles which was caused by the higher adiabatic temperature, while the formation of larger pores was caused by the rapid eviction of gases which resulted.^{81, 84}

1.3.1.5 Fuels

Fuels are the source of carbon and hydrogen, which results in the formation of CO_2 and H_2O upon combustion and thus liberation of heat.^{80, 82} Fuels are known to form complexes with metal ions thus facilitating homogenous mixing of cations in solution. Furthermore, they decompose to form combustible gases like HNCO and NH_3 which ignite with NO_x . In recent studies, fuels such as urea and glycine were shown to produce better catalysts when compared to other fuels, in respect of metal dispersion, surface area, and catalytic activity.^{64, 86} Furthermore, compounds containing N–N bonds in their moieties were observed to assist in combustion.^{80, 82} However, it was observed that fuels tend to be metal-dependent; with urea and glycine being more favoured for the synthesis of alkali metal oxide powders, while fuels such as citric acid and oxalyldihydrazide (ODH) are favoured for the synthesis of the transition metal oxide powders.⁸²

Important properties that qualify an ideal fuel for the solution combustion synthesis are;⁸²

- Being water soluble.
- Having a low ignition temperature ($<500^\circ\text{C}$).
- Being compatible with metal nitrates, i.e. the combustion reaction should be controlled and smooth and not lead to an explosion.
- Evolve large amounts of gases that are of low molecular weight and harmless during combustion.
- Yield no other residual mass except the oxide in question.
- Being readily available or easy to prepare.

Vita *et al.* observed that different fuels affect the nature of the combustion and thus affect the physical and chemical properties of the resulting powder.⁸¹ Furthermore, fuels with a higher enthalpy of combustion result in high adiabatic temperatures, such that the resulting powder has a lower surface area, poorer metal dispersion, and large particle size.⁸¹ Morfin *et al.* observed that glycine resulted in more metal-support interactions.⁸⁶ Although the influence of fuels has been reported; there is no information on how different fuels affect the $\text{Pd}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ system and thus catalytic methane combustion.⁸¹ In this study the influence of different fuels on the properties of solution-combustion synthesized palladium/ceria catalysts for low-temperature methane combustion was investigated. Table 1.1, shows some of the common fuels used in solution combustion synthesis.⁸⁰

Table 1.1 Commonly used fuels in solution combustion synthesis.⁸⁰

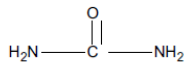
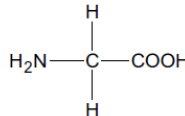
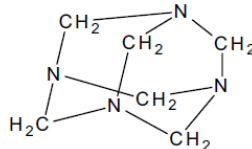
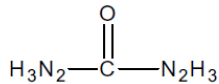
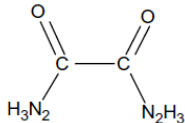
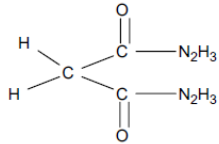
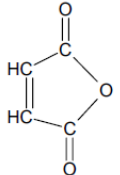
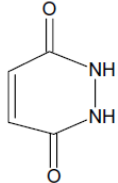
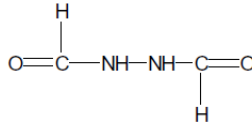
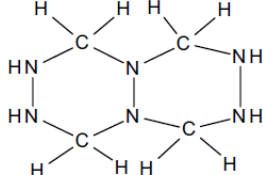
Sl. No.	Fuel	Formula	Reducing valency	Reactants for preparation	Structure
1.	Urea (U)	$\text{CH}_4\text{N}_2\text{O}$	+6	Commercially available	 $\text{H}_2\text{N}-\text{C}(=\text{O})-\text{NH}_2$
2.	Glycine (G)	$\text{C}_2\text{H}_5\text{NO}_2$	+9	Commercially available	 $\text{H}_2\text{N}-\text{CH}(\text{H})-\text{COOH}$
3.	Hexamethylene tetramine (HMT)	$\text{C}_6\text{H}_{12}\text{N}_4$	+36	$4\text{NH}_3 + 6\text{HCHO}$ Commercially available	
4.	Carbohydrazide (CH)	$\text{CH}_6\text{N}_4\text{O}$	+8	$(\text{C}_2\text{H}_5)_2\text{CO} + 2\text{N}_2\text{H}_4\text{H}_2\text{O}$ (Ref. 8)	 $\text{H}_3\text{N}_2-\text{C}(=\text{O})-\text{N}_2\text{H}_3$
5.	Oxalic acid dihydrazide (ODH)	$\text{C}_2\text{H}_6\text{N}_4\text{O}_2$	+10	$(\text{COOC}_2\text{H}_5)_2 + 2\text{N}_2\text{H}_4\text{H}_2\text{O}$ (Ref. 9)	 $\text{H}_3\text{N}_2-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{N}_2\text{H}_3$

Table 1.1 (continued)

Sl. No.	Fuel	Formula	Reducing valency	Reactants for preparation	Structure
6.	Malonic acid dihydrazide (MDH)	$C_3H_8N_4O_2$	+16	$CH_2(COOC_2H_5)_2 + 2N_2H_4H_2O$ (Ref. 10)	
7.	Maleic hydrazide (MH)	$C_4H_4N_2O_2$	+16	 $+ N_2H_6Cl_2$ (Ref. 11)	
8.	Diformyl hydrazide (DFH)	$C_2H_4N_2O_2$	+8	$2HCOOH + N_2H_4H_2O$ (Ref. 12)	
9.	Tetraformal Trisazine (TFTA) 4-amino-3,5-dimethyl-1,2,4-triazole	$C_4H_{12}N_6$	+28	$4HCHO + 3 N_2H_4H_2O$ (Ref. 13)	

Motivation and Objective of this study

Chapter 1 outlined the significance of fuel cells and the components that work to function holistically. Reforming and reformat processing are one of the critical processes involved which have a significant effect on the design, efficiency, volume, weight, and cost of the fuel cell processing subsystem and, in turn, on the total fuel cell power system (refer to Figure 1.2). Steam reforming of natural gas, mostly methane, produces CO and H₂, however, this process is endothermic, as a result it requires an external heat source.⁸ The heat source itself can come in various forms, including traditional heating elements or some kind of heat exchanger. The latter idea will be exploited in this study in the form of methane combustion as a source of heat to drive the reforming reaction. However, it is important to establish low-temperature activity (low temp light-off curve) which will allow for fast start-up of the fuel processor by needing less energy for the reaction.⁸⁸ High catalytic activity and thermally stable catalysts are required to achieve efficient methane combustion. Palladium-based catalysts have been found to be most effective for low-temperature methane combustion compared to other platinum group metals.⁸⁸

In this study, the solution combustion method was used to synthesize Pd/ceria catalysts using the SCS method with different fuels and, subsequently, the catalytic activity of the prepared catalysts was investigated for low-temperature methane combustion.

The objectives of this study were thus;

- To synthesize five Pd/Ceria catalysts containing 2 wt.%. Pd prepared (in triplicate) by the solution combustion synthesis method with different fuels namely:
 - Oxalylhydrazide (ODH)
 - Citric acid monohydrate
 - Urea
 - β -Alanine
 - Tartaric acid

Note; These fuels were chosen based on their heat of combustion, where; Urea and Alanine are classified as fuels with low heat of combustion while the remaining fuels classified as fuels with high heat of combustion.

- To characterize these catalysts using various physisorption and chemisorption techniques, as well as XRD and microscopy techniques; to establish micro-structure, Pd dispersion, and Pd content.
- To test the prepared catalysts for methane combustion (establish light-off curves) activity at temperatures between 25 °C and 600 °C and, furthermore, to monitor deactivation over a period of 100 hours for catalysts that achieved 100% methane conversion.

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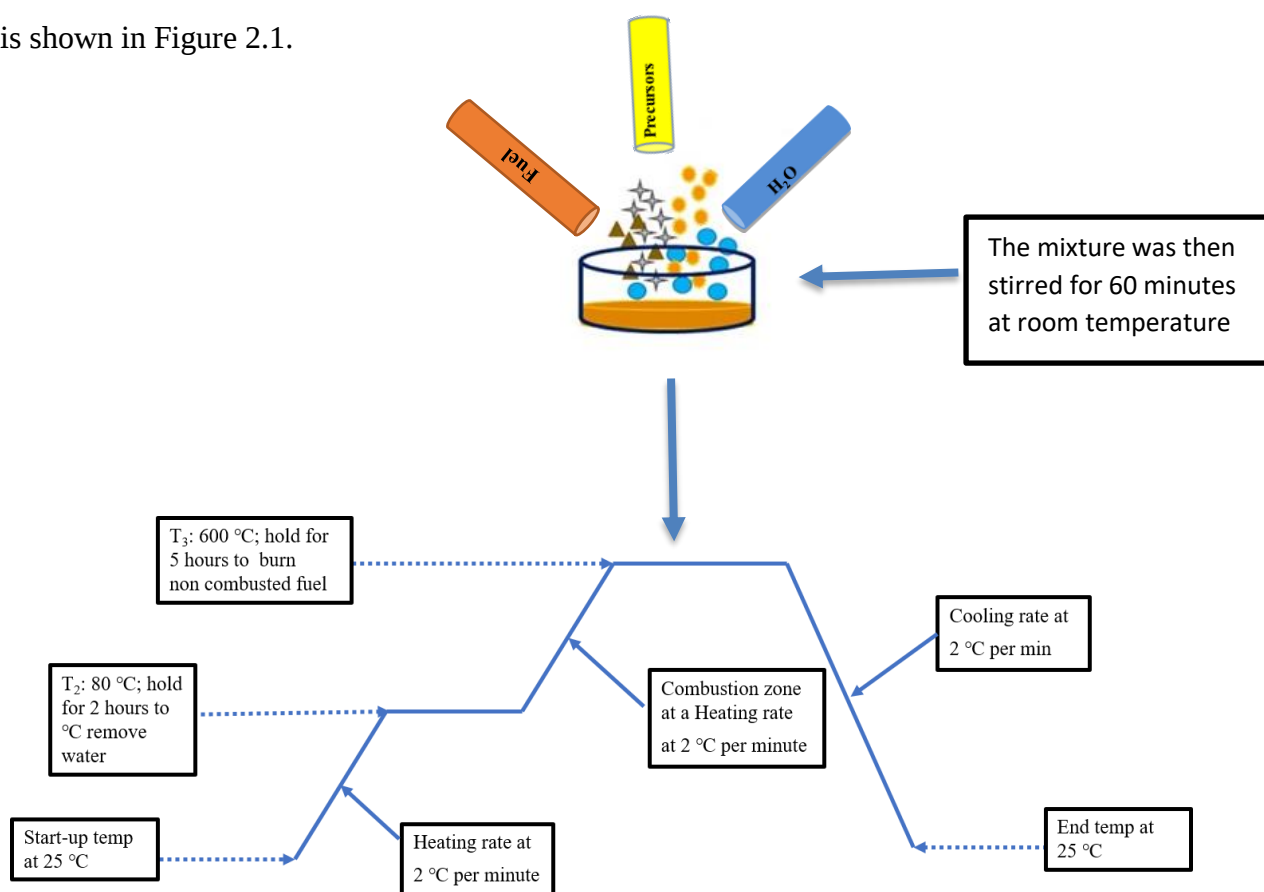
Chapter 2

Experimental

2.1 Catalysts preparation

2.1.1 SCS catalysts preparation

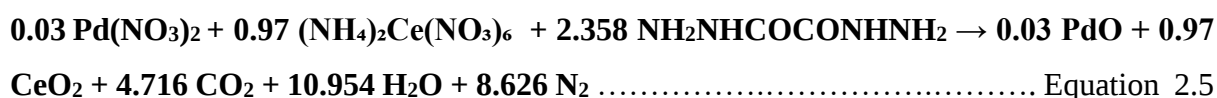
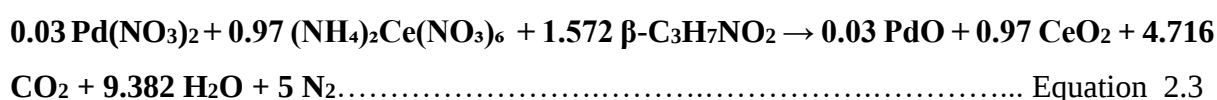
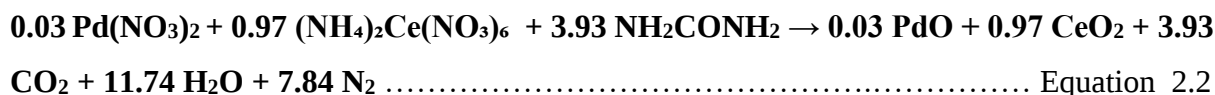
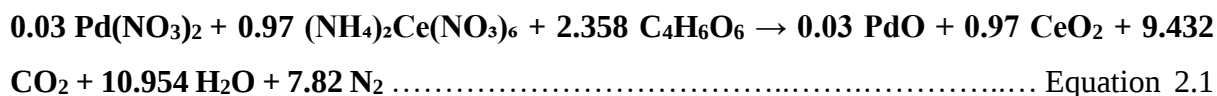
A series of $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{\delta-2}$ catalysts were prepared by the method of solution combustion (SCS). Palladium and Ce precursor salts were mixed with a suitable amount of water and fuel. Ceric ammonium nitrate $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ was used as the CeO_2 precursor, and palladium nitrate $\text{Pd}(\text{NO}_3)_2$ as the Pd precursor. Oxalylhydrazide (ODH), citric acid monohydrate, urea, tartaric acid, and β -alanine were used as fuels. The metal precursors were dissolved in a stoichiometric amount in water containing a suitable amount of the fuel in a ratio of 1:1. The resulting solution was then placed in a programmable furnace for the combustion to take place. The method of preparation as well as the temperature programme used for the combustion step is shown in Figure 2.1.



T_2 and T_3 refers to the temperatures reached after heating up.

Figure 2.1 The schematic diagram of the programmable furnace combustion process.

The resulting powder from the furnace was then crushed into a fine homogeneous mixture. The overall theoretical combustion reactions are shown in Equations (2.1) to (2.5):



2.1.2 Preparation of 2wt.% PdO/CeO₂ using wet impregnation

A supported Pd on ceria catalyst was prepared using the incipient wet impregnation method adapted from the work of Meng *et al.*¹ A mass of commercial CeO₂ (Sigma Aldrich) was made into a slurry using 50 ml of deionised water. Thereafter, the required amount of palladium nitrate was dissolved in a minimum amount of deionised water before it was added dropwise to the slurry of CeO₂ using a separating funnel. The mixture was allowed to mix under constant stirring for 6 hours prior to dehydration at 80 °C. The resulting paste was then dried at 110 °C in an oven overnight. The powder catalyst was then crushed prior to calcination at 600 °C under airflow for 5 hours and the resulting material was called PdO/CeO₂-IWI.

2.2 SCS catalysts characterisation

2.2.1 Powder X-Ray diffraction

Powder XRD (PXRD) was mainly used for finger print identification and structure refinement of the solid materials ². PXRD was also used to determine the phase composition of the catalyst samples, unit cell lattice parameters and lattice symmetry, residual strain of the lattice, and crystal structure.

A PANalytical Empyrean Diffractometer operating at 40 mA and 40 kV equipped with a X'Celerator detector, a CoK α ($\lambda = 1.78901$ nm) radiation source and HighScore Plus software was used to determine the diffraction patterns of the synthesised catalysts and the commercial ceria. The diffraction patterns were obtained in the 2θ range of 5-90°, a step size of 0.0080° per 8.2550 s. The interplanar spacing (d) was calculated by manipulation of Bragg's Law (Equation 2.6) which dictates the conditions required for diffraction to occur:

$$n\lambda = 2d_{hkl}\sin\theta \dots\dots\dots \text{Equation : 2.6}$$

λ – wavelength of the characteristic X – rays

d – lattice interplanar spacing of the crystal

θ – X- ray incidence angle (also known as Bragg's angle)

h,k,l – Miller indices

The Scherrer equation (Equation 2.7) was then used to determine the crystallite size (D) of the catalysts;

$$D_{\text{XRD}} = \frac{K\lambda}{\beta\cos\theta} \dots\dots\dots \text{Equation : 2.7}$$

K = 1 - since the peak profiles were observed to follow the Gaussian peak profile.

$\lambda = 1.78901$ nm

θ = Bragg's angle

β = full width at half – maximum (FWHM) of the (111) plane.

Subsequently, the lattice parameters (**a**) were calculated by the substitution of the corresponding d – spacing and (111) plane. The lattice parameters were calculated by

manipulation of Equation 2.8 since this equation allows for the calculation of the lattice parameters (**a**) given that the D-spacing is known.

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \dots\dots\dots \text{Equation 2.8}$$

2.2.2 Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) analysis

A PerkinElmer Optical Emission Spectrometer – Optima 5300 DV was used to determine the Ce and Pd composition of the synthesised catalysts.

Approximately 25 mg of the catalytic sample was accurately weighed, which was then digested in 10 mL of concentrated H₂SO₄ on a hotplate for 10 hours. The digested samples were then gravimetrically filtered into a 100 mL volumetric flask and made to the mark with deionised water. A 10-fold dilution was then performed on the sample solution.

To obtain a calibration range of 0 – 50 ppm, the respective volumes of Ce and Pd were pipetted into 100 mL volumetric flasks from their respective 1000 ppm commercial stock solutions (Industrial Analytical). To match the matrix of the sample solutions, 10 mL of conc. H₂SO₄ was also pipetted into the 100 mL volumetric flasks and thereafter the volume was made up to the mark with deionised water. All intensities were determined in triplicate.

2.2.3 N₂-physisorption

Physical characteristics, such as surface area, pore volume and particle size, of the ceria based catalysts were determined using the BET surface area Equation 2.9:

$$\frac{C \frac{P}{P_0}}{\left(1 - \frac{P}{P_0}\right)V} = \frac{1}{CV_0} \left(1 - (C - 1) \frac{P}{P_0}\right) \dots\dots\dots \text{Equation : 2.9}$$

C – BET constant

V – gas adsorbed

P/P_0 – relative pressure

V_0 – amount of gas required for the monolayer coverage

Approximately 200 mg of catalytic sample was degassed under a flow of N₂ prior to analysis, using a Micromeritics FlowPrep 060 instrument. Thereafter a Micromeritics TriStar 3000 multipoint analyser was used to obtain the N₂ absorption/desorption isotherms at - 196 °C. Particle sizes of the various ceria based catalysts were calculated from their BET area using Equation 2.10 by assuming all particles were spherical.

$$D_{BET} = \frac{6}{\mu \times S_{BET}} \dots\dots\dots \text{Equation : 2.10}$$

μ – density of ceria: 7.216 g.cm⁻³

S_{BET} – specific surface area determined by BET measurements

The crystallite size was also obtained from Equation 2.10. However, the calculated crystallite size by this method is known to be an estimate of the actual crystallite size, since this calculation doesn't account for pore size and pore volume.

2.2.4 Raman Spectroscopy

Raman spectroscopy was conducted using a DeltaNu Advantage 532 instrument fitted with a 532 nm laser source. A powdered sample was placed in an aluminium sample holder before the laser beam was employed. The laser beam strength was set on high while the sample was exposed to the laser beam for 20 seconds. To compare oxygen vacancy (O_v) density of the various catalysts, the ratio between the areas of the O_v and F_{2g} peaks were used as shown in Equation 2.11.

$$O_v/F_{2g} = \frac{\text{intensity of } O_v \text{ band at } 600 \text{ cm}^{-1}}{\text{intensity of } F_{2g} \text{ band at } 460 \text{ cm}^{-1}} \dots\dots\dots \text{Equation 2.11}$$

2.2.5 Scanning Electron Microscopy

Scanning electron microscopy (SEM) images and Energy dispersion X-ray (EDX) analysis was carried out using a Jeol JSM 6100 Scanning Electron Microscope at 20 kV. Energy dispersion X-ray (EDX) was carried out using a Bruker EDX Detector and analysed by Espirit 1.8.5 software. All samples were dispersed onto double-sided carbon tape mounted on aluminium stubs. Thereafter, all samples were coated with gold using a Polaron E5100 coating unit prior to imaging. All images were taken at random points along the surface of the catalysts.

2.2.6 Transmission Electron Microscopy

All samples were obtained using a Jeol JEM 1010 Transmission Electron Microscope (TEM) operated at a voltage of 100 kV equipped with a MegaView III Soft Imaging System. The samples were first diluted with ethanol in an Eppendorf tube and sonicated for 10 minutes, prior to coating on a formvar copper grid for analysis. A brightfield analysis was then conducted on all samples and the scale was set at 100 nm.

2.2.7 High Resolution Transmission Electron Microscopy

High Resolution Transmission Electron Microscopy images were obtained using a Jeol JEM 2100 High Resolution Transmission Electron Microscope (HRTEM), operated at a voltage of 200 kV equipped with a MegaView III Soft Imaging System. This microscope used a LaB6 gun and it was equipped with a Gatan ultrascan camera for imaging. The catalyst samples were subjected to the same method of sample preparation as for TEM and the imaging scale was set at 20 nm. The line scan EDX was performed on darkfield images obtained using a Gatan ultrascan camera.

2.2.8 H₂ Temperature Programmed Reduction

A Micromeritics AutoChem II Chemisorption Analyser was used to determine the reducibility of the catalyst. Approximately 50 mg of the catalyst sample was placed on top of quartz wool in a U-shaped quartz tube prior to the start of an analysis. The analysis was performed by heating the sample from room temperature to 850 °C, at a rate of 10 °C.min⁻¹ under a flow of 10% hydrogen in argon at 50 ml.min⁻¹. The amount of hydrogen consumed by the sample during reduction was measured using a thermal conductivity detector (TCD).

2.3 Palladium supported catalyst characterisation

The PdO/CeO₂ – IWI catalyst as well as the commercial ceria were characterised using N₂-physisorption, Raman spectroscopy, ICP-OES and XRD equipped with a Cu radiation source prior to testing.

2.4 Catalytic testing

Generally, three types of reactors are employed in heterogeneous catalysis which include a continuous fixed bed, fluidized bed and stirred tank reactor. However, a continuous-fixed bed reactor is widely used due to their cost advantage and industrial implication.

2.4.1 Reactor setup and Reactor tube packing

In this study, a continuous-fixed bed reactor was used to study methane combustion in air. The reactor design is depicted by the schematic diagram shown in Figure 2.2 and pictorially in Appendix A, Figure A-1. The reactor was custom built by the chemical engineering department of the University of Cape Town. The reactor is a PROX prototype reactor with all tubing and fittings supplied by Swagelok. The tubing was made from stainless steel with 1/4 inch (outer diameter) upstream of the reactor tubes and 1/8 inch (outer diameter) downstream of the reactor tubes to the Vici valve. The reactor tubes were made from stainless steel with 3/4 inch (outer

diameter) and 490 mm in length. The reactor consists of a heating block which houses two reactor tubes labelled left and right-hand tube (LHT and RHT).

The catalyst was always packed at the isothermal point within heating zone 2 as shown in Figure 2.3. To determine the isothermal point, a temperature profile for the reactors was determined at various temperatures in the reactor tubes packed with silicon carbide particles (24 gritt, Promark Chemicals) under N₂ flow, as shown in Appendix A, Figure A-2. The reactor was mounted into a heating block with four heating zones. The temperature of each heating zone was adjusted in order to establish an isothermal zone in each of the reactors. A J-type thermocouple was used to measure the temperature every 10 mm along the reactor's length and the results are shown in Appendix B, Figure B-1.

The catalyst (various volume diluted with required carborundum to give a required GHSV) was sandwiched between two layers of quartz wool and the remainder of the tube was filled with carborundum and stoppered with glass wool on both ends. Prior to catalytic testing, leak tests were performed on the reactor tubes by flowing N₂ at a pressure of 2 bars while checking for air bubbles using snoop and soap water. At the end of each experiment, the reactor tubes were carefully emptied, washed with water and soaked in an oxalic acid solution. Furthermore, the tubes were further washed with water and rinsed with acetone before they were dried in an oven (110 °C).

Brooks mass flow controllers (MFC) with a proportional-integral-derivative (PID) control loops were used to control the gas flow rates. Temperature controllers (Gefran 800P) were used to set the reactor as well as the heating line temperatures to the required value. A J-type thermocouple (Uni Temp) was used to measure the temperature of the catalyst bed as well as the heating line (see Appendix A, Figure A-3)

All gases were supplied externally to the test unit from the cylinders (Afrox SA) with the pressure regulated at 20 bar. The exiting gasses from the cylinders were passed through the filters prior to pressure reducing regulators. This pressure regulators were used to maintain the inlet pressure to the mass flow controllers (MFC) between 20 and 15 bar. Upon exiting the MFCs, the gasses were allowed to mix in the blend pot at 3 bar maintained by the spring loaded back pressure regulators (Tescom 150). Thereafter, the gasses were regulated to atmospheric pressure prior to entering the reactor tubes and bypass stream. However, in an event of a significant increase in pressure, pressure relief valves were in place to vent out the excess gas thus reducing the pressure. Upon exiting the reactor tubes and bypass, a 4-way vici-valve with

two inlets and two outlet ports, as shown in Figure 2.2, was used to sample either reactor's product stream or the reactor by-pass stream (i.e. feed). When this valve was set to sample the reactor product on the 3-channel micro GC, the reactor by-pass stream was sent to vent and vice versa when the by-pass stream was sampled. A cooling bath was employed for the knock-out pot (see Appendix A, Figure A-4). A list of chemicals used in the study, reactor conditioning data, flow controller calibration data and data analysis using a micro GC is given in Appendix B.

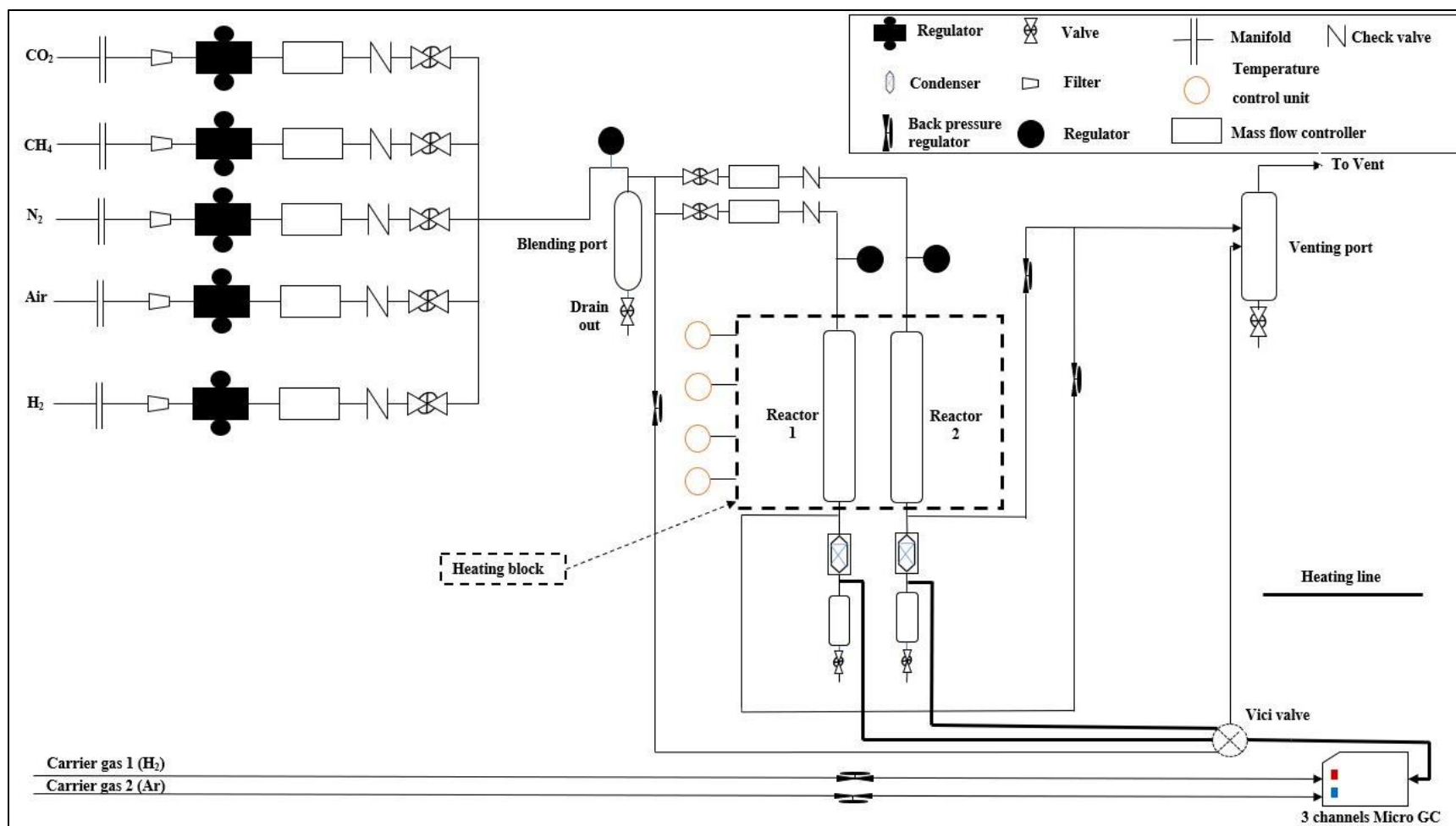


Figure 2.2 Schematic representation of the test unit used in methane combustion.

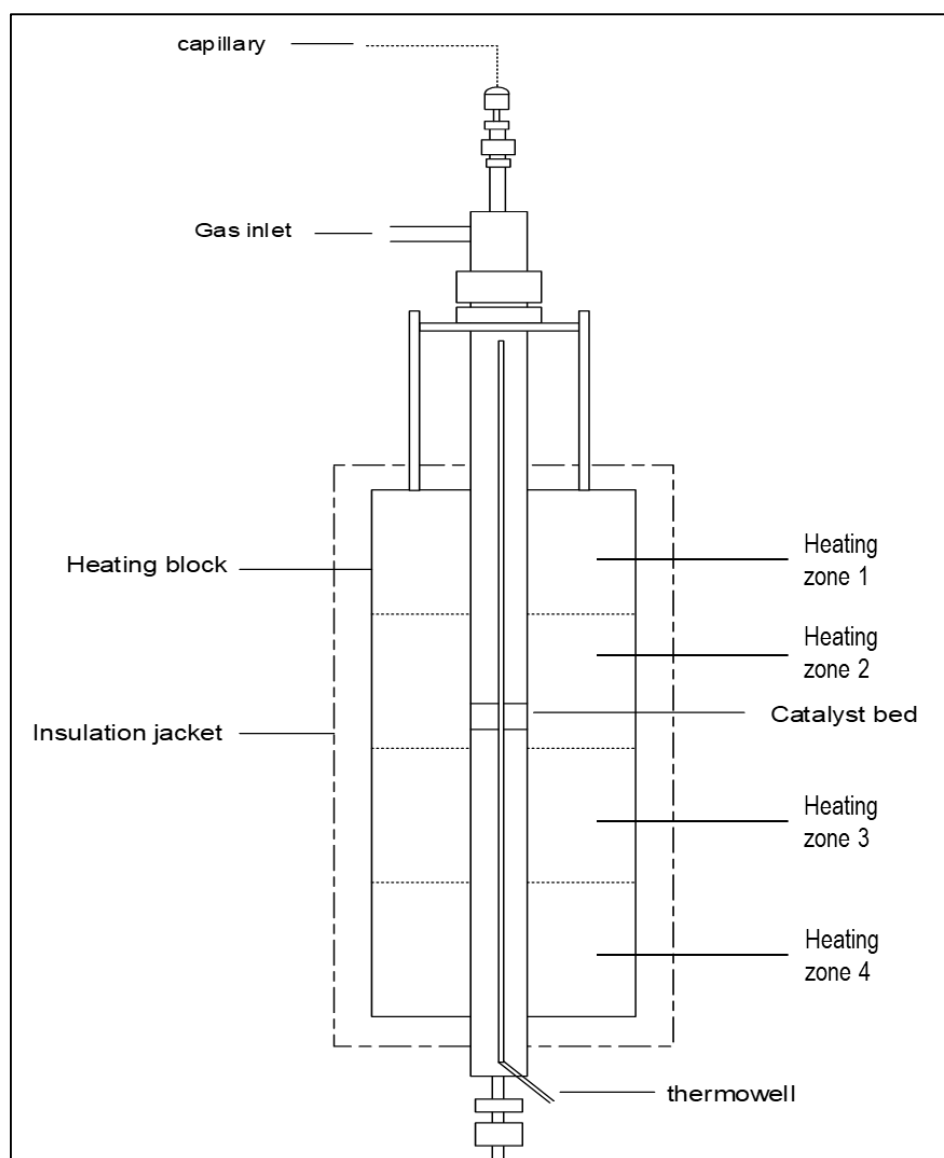


Figure 2.3 The schematic diagram of the reactor tube.

2.5 Methane combustion

Methane combustion was studied at a GHSV of $15\,000\text{ h}^{-1}$ and prior to combustion studies, the catalysts were pre-treated using the feed.

2.5.1 Catalysts pre-treatment

The 4 % methane in air at a GHSV of $15\,000\text{ h}^{-1}$ was used to pre-treat the catalyst by first increasing the temperature from room temperature to $400\text{ }^{\circ}\text{C}$ and holding for 1 hour before cooling to $25\text{ }^{\circ}\text{C}$. Colussi *et al.*, mentioned that it is beneficial to pre-treat using feed, since

methane combustion is an exothermic reaction.^{3, 4} Furthermore, pre-treating with the feed resulted in stable reproducible catalytic reaction data.

2.5.2 Methane combustion over ceria based catalysts

The methane combustion reactions were studied over the ceria-based catalysts using a feed containing 4 vol. % CH₄ in air with a flow rate of 182 mL/min and a GHSV of 15 000 h⁻¹. The catalyst volume used was 0.2 mL consisting of mesh sizes between 300-600 microns. The catalyst was screened within a temperature window from 25 °C to 600 °C with samples taken at 50 °C increments. Prior to sampling, the reaction was given 20 minutes to equilibrate before samples were taken and all the gaseous products were analysed using an online 3 channel micro-GC. Time on stream experiments were conducted using fresh catalysts at various GHSV's from 100 hours to 150 hours to determine the catalyst's stability. Moreover, the heating and cooling curves were obtain using the same feed at a 15 000 h⁻¹ GHSV.

2.5.3 Methane combustion via lattice oxygen

Methane combustion via the lattice oxygen was performed over the best catalyst using 4 % vol methane in nitrogen, in the absence of fed oxygen. The catalyst was degassed in the reactor overnight using nitrogen prior to the introduction of methane. The reaction was then left for an hour to obtain the desired methane-nitrogen feed. The catalyst was then screened at 350 °C for 250 minutes, since at this temperature methane combustion is known to occur at a minimal rate.

2.5.4 Conversion calculations

Methane conversion was calculated using Equation 2.12.

$$XCH_4(\%) = (nCH_4, in - nCH_4, out) / nCH_4, in \times 100 \dots\dots\dots \text{Equation 2.12}$$

Where: nCH_4 refers to the molar flow rate of methane.

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Chapter 3

Characterisation of $\text{Pd}_{0.03}\text{Ce}_{0.097}\text{O}_{2-\delta}$ catalysts synthesized using different fuels

3.1 Enthalpy of combustion

The solution combustion synthesis method has been reported to be affected by several factors including the nature of the combustion. This study focuses on the effect of fuels on the physical and catalytic properties of palladium ceria catalysts. Table 3.1 shows the enthalpy of combustion of each fuel for the respective catalysts prepared. Vita *et al.* showed that different fuels led to changes in physical and structural properties such as morphology, surface area, particle size and oxygen vacancies.¹ Moreover, the powder's morphology and structural properties are related to not only the enthalpy of combustion, but also to the amount of escaped gases during the combustion; which are in turn responsible for the clusters breaking up and for the formation of pores between particles¹. The number of moles of gas evolved per mole of fuel used is reported in Table 3.1. The amount of gas was calculated from the combustion equations mentioned in Chapter 2, Equation s 2.1 to 2.5, assuming that N_2 , CO_2 and H_2O are the only evolved gases.

Table 3.1 The effect of fuels on the nature of combustion.

Catalysts	enthalpy of combustion for each fuel $\Delta H^\circ (\text{kJ.mol}^{-1})$	Amount of gas produced per mol of fuel used (mol)
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Tartaric acid	-1120	28.2
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Urea	-633	23.5
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Alanine	-563	23.7
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Citric acid	-1837	20.9
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ ODH	-1369	24.3

- $2-\delta$ was used to show that the synthesised ceria based catalysts has ceria with lattice oxygen.

As shown in Table 3.1, each fuel has a different enthalpy of combustion and the amount of gases produced also varies. Therefore, the choice of fuel is significant since it determines the exothermicity of the redox reaction and the properties of the resulting powder. The solution mixtures, containing citric acid and ODH, were characterised by a violent combustion with a sudden rise in temperature.¹ However, urea, alanine and tartaric acid containing solutions were characterised by a moderate increment temperature change and the obtained powder was less

voluminous compared with the powders obtained with the other fuels. The nature of the combustion reaction is related to the capability to form complexes between the ligands ($-\text{C}=\text{O}$, $-\text{OH}$, $-\text{NH}_2$) contained in the fuel structure, and the metal cations ($\text{Ce}^{3+}/\text{Ce}^{4+}$, Pd^{2+}).^{1, 2} The more stable the complex, the higher the energy required to break the bonds between the fuel and metal cations. On this basis, ODH forms a strong complex with the metal ions compared to the other amino group containing fuels (alanine and urea). ODH contains two carbonyl groups and four amino groups, while urea contains only two amino groups bonded to one carbonyl group resulting in less energy required to break the bonds and thus giving a lower enthalpy of combustion.¹ In conjunction, β -alanine contains one amino group and one carbonyl group and, thus, a minimum enthalpy of combustion was reported.

3.2 Inductive Coupled Plasma-Optical Emission Spectroscopy

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) was used to quantitatively determine the composition of the catalysts (wt %).

Table 3.2 Metal loading of the prepared catalysts

Catalysts	Nominal Pd [wt.%]	Actual Pd [wt.%]	Composition
PdO/CeO₂ - IWI	2	1.87	-
Pd_{0.03}Ce_{0.97}O_{2-δ} Tart	2	1.80	Pd _{0.03} Ce _{0.97} O _{2-δ}
Pd_{0.03}Ce_{0.97}O_{2-δ} Urea	2	1.80	Pd _{0.03} Ce _{0.97} O _{2-δ}
Pd_{0.03}Ce_{0.97}O_{2-δ} Alanine	2	1.91	Pd _{0.03} Ce _{0.97} O _{2-δ}
Pd_{0.03}Ce_{0.97}O_{2-δ} Citric acid	2	1.74	Pd _{0.03} Ce _{0.97} O _{2-δ}
Pd_{0.03}Ce_{0.97}O_{2-δ} ODH	2	1.74	Pd _{0.03} Ce _{0.97} O _{2-δ}

- IWI stands for incipient wet impregnation

The ICP-OES provides useful information about the total metal content incorporated in the ceria lattice structure. All catalysts gave metal loadings close to the nominal weight percent. The results are given in Table 3.2. However, the catalysts synthesised by ODH and citric acid showed a lower amount of palladium likely because of the flame temperature or the nature of the combustion was severe and thus, resulted in the loss of Pd during the combustion.

3.3 X-Ray diffractogram (XRD) studies

X-ray powder diffraction (XRD) is an analytical technique primarily used for phase identification of a crystalline material and determination of unit cell dimensions. However, this

technique can also be used in conjunction with other mathematical equations, such as the Scherrer and Williamson-Hall equations, to calculate crystallite size and lattice strain respectively.

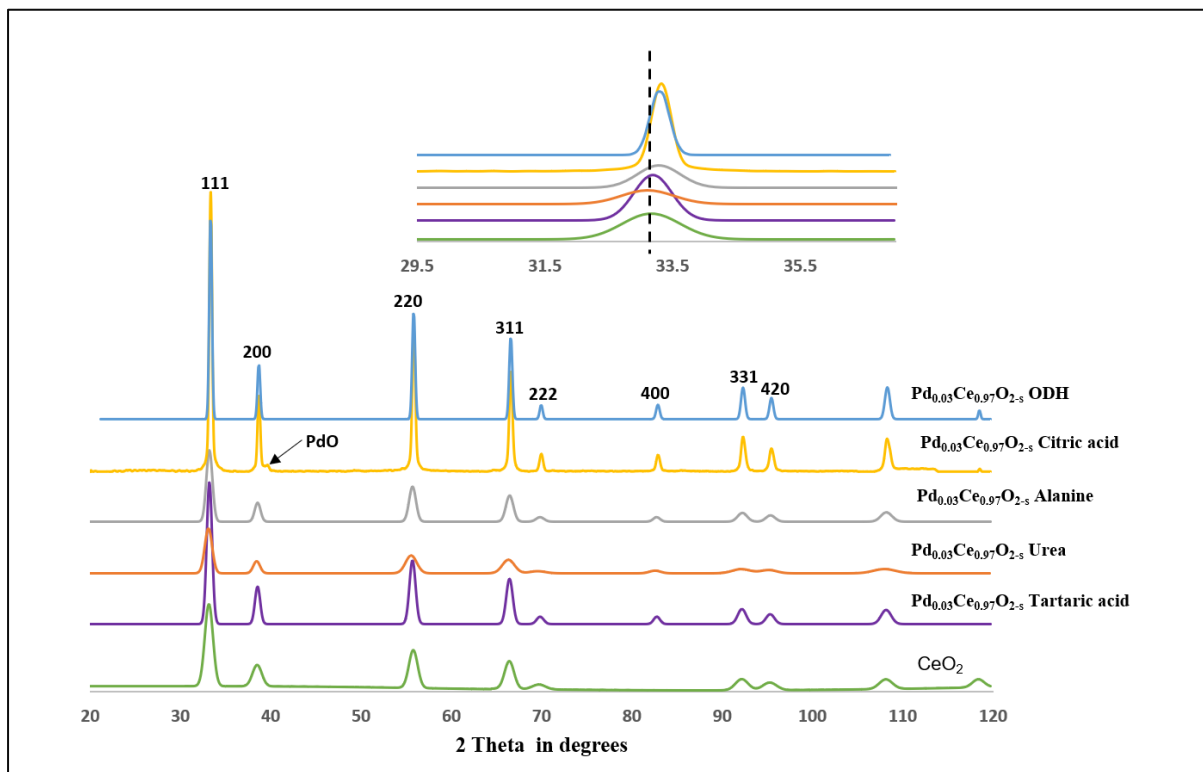


Figure 3.1 X-ray diffractograms of $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ prepared by solution combustion synthesis.

The XRD patterns of all the synthesised Pd/CeO₂ catalysts (Figure 3.1.) are associated with the typical cubic fluorite structure of ceria, corresponding to (111), (200), (220), (311), (222) and (400) planes when Pd is incorporated into the ceria matrix. However, when there is Pd “spillover”, this is seen as PdO at $2\theta = 40^\circ$,^{1, 3-5} as observed for the citric acid prepared catalyst. The presence of the PdO peak in the X-ray diffractogram of $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ citric acid, caused by the presence of PdO on ceria, is thought to be due to the high combustion enthalpy of citric acid. It was also noticed that the samples prepared with lower enthalpy of combustion fuels, such as urea, show diffraction patterns characterized by more broad peaks than the catalysts synthesized by the other fuels (ODH, citric acid). The sharp peak observed for the ODH and citric acid synthesised catalysts suggests the formation of catalysts with large crystallite sizes, which result from agglomeration caused by the high enthalpy of combustion and temperatures reached during the combustion.⁶

Table 3.3 Crystallite size, d-spacing and lattice strains for $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ prepared by solution combustion synthesis

Catalysts	Crystallite size nm	enthalpy of combustion for each fuel ΔH° (kJ.mol ⁻¹)	d-spacing	a (Å)	Lattice strains
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Tart	14.4	-1120	3.13	5.4214	0.0103
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Urea	10.9	-633	3.14	5.4341	0.0141
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Alanine	12.8	-563	3.14	5.4325	0.0115
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Citric acid	26.4	-1837	3.12	5.4103	0.0056
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ ODH	28.5	-1369	3.12	5.4109	0.0052

In Table 3.3, it is evident that the crystallite size, calculated using the Scherrer equation, has a proportional relationship with the enthalpy of combustion, while the lattice parameter, **a**, has an inversely proportional relationship. Furthermore, the CeO_2 (111) reflections of all the catalysts were shifted slightly to higher angles when compared to the blank CeO_2 . This shift suggests an incorporation of Pd^{2+} into the CeO_2 lattice structure resulting in oxygen vacancies because Pd^{2+} is square planar and 4 co-ordinate while Ce^{4+} is 8 co-ordinate.^{4, 6, 7} The difference in lattice strain can be attributed to the distortion of the fluorite structure of ceria and this can be explained by the defect equation using Kroger–Vink notations.⁸

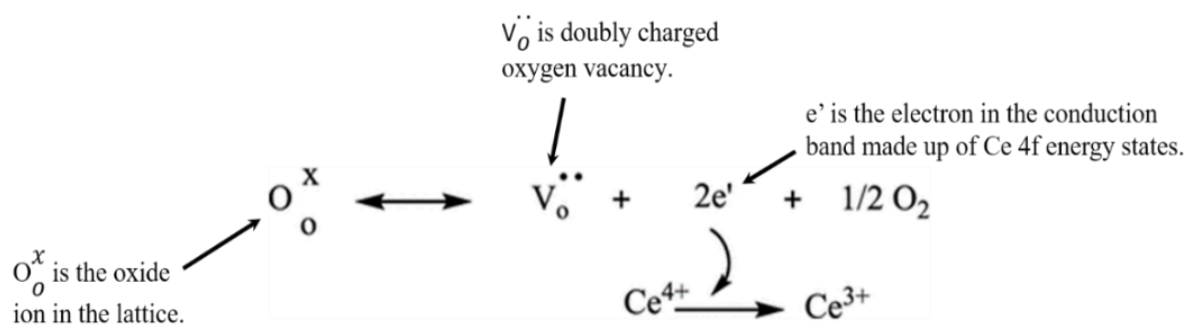


Figure 3.2 Schematic diagram showing incorporation of oxide ion into ceria lattice using Kroger-Vink notation.⁸

Figure 3.2, illustrates the incorporation of an oxide ion into the lattice structure of ceria which further results in the formation of an oxygen vacancy as represented by the presence of Ce^{3+}

and thus results in a distorted lattice structure.⁸ The degree of distortion depends on the size of an incorporated metal, in which case the different sizes will result in different Ce-O bond lengths.⁸⁻¹⁰ For larger crystallite sizes, the loss of one oxygen atom does not lead to significant lattice strain.⁸⁻¹⁰ However, for small crystallites, the loss of one oxygen results in significant lattice strain due to an increase in the Ce-O bond length leading to lattice expansion.⁸⁻¹⁰ To this effect, the crystallite size of the prepared catalysts has an inversely proportional relationship to the lattice strain as shown in Table 3.3. The decrease in crystallite size is in order of $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ citric acid > $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ ODH > $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ tartaric acid > $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ alanine > $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ urea. The diffractogram of PdO/CeO_2 -IWI was observed to be similar to the diffractogram of commercial ceria, as shown in Figure 4.3. Furthermore, PdO and Pd^0 peaks were not observed, suggesting that PdO may be well dispersed or exist as an amorphous phase on the surface of the catalyst.

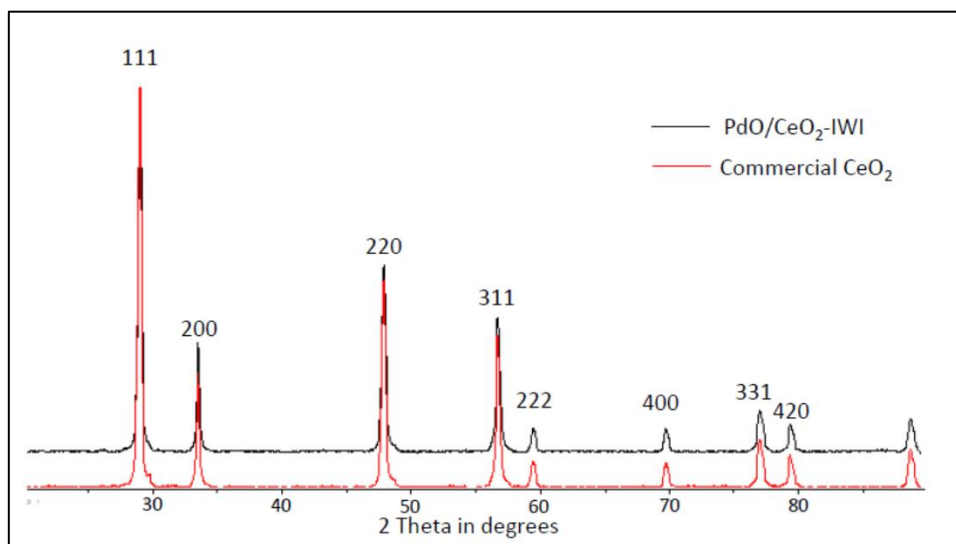


Figure 3.3 X-ray diffractograms of commercial CeO_2 and PdO/CeO_2 -IWI catalysts.

From the studies of Meng *et al.*, it was observed that a PdO/CeO_2 catalyst prepared by wet impregnation had the same X-ray pattern compared to commercial ceria with no peaks for PdO and Pd^0 being visible.¹¹ Meng *et al.* also proposed that the absence of PdO and Pd^0 peaks may be due to the low loading of Pd which may be below the instrument detection limits.¹¹ Colussi *et al.* made similar observations to Meng *et al.* and further stated that PdO could be well dispersed on the surface of ceria.¹² The crystallite size of PdO/CeO_2 and commercial ceria were calculated to be 28.7 nm and 28.3 nm respectively, while the lattice parameters were observed to be 5.4118 Å and 5.4115 Å respectively.

3.4 N₂-Physisorption analysis

The catalysts were characterized using N₂-physisorption analysis to determine the total specific surface area, pore volume and pore size. In Table 3.4, it is evident that the catalysts have different surface areas, pore volumes and pore sizes; which is due to the different maximum combustion temperatures reached during the synthesis and the amount of produced gases with each of the different fuels that were used.^{13, 14}

From the results presented in the Table 3.4, it is also observed that the surface area has an inverse relationship to the pore size whereby an increase in the surface area is accompanied by a decrease in the pore size. Furthermore, the catalysts synthesized from ODH and citric acid were observed to have larger pore sizes due to the voluminous nature of the combustion resulting from the high enthalpy of combustion of these fuels.¹

Table 3.4 The surface area, pore sizes and pore volume of the $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ prepared by solution combustion synthesis.

Catalysts	Surface Area (m ² /g)	Pore volume (cm ³ /g)	Pore size (Å)	Crystallite size nm
Commercial CeO ₂	7	0.0211	119	118.72
CeO ₂ -SCS-urea	85	0.0540	24	9.97
PdO/CeO ₂ - IWI	5	0.0123	105	166.21
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Tart	35	0.0696	81	23.74
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Urea	65	0.0400	24	12.78
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Alanine	12	0.0170	57	69.23
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Citric acid	7	0.0200	121	118.72
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ ODH	4	0.0120	111	207.26

However, the catalysts synthesized by urea, β -alanine and tartaric acid were observed to have smaller pores and higher surface areas due to the minum amount of gases escaped during the combustion, which is caused by the low enthalpy of combustion of these fuels.¹ To this effect, the surface area of the catalysts prepared by the different fuels decreased by the following trend; $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ urea > $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ tartaric acid > $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ alanine > $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ citric acid > $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ ODH. However, no corresponding order was observed in the case of the pore volume. From Table 3.4, commercial CeO₂ having a surface

area of $7 \text{ m}^2/\text{g}$ is observed to be approximately 12 times smaller than the solution combustion synthesised ceria. However, the PdO/CeO_2 - IWI, was observed to have a similar surface area to the commercial ceria as well as with catalysts prepared by fuels with a high enthalpy of combustion. Moreover, the crystallite size of the SCS catalysts was observed to show a similar trend as compared to the XRD results (see Table 3.3).

3.5 Raman spectroscopy studies

Raman spectroscopy is a powerful tool used to observe vibrational, rotational and low-frequency modes in the CeO_2 system, and it is normally used to provide fingerprints with which molecules can be characterised.¹⁵ The Raman spectroscope was used to determine the presence of oxygen vacancies and quantify them using the intensity ratios of the oxygen vacancy peak, O_v and the F_{2g} mode peak which is Raman active for the fluorite structure of ceria.^{16,4, 17}

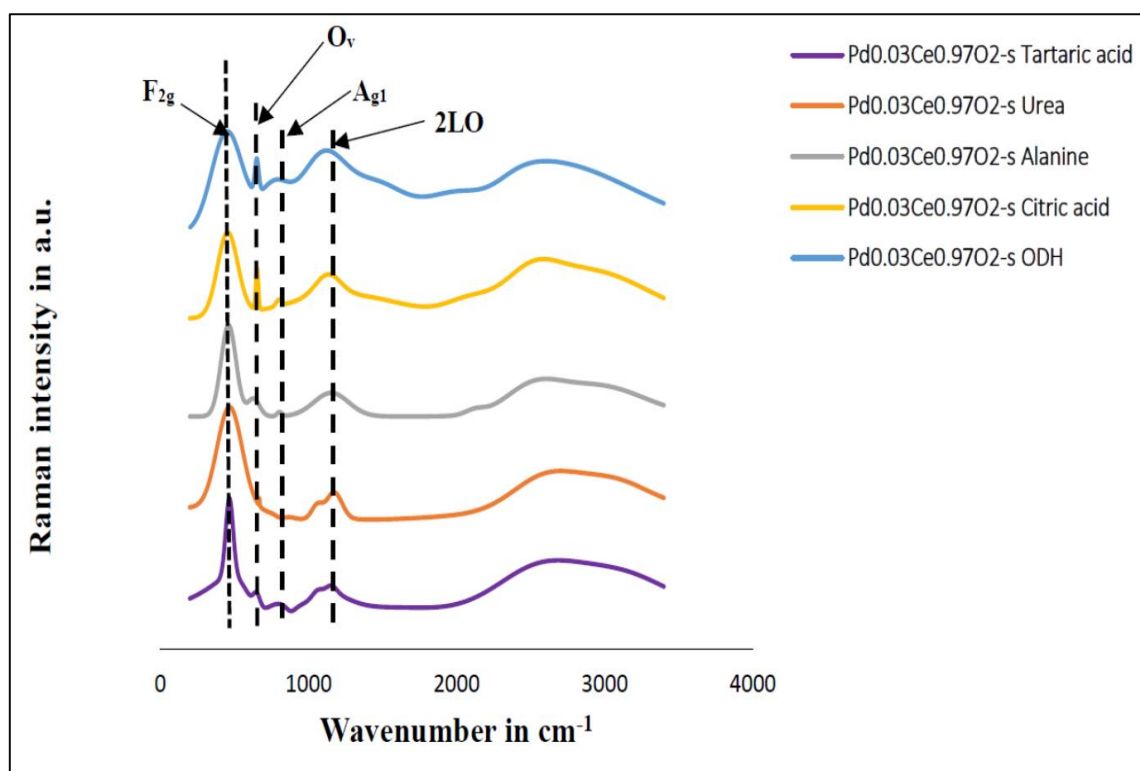


Figure 3.4 Raman spectra of $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-s}$ prepared by solution combustion synthesis.

The Raman spectra of the prepared catalysts are presented in Figure 3.4. All spectra showed a broad peak at approximately 500 cm^{-1} (Figure 3.4) due to the triply degenerate F_{2g} active mode, which is characteristic of fluorite-type structures like ceria.^{4, 16, 18-21} This peak was observed to be symmetrical in all samples and its contribution can be viewed as the symmetric broadening of the oxygen ions surrounding cerium ions.¹⁹ The peak at $590 - 595 \text{ cm}^{-1}$, which is of lower intensity, denotes the oxygen vacancies (O_v) which normally form due to the disorder-induced

components which are commonly associated with the presence of oxygen vacancies.^{17, 19} This is due to the non-degenerate Raman inactive LO mode (O_v) caused by an agitation of the local Ce-O bond symmetry that leads to the relaxation of the symmetry selection rules.^{4, 17, 19} Thus, increased intensities of this peak shows the ceria lattice agitation caused by insertion of Pd cations in the ceria lattice which resulted in the O_v formation.^{17, 19, 20}

Table 3.5 Oxygen vacancies of the synthesised catalysts.

Catalysts	oxygen vacancy ^a (O_v/F_{2g} intensity ratio)
Commercial CeO_2	0.001
CeO_2-SCS-urea	0.018
PdO/CeO_2- IWI	0.019
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Tartaric Acid	0.175
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Urea	0.035
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Alanine	0.194
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Citric Acid	0.495
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ ODH	0.328

^a Oxygen vacancy calculated based on intensity ratio [$I_{660\text{cm}^{-1}}/I_{500\text{cm}^{-1}}$]

The $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ citric acid catalyst showed the highest O_v/F_{2g} intensity ratio, which suggests that this catalyst had more defects compared to the other catalysts, and this was further confirmed using the O_v/F_{2g} intensity ratio presented in Table 3.5. Furthermore, Priolkar *et al.* outlined that most Pd^{2+} incorporation occurs in CeO_2 when the crystallite size is around 30 nm which correlates with the experimental results.²² The peaks at approximately 827 cm^{-1} and 1127 cm^{-1} denotes the A_{g1} and 2LO modes respectively.^{17, 23, 24} The presence of the A_{g1} peak confirm the O-O vibrational stretching of peroxides originating from adsorption of molecular oxygen onto two electron defects.^{4, 17, 20, 21} Moreover, this peak is observed in the presence of oxygen vacancies. The 2LO mode peak is referred as a second-order Raman mode.^{17, 20, 23-26} Cwele *et al.* showed that $\text{Pd}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ prepared by urea promoted high oxygen vacancy which is due to the small crystallite size of CeO_2 obtained and these results were in agreement with the results obtained by other authors including Filtschew *et al.*¹⁷ However, in this study, all catalysts with a CeO_2 crystallite size ranging from 10 nm – 18 nm exhibited a small amount of oxygen vacancies which is in contradiction to the results of Filtschew *et al.* Furthermore, it was observed that the catalysts with a crystallite size closer to 30 nm exhibited a high amount of oxygen vacancies which is in accordance with the results obtained by Priolkar *et al.*²²

From Table 3.5, The O_v/F_{2g} ratio was observed to decrease in the order of $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ citric acid > $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ ODH > $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ alanine > $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ tartaric acid > $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ urea when comparing fuels. However, the commercial CeO_2 material showed a smaller amount of defect sites when compared to CeO_2 -SCS-urea. A similar trend was observed when comparing the PdO/CeO_2 - IWI and $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ urea catalysts, suggesting SCS catalysts may have enhanced redox properties due to an elevated number of oxygen vacancies.

3.6 Scanning electron microscopy

Scanning electron microscopy was used to view the morphology of the prepared catalysts. A correlation between the enthalpy of combustion and the amount of produced gases by the combustion reactions of (tartaric acid, urea, β -alanine, citric acid and ODH) and the morphology of the resultant powders can be observed in Figure 3.5.^{1, 13, 14} The $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ tartaric acid showed a sponge like morphology with irregular pore sizes which can be attributed to the voluminous nature of the combustion. The urea synthesised catalyst showed a spherical like morphology caused by the low enthalpy of combustion associated with this fuel.^{1, 4} Moreover, Vita *et al.* outlined that the combustion via urea as fuel is a controlled combustion with less voluminous gases, thus resulting in ceria catalysts with a high surface area as also seen in this study.¹ The alanine catalysts showed a foam like morphology with irregular pore size and rudimentary particles.

The citric acid catalyst also showed a sponge like morphology and it was observed to be very porous. This catalyst showed a similar morphology to the tartaric acid catalyst; however, it was observed that the crystallite sizes, surface area and oxygen vacancies were different. The ODH catalyst was observed to have a layered morphology which was formed due to the high temperatures reached during the combustion. Vita *et al.* noted that a fuel with high a enthalpy of combustion exhibited a high adiabatic temperature increase during the combustion synthesis with ODH assisted combustion reaching temperatures close to 1000 °C and presented a material with similar morphology to that obtained in this study.¹

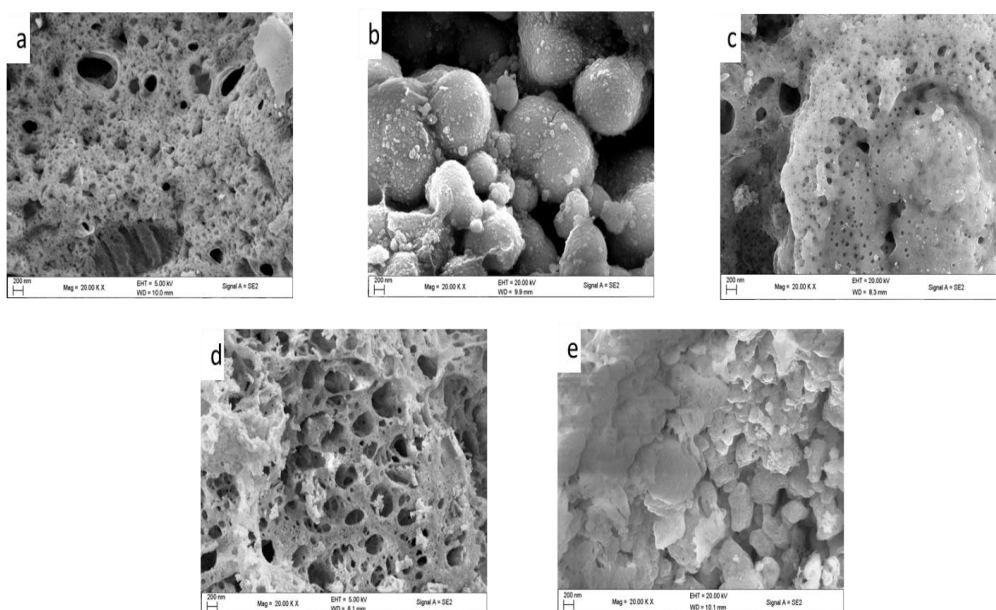


Figure 3.5 SEM images of $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ synthesised using a) Tartaric acid, b) Urea, c) Alanine, d) Citric acid and e) ODH

3.7 Transmission electron microscopy

The transmission electron microscope (TEM) was used to obtain the particle size, metal distribution, particle shape and surface morphology of the various catalysts.

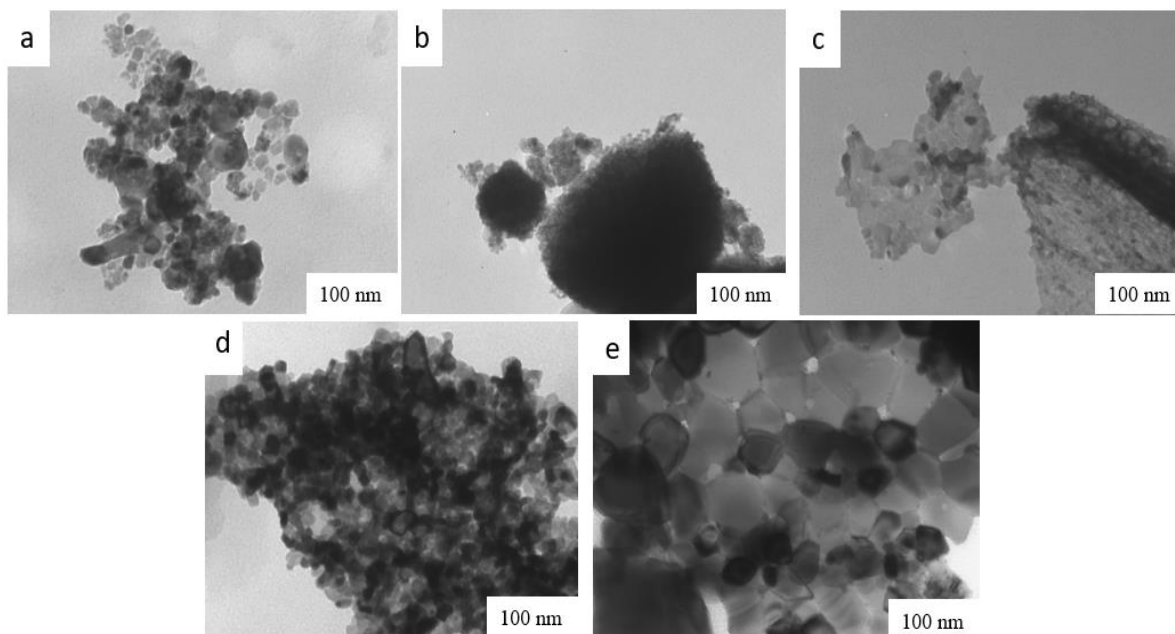


Figure 3.6 TEM images of $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ synthesised using a) Tartaric acid, b) Urea, c) Alanine, d) Citric acid and e) ODH

The TEM images, shown in Figure 3.6, show that the Pd (dark spots) is well distributed in all the catalysts prepared, however, in most cases, the Pd particle size proved difficult to obtain. The lack of visible and distinctive Pd on the surface could be attributed to the incorporation of the metal as Pd^{2+} and this could also be attributed to instrument limitations, such as resolution and magnification. Therefore, high resolution TEM was performed to confirm the structural differences and extent of substitution. The morphology and particle sizes were observed to be different for the various catalysts as similarly observed from the SEM images.

3.8 High-resolution Transmission electron microscopy

The prepared catalysts were further analysed using high-resolution transmission electron microscopy (HRTEM) to obtain the surface morphology, metal dispersion and d-spacing of the lattice planes. The interplanar spacings between the adjacent fringes were measured to be 0.32 nm for all the prepared catalysts, which is known to be due to the d_{111} lattice plane of ceria.^{4, 27} The $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ citric acid system was observed to have a cubic like morphology with larger particles of ceria. However, the other catalysts' morphologies were without any specific crystal form as shown in Figure 3.7.

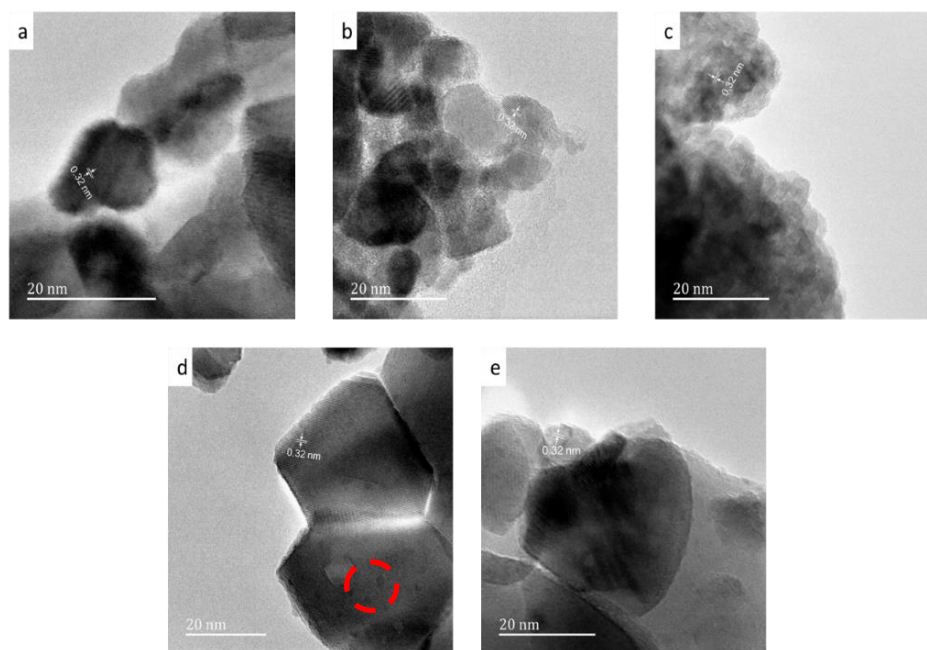


Figure 3.7 HRTEM images of $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ using a) Tartaric acid, b) Urea, c) Alanine, d) Citric acid and e) ODH

The HRTEM line scan was performed to confirm the distribution of Pd and it was observed that all the prepared catalysts showed an even dispersion of Pd across the particle as shown in Figure 3.8.

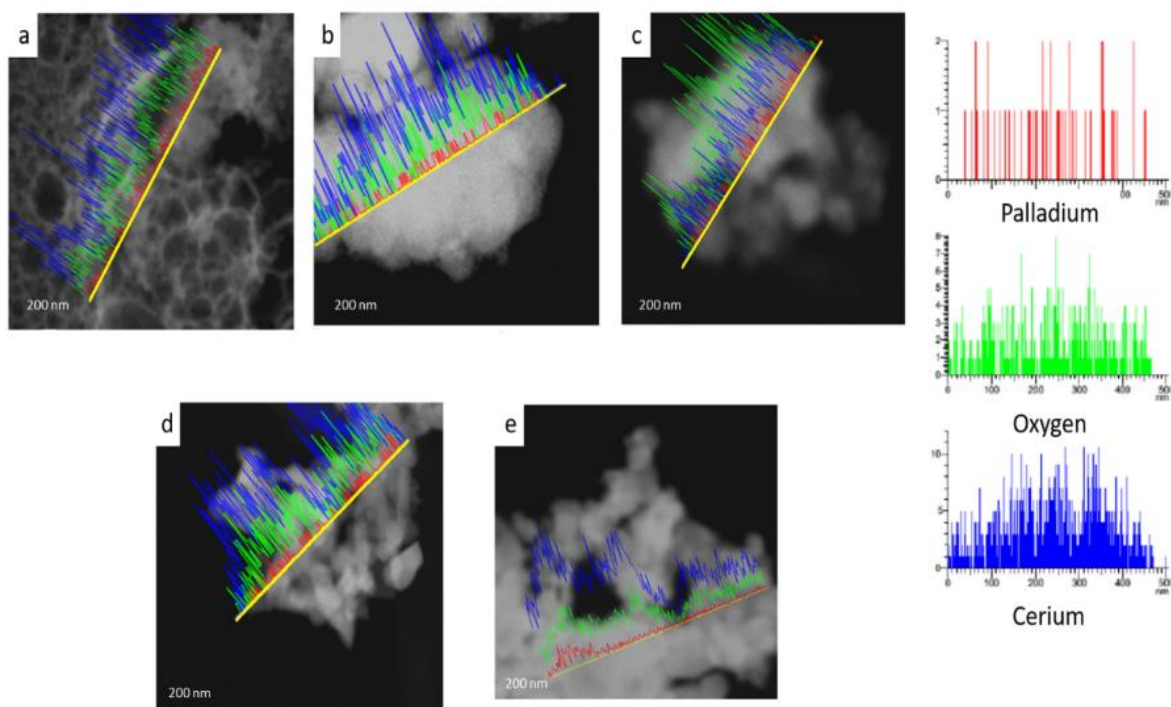


Figure 3.8 HRTEM (line scan images) of $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ synthesised using a) Tartaric acid, b) Urea, c) Alanine, d) Citric acid and e) ODH

3.9 Temperature programmed reduction (TPR) studies

Hydrogen TPR is a characterisation technique that provides a better understanding of the reduction capability of a metal oxide. In addition, this technique can also be used to quantify the presence of active metal species via hydrogen consumption.³ The hydrogen consumption by the active metal cannot be more than 100%. Thus, when H_2 consumption is greater than 100%, it indicates H_2 spill over, which is known to occur during the supporting of precious metals.³ From the studies of Colussi *et al.*, it was seen that $\text{Pd}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ prepared by solution combustion synthesis and palladium nitrate as a palladium precursor presented a Ce-O-Pd supercell, which also contributed to the H_2 spill over.³ The TPR profiles of the prepared catalysts are presented in Figure 3.9. All samples showed three reduction peaks in the H_2 -TPR analysis. The first peaks was observed at lower temperatures, around 38 °C to 110 °C, which was attributed to the reduction of Pd species (PdO) in the presence of Pd-Ce which is known to reduce the reduction temperature of PdO.^{3, 28} However, the catalysts prepared by ODH and citric acid as fuel showed a peak for hydrogen release assigned to the decomposition of β -Pd hydride species. These observations were also made by Colussi *et al.*, who further outlined that the hydrogen adsorption on $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ prepared by ODH occurs at temperatures around 20 to 30 °C, which is below the initial analysis temperature used here.³

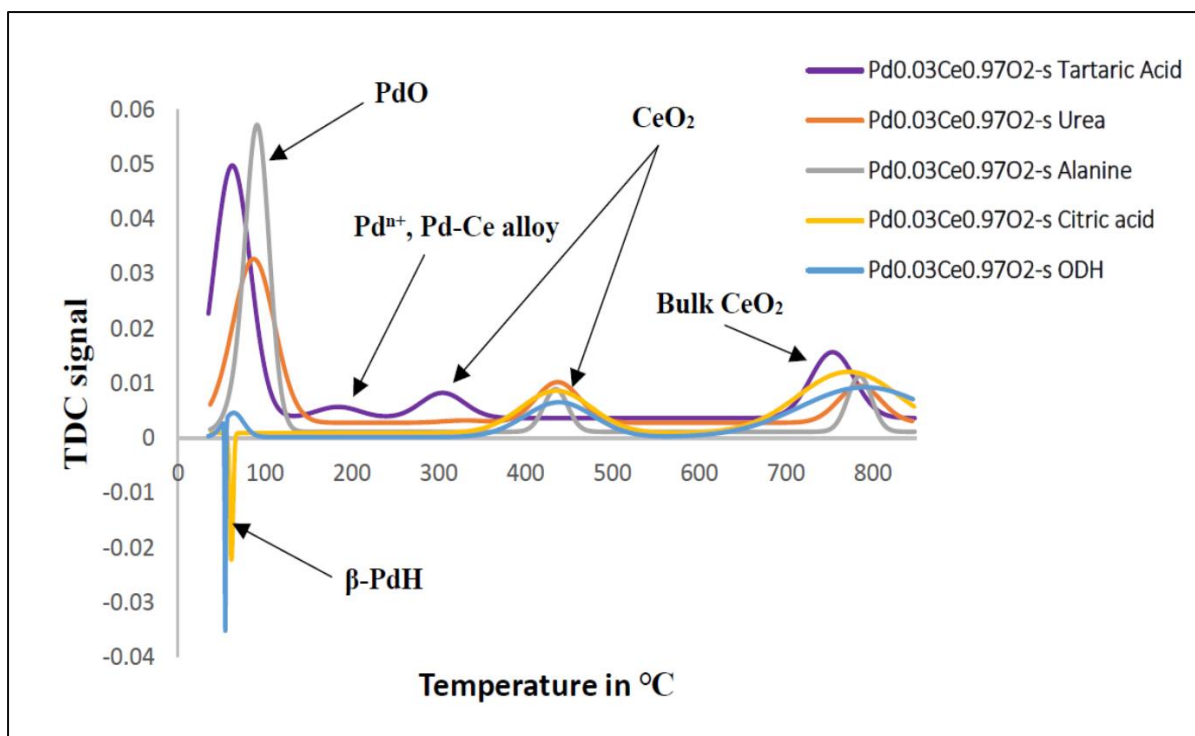


Figure 3.9 TPR of $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ prepared by solution combustion synthesis.

The presence of $\beta\text{-PdH}$ suggested that $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ prepared by ODH and citric acid have large particles of unsupported PdO and a minimum amount of supported PdO. This is also observed in the XRD of the citric acid catalyst in which peaks for PdO are observed, suggesting it is supported on the $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ surface. Furthermore, this suggests there is hydrogen spill over or a reduction of ceria, which is known to occur on reducible supports supporting noble metals. The peaks obtained at temperatures between 140 °C to 450 °C were attributed to the reduction of bulk PdO, Pd-O-Ce and the partial reduction of ceria. However, the tartaric acid catalyst was observed to show a reduction peak at 200 °C which could be attributed to the presence of Pd^{n+} species and the decoration of Pd, Pd^{n+} and PdO by cerium ions which results in the formation of Pd-Ce alloy type species.^{3, 28, 29} All peaks obtained at temperatures above 640 °C were attributed to reduction of bulk ceria.³ As observed from Figure 3.9, the highest extent of reduction occurred at temperatures below 250 °C and it was attributed to the reduction of Pd species and thus the hydrogen consumption of Pd species was calculated below 250 °C.

Table 3.6 The hydrogen consumption and release calculated below 250 °C.

Catalysts	Hydrogen consumption (mmol)	Hydrogen release (mmol)
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Tartaric Acid	0.328	-
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Urea	0.603	-
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Alanine	0.642	-
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Citric Acid	-	0.0379
$\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ ODH	-	0.0222

The $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ alanine catalyst showed a high hydrogen consumption, like the hydrogen consumption of the $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ urea catalyst. The $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ tartaric acid was observed to have half the hydrogen consumption of $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ urea suggesting that some Pd species were not accessible, thus probably being shielded by Ce ion. This also suggests that the Ce-O-Pd and Ce-O-Ce bonds are stronger in the tartaric acid prepared catalysts and thus were difficult to reduce.

3.10 The XPS analysis of $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$

The XP spectra of the 3d lines of Ce for all catalysts are shown in Figure 3.10. These spectra are labelled using the reported system by Burroughs *et al.*,³⁰ where v and u represent the spin-orbit coupling of $3d_{5/2}$ and $3d_{3/2}$, respectively and v , v'' and v''' are assigned to Ce^{4+} , while v_0 and v' belong to Ce^{3+} . The same order is applicable for the u lines. As can be seen in Figure 3.10, the surface of all the catalysts contain mainly Ce^{4+} with some Ce^{3+} , as was also seen with Raman. The presence of Ce^{3+} on the surfaces of these catalysts indicates the high potential of the SC technique to form defects in ceria-based materials. The population of defect sites was calculated using the suggested method by Zhang and Shen.³¹ The catalysts prepared using citric acid produced the highest quantity of Ce^{3+} on its surface, while the use of ODH as a fuel resulted in the lowest number of Ce^{3+} on the surface of the corresponding catalyst, as shown in Table 3.7.

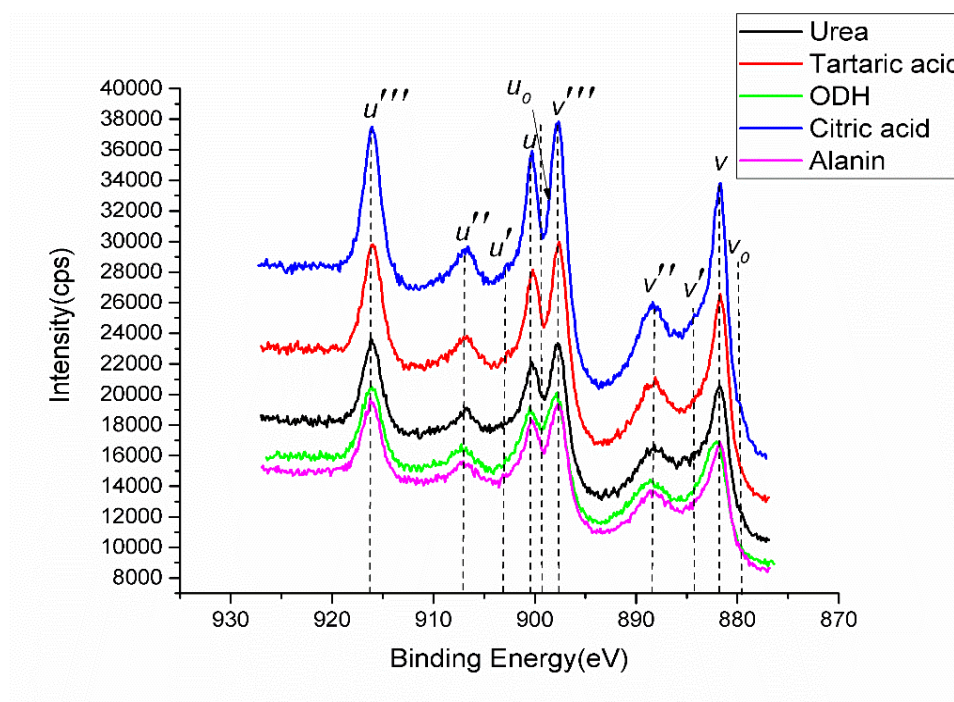


Figure 3.10 The XP spectra of Ce3d of catalysts prepared by SC using different fuels.

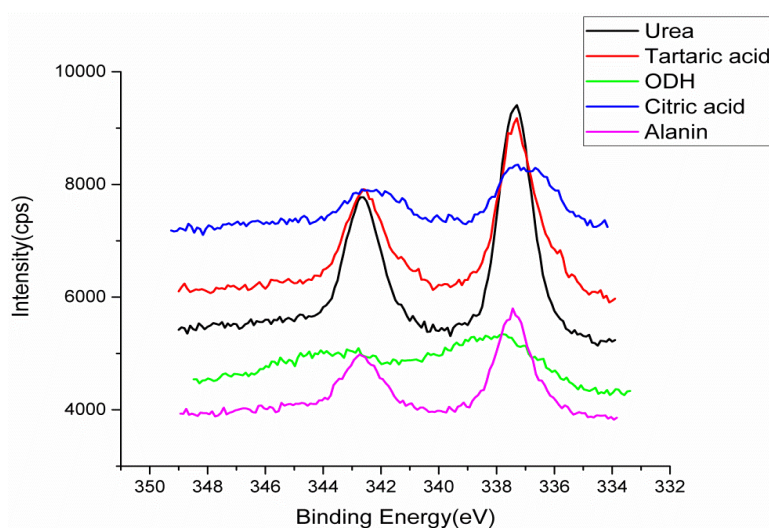
The presence of Ce^{3+} has a direct correlation with the number of defect sites on the surfaces of these ceria-based catalysts. The increases of these defect sites are believed to increase the formation of Frankel-type oxygen vacancies on the surface, and therefore, enhance the redox properties of these materials.³² The amount of these defect sites was compared to different characteristics of each fuel, such as the enthalpy of combustion, and oxygen/carbon ratio, without any correlation being found. This complexity indicates that various parameters such as the chelating capability of the synthesis matrix and the amount of substituted Pd during the SC synthesis may affect the densities of these sites in the final catalysts.

The $3d_{5/2}$ of Pd in PdO shows a peak at ~ 336.6 eV,³³ while the $3d_{5/2}$ of Pd in PdO₂ appears at 338 eV as shown in Figure 3.11.³⁴ However, recent studies on CePd solid solutions have shown that the high binding energy of 337.7 eV observed for Pd in ceria, is not for the 4^+ state.^{12, 35-37} The EXAFS, XRD and computational analyses have shown that these Pd species are still Pd^{2+} with a shorter Pd-O bond length (with ionic nature) and highly oxidizing environment imposed by oxygen atoms in the lattice of ceria.^{36, 37} Based on the findings of Senftle *et al.*, it seems the Pd^{4+} forms *in situ* and under the reaction conditions, facilitates the methane combustion reaction.^{38, 39}

Table 3.7 The population of Ce^{3+} on the surfaces of catalysts prepared using SCS with different fuels.

Catalyst	Ce^{3+} (%)
Urea	11.5
Tartaric acid	10.5
ODH	10.3
Citric acid	12.6
Alanin	11.2

The increase in the oxidation state of Pd^{2+} and the formation of Pd^{4+} seems to originate from the ionic nature of Pd-O in ceria, the oxidizing environment supplied by oxygen atoms in the ceria lattice and the high temperature during the catalytic methane combustion reaction. The XPS data for $3d_{5/2}$ and $3d_{3/2}$ of Pd are shown for all catalysts in Figure 3.11. Urea, tartaric acid, and alanine showed only the Pd^{2+} in the lattice of ceria, which shows a high propensity of these fuels to cause full substitution of Pd in the lattice of ceria with the chosen loading in this study. ODH and citric acid showed Pd^{2+} in the lattice of ceria and a segregated phase of PdO. The observed PdO, out of the lattice of ceria, for catalysts prepared using ODH and citric acids as the fuels were also confirmed by H_2 -TPR analyses by the detection of a PdH_2 peak.

**Figure 3.11** The XP spectra of Pd 3d of catalysts prepared by SC using different fuels.

The surface compositions of all catalysts are shown in Table 3.8. None of the catalysts showed 2 wt.% of Pd on the surface, which suggests that most of the Pd is substituted in the bulk structure of ceria. Furthermore, urea showed 0.01 atom% of Pd in the outermost lattice of the ceria, while the smallest loading was observed for the catalyst prepared using citric acid. As

mentioned, citric acid and ODH showed some PdO on their surfaces. The deconvolution of the Pd 3d lines for these catalysts showed that 36.0% and 17.3% of Pd on the surface is in the form of PdO for citric acid and ODH, respectively.

Table 3.8 The population of Pd^{2+} on the surfaces of catalysts prepared using SCS with different fuels from XPS analysis.

Catalysts		Surface composition			
		Type of Pd^{2+} (%)		Pd loading (wt.%)	
		Pd^{2+} in CeO_2	PdO	Pd^{2+} in CeO_2	Supported PdO
Urea	0.0100	100.0	0	1.80	0
Tartaric acid	0.0060	100.0	0	1.80	0
ODH	0.0030	82.7	17.3	1.44	0.30
Citric acid	0.0005	64.0	36.0	1.11	0.63
Alanine	0.0060	100.0	0	1.91	0

XP spectra of O1S lines of all catalysts were investigated to gain a better understanding of the oxygen species on the surface of these catalysts (Figure 3.12). The peak at ~ 529.0 eV is representative of lattice oxygen that is bonded to the metal.³² The peak at ~ 531.0 eV shows chemisorbed oxygen species on the surface, while the peak at ~ 534.0 eV is indicative of physisorbed oxygen species on the surfaces of these catalysts.³²

The urea, alanine and tartaric acid synthesised catalyst, showed similar O1s XPS spectra that contain all types of oxygen that were discussed and can be found on the surface of ceria (Figure 3.12). The peak corresponding to physisorbed oxygen species was absent for the catalyst that was prepared using citric acid as a fuel. Furthermore, a shift towards higher binding energies was observed for both lattice and chemisorbed oxygen species for catalysts prepared using citric acid (Figure 3.12). This observation is a common phenomenon and frequently occurs for ceria with a highly defected surface (with a high density of Ce (III)).⁴⁰ The prepared catalyst using ODH as a fuel showed two types of lattice oxygen that demonstrate that the M-O bonds in this catalyst have similar characteristics to both citric acid and other fuels synthesised catalysts. Furthermore, the intensity of peaks corresponding to the chemisorbed oxygen species

was relatively more abundant for the ODH synthesised catalyst when compared with the other fuel synthesised catalysts (Figure 3.12). This might indicate the high oxygen storage capacity of this catalyst.

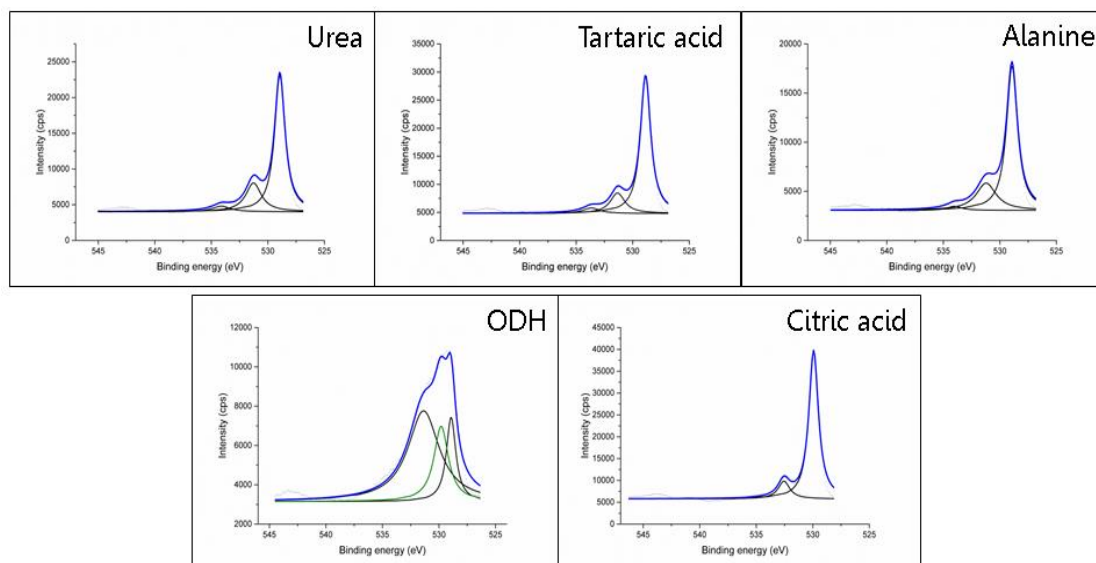


Figure 3.12 The XP spectra of O1s of catalysts prepared by SC using different fuels.

As was seen in the XPS analysis of the Ce3d lines, the use of citric acid resulted in a catalyst with the highest number of Ce^{3+} on its surface. These defect sites are believed to enhance the formation of oxygen vacancies on the surface of ceria and improve the redox nature of the ceria-based catalysts. Thus, a highly oxidized surface, even in the presence of methane, is expected for the catalyst prepared using citric acid as a fuel. Also, several studies have shown that PdO in the lattice of ceria transforms to PdO_2 during the methane combustion catalytic reaction, and these species are believed to be the *in situ* active sites for this reaction.^{38, 39}

The use of citric acid and ODH as fuels during the SCS of these catalysts resulted in some segregated PdO. This PdO phase seems to have a large crystallite size, since both catalysts showed negative signals in the H_2 -TPR analysis. According to the report by Lang et al., Pd_x^+ and Pd_xO^+ species have high potential to dehydrogenate CH_4 molecules.⁴¹ This dehydrogenation is known as a rate-determining step in the methane combustion reaction.⁴² The facile transformation of existing PdO (detected using XPS) to PdH_2 (identified using H_2 -TPR analysis) shows the possible presence of reduced species of Pd under the reaction conditions that can lower the energy barrier of the dehydrogenation step. Afterward, the *in situ* formed PdO_2 species in the lattice of ceria seems to accelerate the oxygen insertion step and result in complete combustion of methane as was suggested by Senftle et al.^{38, 39} The explained

synergic effect between the PdO phase and *in situ* formed PdO_2 in the lattice of ceria is required for the low-temperature methane combustion reaction over $\text{Ce}_{1-x}\text{Pd}_x\text{O}_{2-\delta}$ catalysts.

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Chapter 4

4.1 Methane combustion over ceria-based catalysts

Catalytic methane combustion is known to play a significant role in both environmental and industrial sectors. Methane is known to be 20 to 30 times more potent than carbon dioxide as a greenhouse gas.^{1,2} Recently, catalytic methane combustion has been viewed as a viable route to minimise unburned hydrocarbons in automobiles engines. Moreover, the heat generated from methane combustion can be used to heat the steam reforming processes in and integrated fuel cell.³ Palladium-ceria-based catalysts are known to catalytically combust methane at low-temperature.^{2,4-6} In this study, solution combustion synthesis (SCS) and wet impregnation were investigated as methods to synthesise Pd-Ce catalysts for the purpose of methane combustion.

4.1.1 Methane combustion over commercial and SCS ceria

Methane combustion is known to occur over ceria-based catalysts⁶⁻¹⁰, however, no direct correlation between the catalyst synthesis methodology and activity has been reported. A major component of the Pd-Ce based catalysts is the support. However, it is not known how the method of synthesis of the support itself can affect methane combustion. To investigate this, commercial ceria was compared with SCS prepared ceria. The commercial-ceria and SCS-ceria (synthesised using urea as a fuel) were then investigated for methane combustion with 4% methane in air at a GHSV of 15 000 h⁻¹. Figure 4.1 gives the conversion of the methane over the two types of ceria prepared.

In general, SCS ceria-based catalysts are known to contain more oxygen vacancies and improved redox properties than commercial ones.¹⁰⁻¹² Oxygen vacancies are known to positively affect methane combustion, as they ease the release of lattice oxygen which plays a key role in methane combustion.^{10, 11, 13, 14}

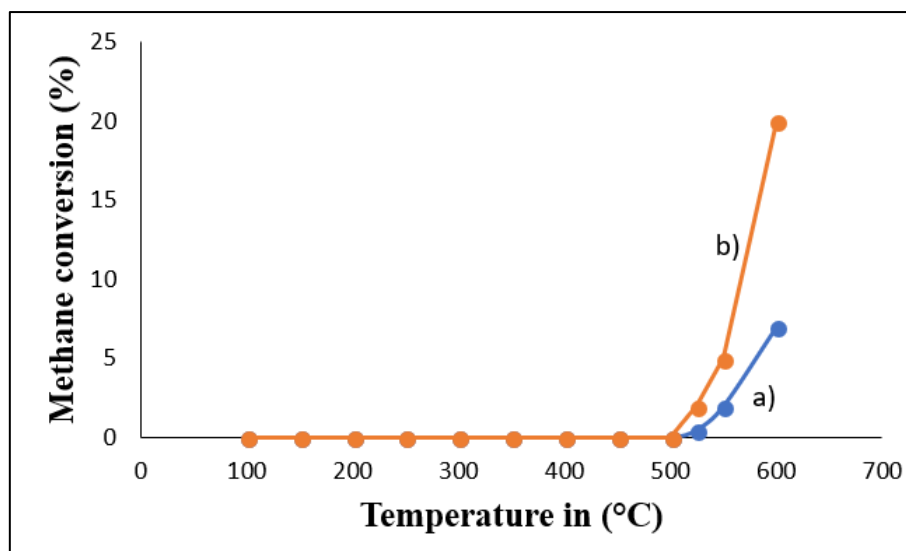


Figure 4.1 Methane combustion over a) CeO₂-comm and b) CeO₂-SCS with 4% CH₄ in air and at a GHSV of 15 000 h⁻¹

From Figure 4.1, it is observed that SCS-ceria became active and showed conversion at temperatures above 500 °C. Additionally, the SCS-ceria showed a higher methane conversion, 20 % in comparison to the 7 % observed for the commercial ceria, when compared at 600 °C. This difference in conversion can be attributed to the various physical properties such as surface area, crystallite size and oxygen vacancies which is explained in more detail herein. In general, catalytic methane combustion is not favoured at low-temperatures and thus it can be assumed that the activation of methane above 500 °C is thermodynamically favoured. However, the rate of the combustion reaction is also related to the surface area and oxygen vacancies. As observed in the Table 3.4 and Table 3.5, the SCS-ceria has a higher surface area and order of magnitude more oxygen vacancies than commercial ceria. In general, the higher the surface area, the higher the population of available sites for the reaction to take place which in turn increases the activity.¹⁵

Müller *et al.* observed that the catalyst with the higher surface area resulted in a higher methane combustion and further stated that this is due to more available sites and more space for a reaction to occur.¹⁵ In contrast, Pu *et al.* observed a higher methane combustion over a small surface area catalyst and attributed the increase in catalytic activity to the elevated redox properties.¹⁶ However, several researchers have agreed that catalysts with higher oxygen storage capacity (OSC) result in higher methane combustion.^{14, 17-19} Jin *et al.* also stated that the high methane combustion over ceria is due to its facile redox ability and high oxygen storage capacity.^{10, 14} Ceria is known to switch between reduced and oxidized states, thus, resulting in easy oxygen exchange within its lattice structure for the various composition of the

reactants.^{10, 20, 21} Furthermore, the participation of surface oxygen species and vacancies ensures the availability of oxygen for the oxidation of methane.^{10, 19}

4.2 Methane combustion over palladium-ceria based catalysts

Among various metals employed for methane combustion, noble metals such as palladium were investigated due to its superior activity compared to that of transition metals.^{7, 19, 22} However, few studies have been conducted on the effect of the synthesis method, therefore, this study investigates the effect of the synthesis routes. The 2 wt.% PdO/CeO₂ prepared by wet impregnation using a commercial ceria and by the solution combustion method were compared for methane combustion by testing with 4 % methane in air mixture at a GHSV of 15 000 h⁻¹. Figure 4.2 illustrates methane combustion activity over PdO/CeO₂ prepared via incipient wet impregnation and PdO/CeO₂ prepared via the solution combustion synthesis method using urea as fuel.

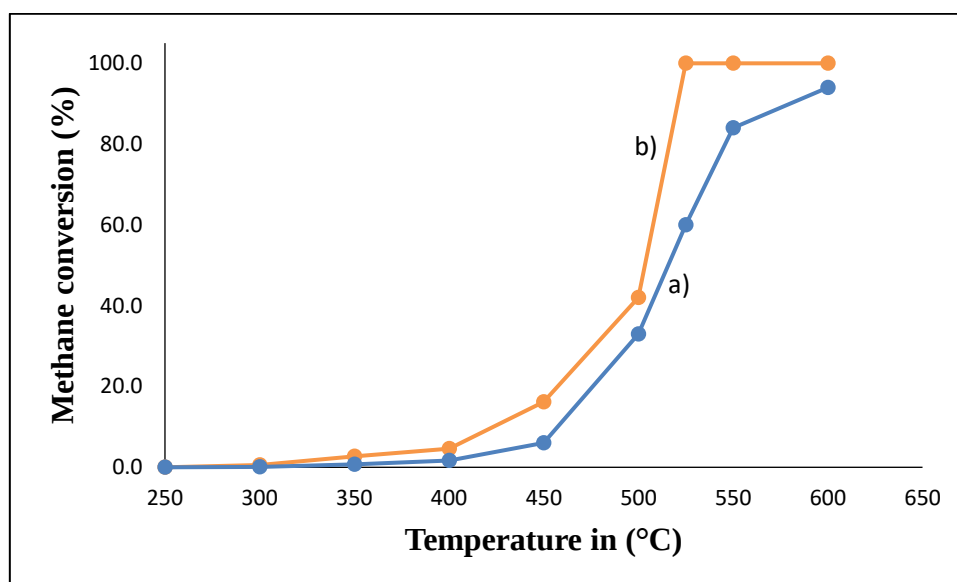


Figure 4.2 Methane combustion over a) PdO/CeO₂- wet impregnation and b) PdO/CeO₂-SCS at 4% CH₄ in air and at a GHSV of 15 000 h⁻¹

From Figure 4.2, it can be observed that the SCS catalyst gives a higher conversion in comparison to the wet impregnation catalyst at temperatures above 300 °C. In addition, the SCS catalyst was observed to reach T₁₀₀ at 500 °C, while T₁₀₀ could not be established for the wet impregnation catalyst in the reaction temperature range studied, that is, up to 600 °C. The reasons for this difference in catalytic activity were attributed to differences in physical properties such as surface area, metal support interactions and surface morphology, as speculated also by other authors.^{14, 19, 22} The increase in conversion over the SCS catalyst can

also be attributed to the increased oxygen vacancies due to palladium doping and strong metal-support interactions. Thevenin *et al.* outlined the importance of the palladium-ceria interaction and further stated that the palladium-ceria interactions are mostly responsible for the increase in activity for a PdO/Ce/Al₂O₃ catalyst in comparison to PdO/Al₂O₃.²³ Jin *et al.* observed that ceria catalysts promoted by palladium or ceria-based solid solutions exhibit higher activity and stability for methane combustion.¹⁰ The strong interaction between palladium and ceria, which leads to the formation of a kind of cationic palladium species, can be used to explain this outstanding property.²⁴ Jin and Cwele co-workers further explained that the dispersed ionic Pd on CeO₂ and the presence of Pd in the lattice structure of ceria could lead to high dispersion for a given Pd loading.^{10,25} This results in improved chemical and structural stability of Pd²⁺ ions due to the formation of a Pd–O–Ce supercell structure.¹⁴ Colussi *et al.* also observed that PdO/CeO₂ -SCS exhibited a higher surface area in comparison to the wet-impregnation catalyst, which is in good agreement with the obtained results in this study.¹⁴ Moreover, Colussi *et al.* further stated that PdO/CeO₂ -SCS presented a distinct Pd-O-Ce which stabilizes the PdO resulting in the low temperature needed to obtain 100 % methane conversion.¹⁴

4.2.1 Methane combustion with SCS catalysts

The PdO/CeO₂ -SCS catalyst was found to be highly active in comparison to the wet-impregnation catalyst. However, there are several parameters in solution combustion synthesis that affect the SCS catalyst.²⁶ These parameters include the ignition temperature, amount of water, fuel to oxygen ratio and the type of fuel. However, in literature, there is minimal knowledge on how the type of fuel affects the physical and chemical properties of the SCS catalyst and, consequently, the catalytic activity for methane combustion.

4.2.2 Effect of fuels on methane combustion

To evaluate the effect of fuels on methane combustion, a series of Pd/ceria catalysts containing 2 wt.%. Pd were prepared by the SCS method with different fuels, namely tartaric acid, urea, β-alanine, citric acid monohydrate and oxalyl hydrazide (ODH). These catalysts were then tested for methane combustion with 4 vol% methane in air and at a GHSV of 15 000 h⁻¹.

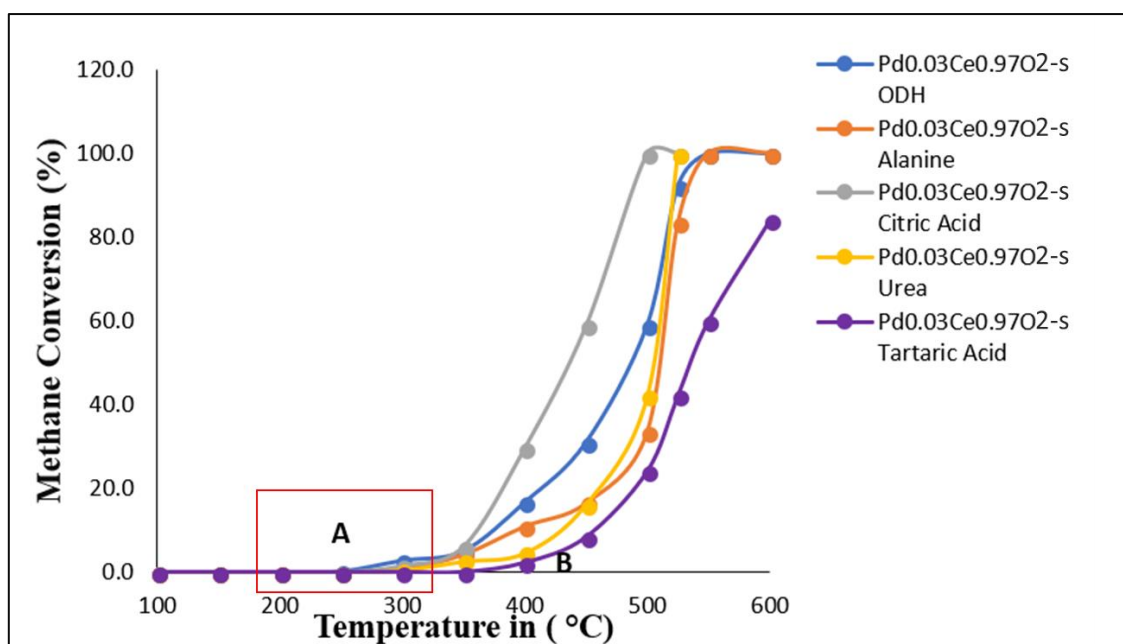


Figure 4.3 Methane combustion over $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ prepared by various fuels at 4% CH_4 in air and at a GHSV of $15\,000\text{ h}^{-1}$

All catalyst showed acceptable methane combustion activity at temperatures below and up to $600\text{ }^\circ\text{C}$ as shown in Figure 4.3. The $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ citric acid showed the highest methane conversion at all temperatures in comparison to the other $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ catalysts prepared using different fuels. At temperatures below $350\text{ }^\circ\text{C}$ (section A in Figure 4.3 and in Figure 4.4), it is seen that the methane activity decreased in the following order: $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}\text{ODH} > \text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}\text{citric acid} > \text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}\text{alanine} > \text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}\text{urea}$. From the studies of Price *et al.*, it was observed that at low temperatures, the methane combustion activity depended on the palladium crystallite size and, thus, the particle size.²⁷ Additionally, the methane binding energy depended on the crystallite size and particle size. A smaller binding energy is required to bind methane to a larger crystallite size than a smaller crystallite size.²⁷ In this study, the crystallite size effect was observed to influence the activity and, thus, a larger crystallite size resulted in the higher methane combustion activity as shown in Figure 4.4. However, from XRD and H_2 -TPR results, these differences in activity can also be attributed to the presence of a low amount of large crystals of the supported PdO.

From Figures 4.3 and 4.4, at temperatures below $350\text{ }^\circ\text{C}$, the reaction can be assumed to occur via the Langmuir Hinshelwood (LH) mechanism, wherein methane combustion occurs via the interaction between the CH_x species and oxygen on the Pd surface as shown in Scheme 1.1 and Figure 1.12.²⁸ However, this quickly changes as the reaction temperature is increased toward $600\text{ }^\circ\text{C}$.

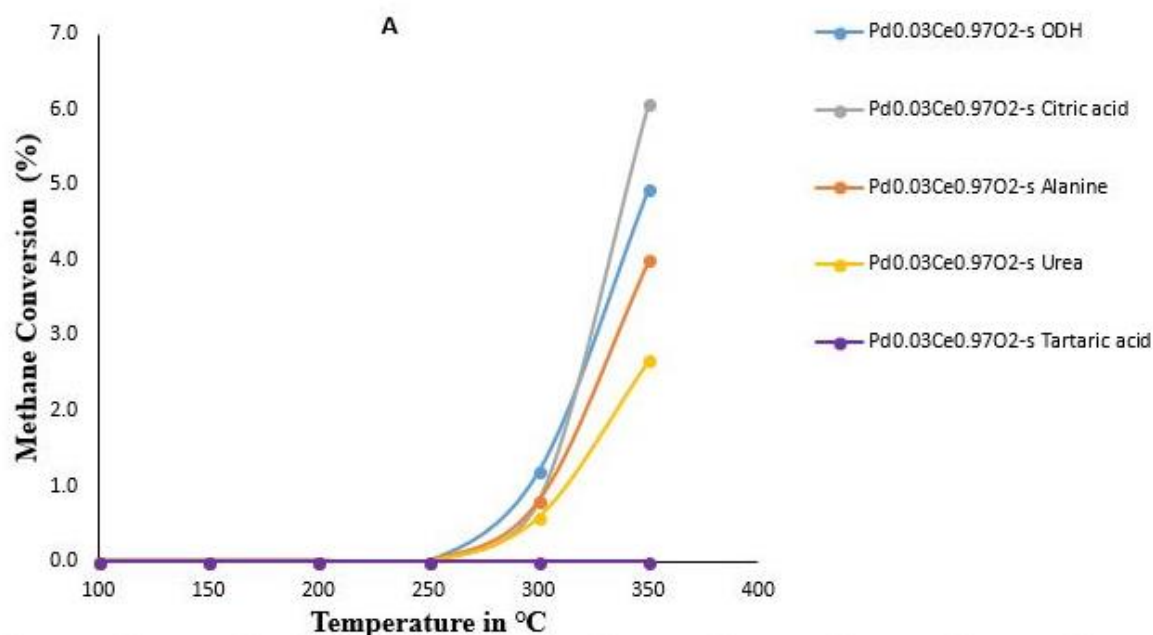


Figure 4.4 The effect of crystallite on methane combustion under 350 °C

At 350 °C, all catalyst gave a methane conversion below 10 % and the reaction is expected to be heat and mass transfer limited. This can further explain the increase in methane conversion over larger PdO particles.^{27, 28} At temperatures above 350 °C, the activity depends on the microstructure, porosity, redox properties and the morphology of the catalysts/supports. Methane combustion activity was observed to decrease in the order of Pd_{0.03}Ce_{0.97}O_{2-δ} citric acid > Pd_{0.03}Ce_{0.97}O_{2-δ} urea > Pd_{0.03}Ce_{0.97}O_{2-δ} ODH > Pd_{0.03}Ce_{0.97}O_{2-δ} alanine > Pd_{0.03}Ce_{0.97}O_{2-δ} tartaric acid. From XRD and H₂-TPR studies, it was observed that the ODH and citric acid catalysts contained supported PdO. Moreover, the XPS studies of these catalysts confirmed the presence of supported PdO_x in highly oxidised states that can transform to PdO₂ during the methane combustion reaction. The ODH and citric acid catalysts were observed to oxidise PdO_x species which were absent in the alanine, tartaric acid and urea catalytic systems. From DFT studies by Senftle *et al.*, PdO₂ was observed to require a low energy to bind with methane in comparison to PdO.^{29, 30} Colussi *et al.* further observed that the presence of PdO_x and oxygen vacancies increased the oxygen mobility and thus the redox properties.¹⁴ The citric acid catalyst was observed to have a lower T₅₀ and T₁₀₀ in comparison to the other catalysts due to the elevated levels of PdO_x, and oxygen vacancies. From the PdO_x containing catalysts, the activity was observed to increase with an increase in the amount of PdO_x and oxygen vacancies. To clarify, PdO_x refers to PdO species in a highly oxidised environment of the CeO₂ lattice.

In the catalysts with non PdO_x species, the surface area and Pd availability played a significant role. As observed in Figure 4.3, the urea synthesized catalyst exhibited a higher methane

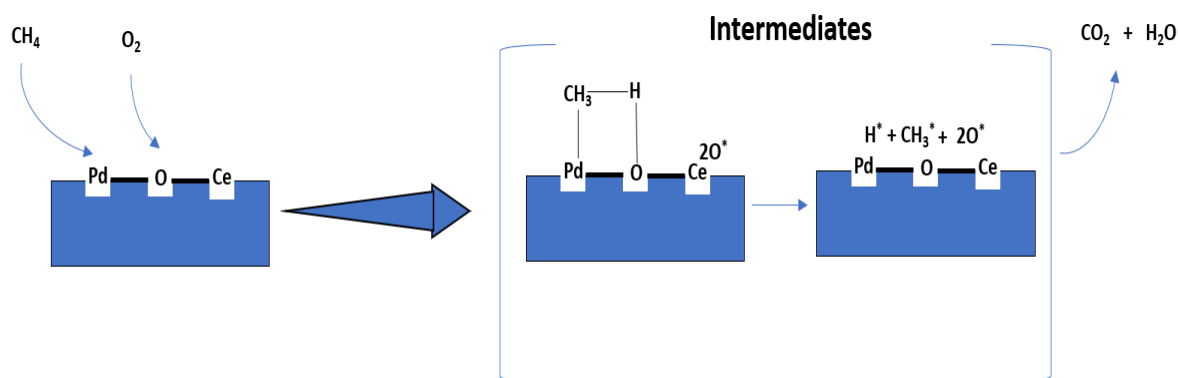
conversion in comparison to the alanine and tartaric acid catalysts due to the higher surface area as shown in Table 3.4. According to Ercolino *et al.*, a high surface area can result in more active sites for the reaction to occur resulting in an increase in the reaction activity.²² From Figure 4.3, it was further observed that the tartaric acid synthesized catalyst showed a poorer methane combustion activity which could be attributed to several factors such as surface area, amount of oxygen species and Pd species present. However, there was no clear indication of the surface area, oxygen vacancies and crystallite size effect on methane conversion obtained over this catalyst. Since this catalyst exhibited a high surface area, crystallite size and a similar amount of oxygen vacancies in comparison to the alanine catalyst, the identified poor activity of this catalyst could be attributed to Pd availability. From the H₂-TPR studies, the tartaric acid catalyst was observed to consume half the amount of hydrogen in comparison to the alanine and urea catalysts. These differences in hydrogen consumption were attributed to the Pd availability. From the TPR and XPS studies, the Pd in the tartaric acid catalyst was observed to be encapsulated by Ce³⁺/Ce⁴⁺ which resulted in less Pd being available for catalytic activity. However, the alanine catalyst was observed to have a similar methane conversion compared to the urea synthesised catalyst. This suggests that the catalyst prepared using the tartaric acid as fuel has poorer redox properties in comparison to the urea and alanine synthesised catalysts.

4.2.3 Comparison between the citric acid synthesised catalyst with the urea synthesised catalyst in methane combustion.

The citric acid synthesised catalyst was observed to be superior in methane combustion at temperatures below 500 °C. However, this catalyst was observed to have a similar T₁₀₀ (minimum temperature needed to obtain 100 % methane conversion) to the urea synthesised catalyst. In fact, the urea catalyst was observed to reach T₁₀₀ at a lower temperature in comparison to other catalysts with the exception of the citric acid catalyst. It is clear that the presences of PdO_x species on the surface of this catalyst enhances the catalyst activity. However, the surface area is also observed to play a role at temperatures above 350 °C. From the studies of Ercolino *et al.*, on methane combustion over Pd/Co₃O₄ (SCS) and PdO supported on Pd/Co₃O₄ (IWI+SCS), it was shown that the PdO supported on Pd/Co₃O₄ (IWI+SCS) exhibited higher methane conversion with a similar T₁₀₀ compared to Pd/Co₃O₄ prepared via SCS.²² They explained that the similar T₁₀₀ observed for these catalysts is due to the high surface area obtained in the Pd/Co₃O₄ (SCS) catalyst.²² Therefore, for an optimum catalyst, it appears that a minimal amount of supported PdO_x is required in conjunction with a high surface area.

4.2.4 Reaction mechanisms

At temperatures below 350 °C, the reaction mechanism is proposed to occur as shown in Scheme 4.1, wherein methane adsorbs on the catalyst surface and further dissociates to form the CH_x and H^* species. These species then react with the dissociated oxygen species resulting in the production of CO_2 and H_2O .

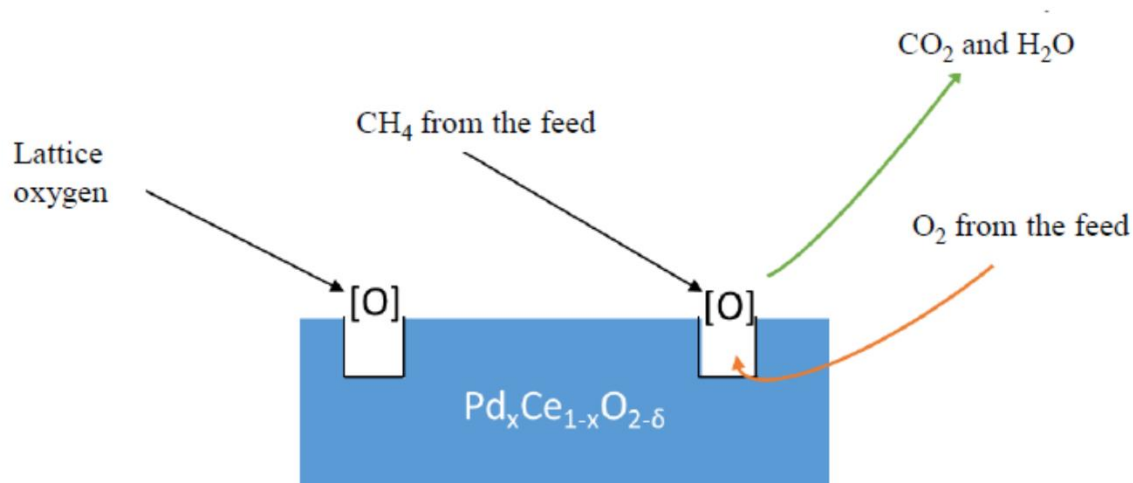


Scheme 4.1 Methane combustion via the LH mechanism.²⁸

At temperatures above 350 °C, all SCS prepared catalysts are proposed to combust methane via the Mars–van Krevelen (MvK) mechanism, wherein the CH_x species produced from the dissociation of methane react with the lattice oxygen of PdO_x to produce carbon dioxide and water. From the studies of Jin *et al.*, methane was shown to react with lattice oxygen resulting in the direct combustion of methane to CO_2 and H_2O as shown in Scheme 4.2. The lattice oxygen is then replenished by the feed oxygen. However, an in-depth study by Chen and Chin co-workers showed that methane adsorbs on the surface of Pd-O-Ce and reacts with the lattice oxygen to give OH^- and CH_3^* . The CH_3^* then quickly reacts with oxygen species to form CO_2 and H_2O in the presence of OH^- , which is in agreement with the results obtained in this study.^{31,}

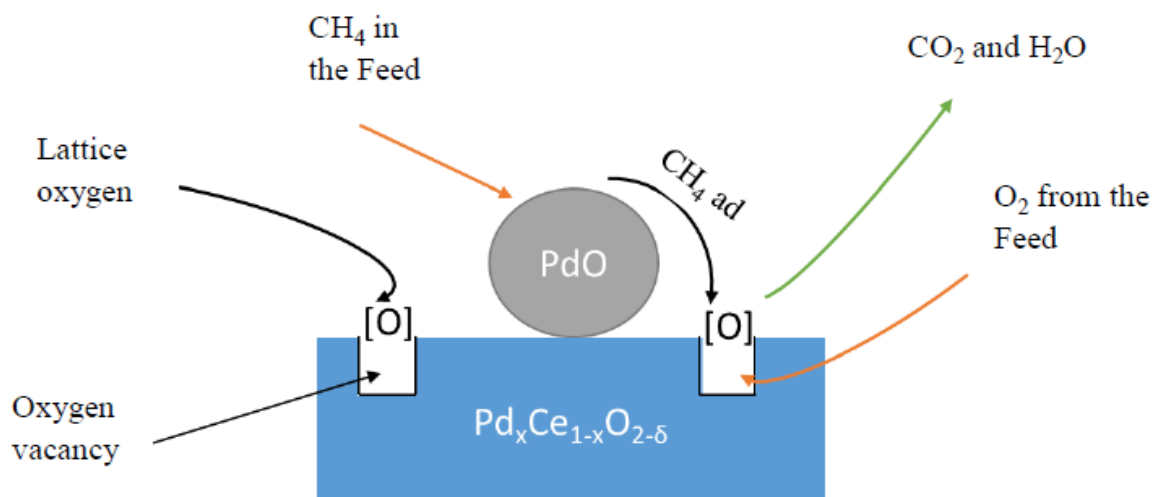
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From the XPS, XRD, and H_2 -TPR studies, the reaction mechanism for the prepared catalysts can be divided based on the Pd species contained in the catalysts. The urea, alanine and tartaric acid catalysts combust methane via the MvK mechanism, while the mechanism over the ODH and the citric acid catalysts occurs via a combination of the MvK and LH mechanisms.



Scheme 4.2 The MvK mechanism of methane combustion over $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ catalyst synthesised by urea, alanine, ODH, citric acid and tartaric acid as fuels

Citric acid and the ODH catalysts are proposed to follow an additional reaction mechanism, where methane adsorbs on the supported PdO and thereafter reacts with the lattice oxygen of the support to produce CO_2 and H_2O as shown in Scheme 4.3. Meng *et al.* stated that the adsorption of CO onto the supported $\text{PdO}/\text{Pd}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ was faster and resulted in a higher CO conversion.³³ Jin *et al.* also observed elevated redox properties in this type of catalyst and consequently higher methane combustion activity.¹⁰



Scheme 4.3 The schematic diagram of the reaction mechanism of methane combustion over $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ citric acid and $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ ODH

They further explained that the methane adsorption onto the supported PdO over $\text{Pd}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ support results in high methane combustion due to the synergistic effect between the supported

PdO and lattice oxygen mobility which seems to be present in the catalysts prepared for this study, as shown in Scheme 4.3.¹⁰ From the studies of Meng *et al.*, it was observed that the rate of CO oxidation over free PdO on PdO/Ce_{1-x}Pd_xO_{2-δ} catalyst is approximately seventy times faster than the rate over free PdO on PdO-CeO₂ catalyst as shown in Figure 4.5.³³

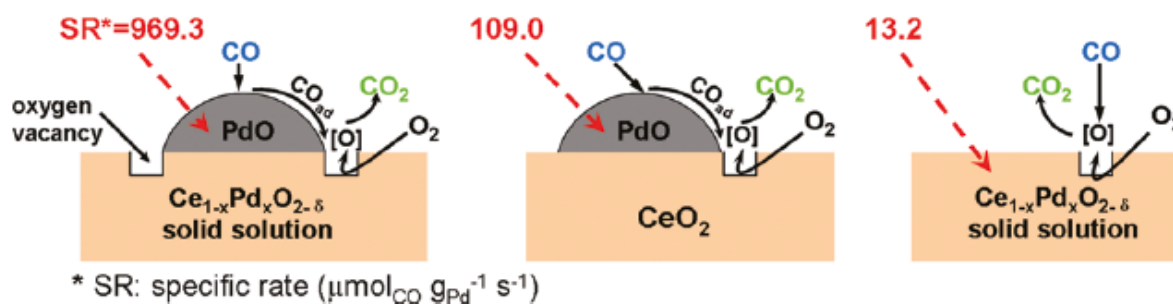


Figure 4.5 Reaction model over the Catalysts.³³

Meng and co-workers concluded that the PdO/Ce_{1-x}Pd_xO_{2-δ} catalyst exhibited a higher reaction rate due to the easy chemisorption of CO on the free surface PdO species compared to that of the Pd²⁺ species in the CeO₂ lattice structure, which could significantly lower the activation energy barrier of the reaction.

4.3 Methane combustion over the citric acid catalyst

From all catalysts tested, the Pd_{0.03}Ce_{0.97}O_{2-δ} citric acid catalyst was observed to have the best catalytic activity. However, further tests were needed at various reaction conditions to establish other important features of this catalyst such as catalyst stability, behaviour at various GHSVs and catalytic activity upon heating and cooling.

4.3.1 Heating and cooling curves

Methane combustion catalysts are known to deactivate via heating and cooling due to structural changes. At elevated temperatures, PdO tends to form Pd⁰ resulting in the catalyst's deactivation, while upon cooling, Pd⁰ re-oxidises to PdO resulting in an increase in catalyst activity. To evaluate the effect of heating and cooling on methane combustion over Pd_{0.03}Ce_{0.97}O_{2-δ} citric acid, 4vol% methane at a GHSV of 15 000 h⁻¹ was used. Figure 4.6 shows the hysteresis behaviour of the citric acid synthesised catalyst during a heating and cooling cycle. From various studies conducted on methane combustion over Pd-based catalysts, it was found that the PdO containing catalysts tend to deactivate due to the transformation of PdO to Pd⁰ which is less active.^{10, 34} In this study, it was observed that upon heating, the catalyst

attained 100 % methane conversion at 500 °C. However, upon cooling, the catalyst maintained a methane conversion above 95 % from 600 °C to 350 °C as shown in Figure 4.6 and this can be attributed to the formation of stable PdO₂.

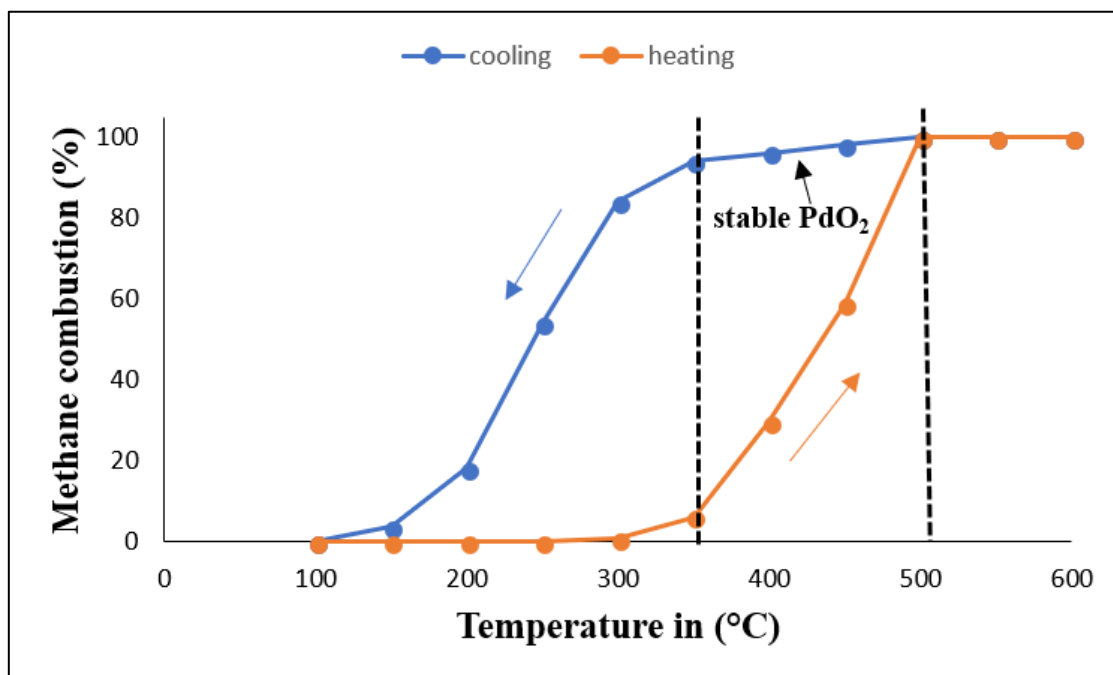


Figure 4.6 Methane combustion heating and cooling curve over Pd_{0.03}Ce_{0.97}O_{2-δ} citric acid at 4% methane in air, 15 000 h⁻¹ GHSV

From the studies of Matam *et al.*, it was observed that upon cooling in an oxygen rich environment, the PdO/Al₂O₃ catalyst was over-oxidised resulting in the increase in methane conversion.³⁵ In conjunction, Senftle *et al.* observed a similar trend over the Pd-Ce based catalyst and further stated that this increase in conversion was due to the oxidation of the Pd²⁺ species to the Pd⁴⁺ species.³⁰ Therefore, upon cooling, the PdO_x species are transformed to the PdO₂ species which are known to be the most active phase of Pd in methane combustion. In Figure 4.6, it is further observed that as the temperature decreases to below 350 °C, the conversion decreased significantly until T₀ was reached and this could be attributed to the loss of the minimum energy required for the combustion of methane.

4.3.2 Effect of different GHSV studies

The contact time has been reported to also play a key role in catalytic oxidation of methane due to the secondary oxidation of the hydrocarbon products and deactivation of the catalyst. A high gas hourly space velocity (GHSV) (i.e. low contact time) results in a low methane conversion. However, a low gas hourly space velocity (i.e. high contact time) results in optimum methane

combustion activity. From the studies by Colussi *et al.* the rate equation of methane combustion was derived as¹⁴:

$$r = k (\text{CH}_4)^{1.0} (\text{O}_2)^0 (\text{H}_2\text{O})^{-1.0} \dots\dots\dots \text{Equation 4.2}$$

Equation 4.2 shows that water has a negative influence on the rate, whilst CH_4 has a positive influence. Furthermore, the formation of water plays a significant role at low GHSVs and temperatures. Under these conditions, water desorption occurs very slowly resulting in a blockage of oxygen vacancies and subsequent loss of active sites and catalytic activity.³² To evaluate the effect of the contact time, the methane combustion reaction was performed using 4 % methane in air over the $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ citric acid catalyst at a GHSV of $30\,000\text{ h}^{-1}$ and $15\,000\text{ h}^{-1}$ as shown in Figure 4.7.

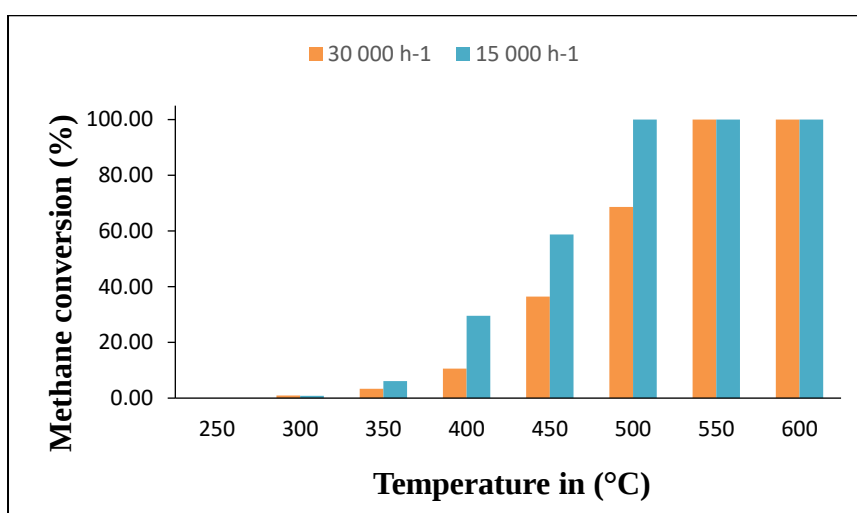


Figure 4.7 Methane combustion over $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ citric acid at 4 % methane in air, GHSV of $15\,000\text{ h}^{-1}$ and $30\,000\text{ h}^{-1}$

As observed in Figure 4.7, a low GHSV ($15\,000\text{ h}^{-1}$) is observed to result in high activity at low temperatures and thus, T_{100} was observed at $500\text{ }^{\circ}\text{C}$. When the GHSV was doubled to $30\,000\text{ h}^{-1}$, the T_{100} was observed at approximately $550\text{ }^{\circ}\text{C}$. It thus appears that at the lower GHSV, water did not affect the rate as per equation 4.2, resulting in a higher methane combustion activity when compared to the results at the higher GHSV. Yaghobi and co-workers also observed that a high GHSV led to a decrease in methane conversion, while a low GHSV resulted in an increase in methane conversion. However, the catalyst studied here shows that even when the space velocity is doubled, it still has excellent activity. Therefore, it has the

ability to achieve T_{100} at different contact times which makes it suitable for fuel cell applications where the GHSV can vary by variation of the feed flow rate.

4.3.3 Time on stream studies

Stability is one of the key criteria when assessing a catalyst since the sustainability of the structure and surface components are essential for catalysts to have long lifetime. Time on stream studies were conducted to evaluate the stability of the $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ citric acid catalyst at T_{100} and a GHSV of $15\,000\text{ h}^{-1}$. Figure 4.8 displays the data for the time on stream studies.

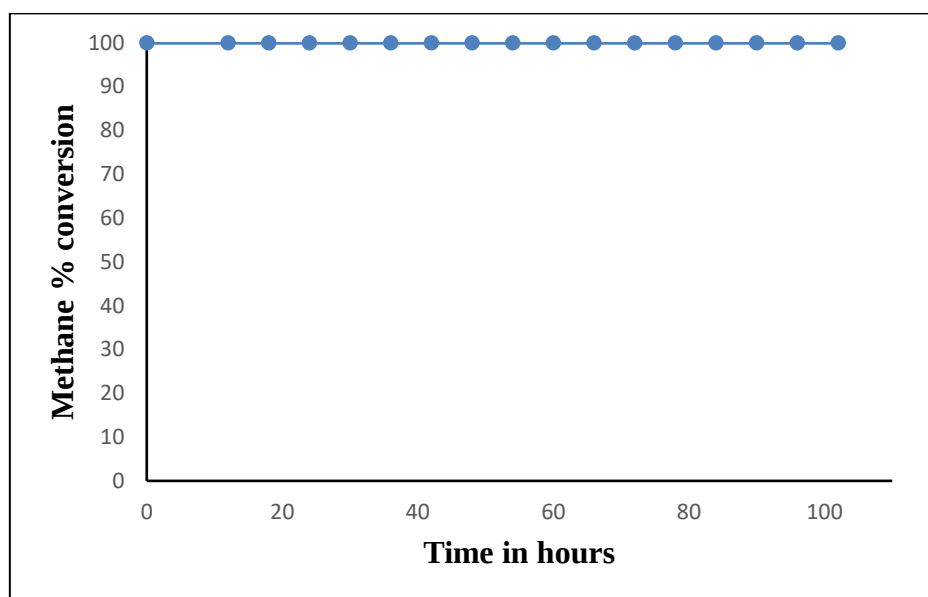


Figure 4.8 Time on stream over $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ citric acid using 4 % methane in air, at $500\text{ }^{\circ}\text{C}$ and a GHSV of $15\,000\text{ h}^{-1}$

The catalyst was observed to be stable at T_{100} for more the 100 hours. Colussi *et al.* also outlined that these types of materials were stable at elevated temperatures and this was due to the formation of the Pd-O-Ce bonds which stabilize PdO.¹⁴ Additionally, Persson *et al.* observed that $\text{PdO}/\text{Al}_2\text{O}_3$, in contrast, had a severe deactivation under reaction conditions after 50 minutes and attributed this deactivation to the loss of the active PdO.³⁴ As observed from Figure 3.1 and Figure 3.6 in Chapter 3, the $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ citric acid catalysts contain supported PdO and this PdO is likely stabilized and re-oxidized by the lattice oxygen. However, to evaluate the stability, the time on stream was further conducted at various GHSVs and at $600\text{ }^{\circ}\text{C}$ where PdO is known to decompose to Pd^0 .

4.3.4 Time on stream at different GHSVS

Figure 4.9 displays the data for the time on stream studies at 600 °C at a GHSV of 15 000 h⁻¹ for the Pd_{0.03}Ce_{0.97}O_{2-δ} citric acid catalyst, while Figure 4.10 illustrates the time on stream data at 600 °C at a GHSV of 30 000 h⁻¹.

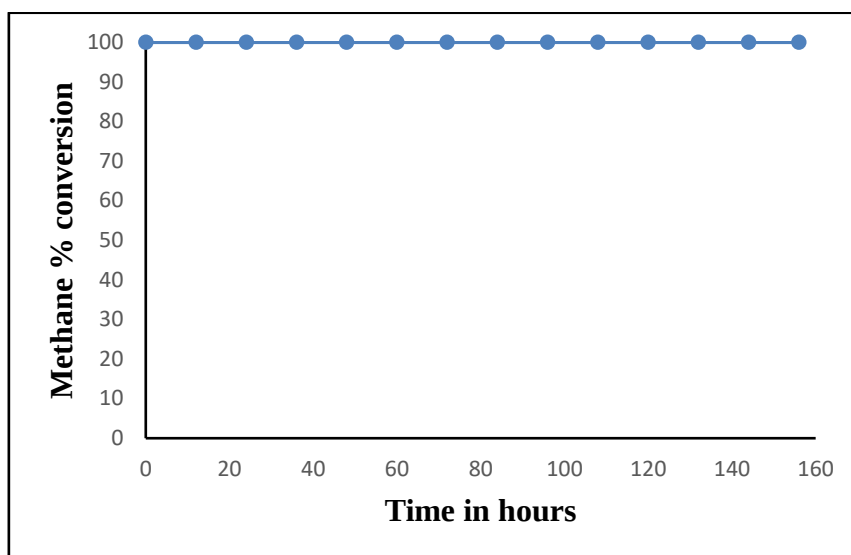


Figure 4.9 Time on stream over Pd_{0.03}Ce_{0.97}O_{2-δ} citric acid at 600 °C, 4 % methane in air and a GHSV of 15 000 h⁻¹

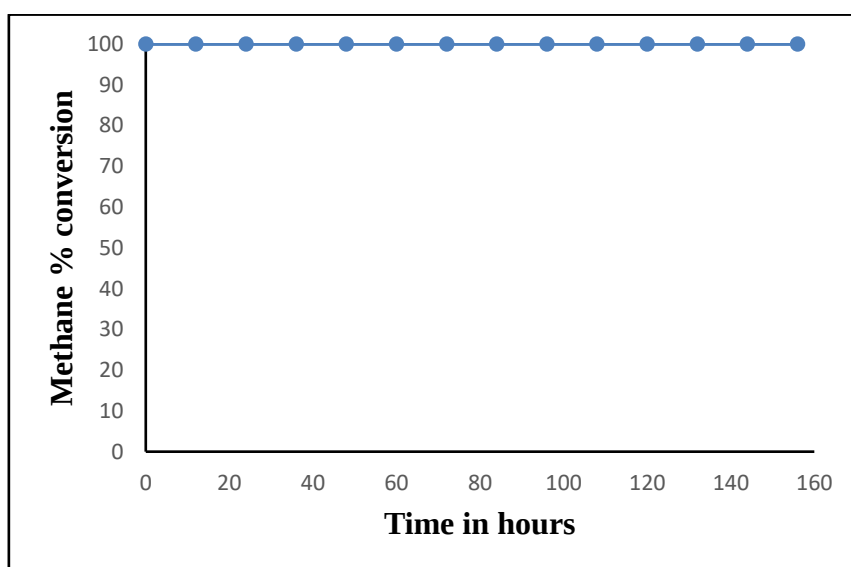


Figure 4.10 Time on stream over Pd_{0.03}Ce_{0.97}O_{2-δ} citric acid at 600 °C, 4 % methane in air and a GHSV of 30 000 h⁻¹

As observed in both Figure 4.9 and Figure 4.10, the catalyst exhibited excellent stability even though PdO is known to decompose at 600°C, which was ascribed to the enhanced redox properties, oxygen mobility and re-oxidation of the supported PdO by lattice oxygen of the

support. It has been reported that conventional (wet-impregnation and hydrothermal) synthesized PdO/CeO₂ shows deactivation when subjected to high temperatures.^{8, 18, 34}

4.3.5 The role of lattice oxygen

Oxygen vacancies are known to play an important role in methane combustion, however, there hasn't been any direct link established between activity and oxygen mobility from the lattice to the surface. To evaluate the extent to which methane combustion can occur via lattice oxygen; 4 % methane in nitrogen was used as feed at a GHSV of 15 000 h⁻¹ over Pd_{0.03}Ce_{0.97}O_{2-δ} citric acid degassed at 350 °C overnight. Figure 4.11 illustrates the combustion of methane via the lattice and bulk oxygen. A temperature of 350 °C was used to decrease the rate of the reaction in order to sample over the specified period. Increasing the temperature further reduces the catalysts within minutes and kills the activity.

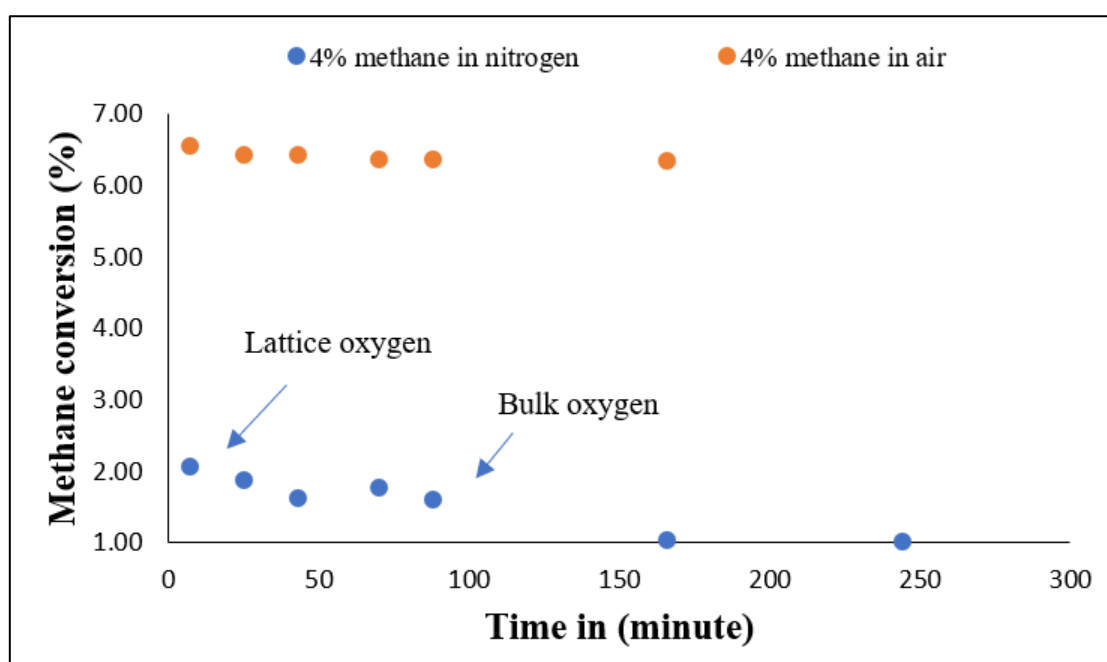


Figure 4.11 Methane combustion over Pd_{0.03}Ce_{0.97}O_{2-δ} citric acid with 4 % methane in nitrogen and 4 % methane in air, at a GHSV of 15 000 h⁻¹, and 350 °C

From Figure 4.11, methane combustion was observed to occur without oxygen in the feed, thus showing that the reaction is occurring via the lattice oxygen. However, the activity was observed to be very low and not stable over the period monitored due to the limited amount of lattice oxygen in the catalyst. Furthermore, the conversion continued to decline as the bulk oxygen was consumed. In contrast, when methane was co-fed with air, the conversion was observed to be higher showing the importance of oxygen replenishment into the lattice of the support of the Pd_{0.03}Ce_{0.97}O_{2-δ} catalyst via the MvK reaction mechanism.

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Chapter 5

Summary and Conclusions

In this study, the effect of the synthesis method of the support was evaluated prior to the evaluation of the effect of fuels on solution combustion synthesized Pd-ceria catalysts for methane combustion. All catalysts were characterized using various physical and chemical techniques prior to the methane combustion activity studies.

The solution combustion ceria was found to have a high surface area and oxygen vacancies in comparison to the commercial ceria. Accordingly, the SCS synthesized ceria achieved 2.5 times higher methane combustion at 600 °C in comparison to the commercial ceria. The 2 wt.% Pd-CeO₂ catalyst synthesized via the solution combustion method using urea as fuel (Pd_{0.03}Ce_{0.97}O_{2-δ} urea) was observed to have a high surface area and smaller crystallite size in comparison to the wet impregnation synthesized counterpart. The Pd_{0.03}Ce_{0.97}O_{2-δ} urea catalyst was further observed to be highly defective, containing a high amount of oxygen vacancies. This catalyst achieved a higher methane combustion activity at all temperatures studied in comparison to the IWI catalyst. In addition, the Pd_{0.03}Ce_{0.97}O_{2-δ} urea catalyst achieved a T₅₀ at 515 °C which was 25 °C lower than the T₅₀ achieved by the IWI catalyst. The Pd_{0.03}Ce_{0.97}O_{2-δ} urea catalyst achieved a T₁₀₀ at 525 °C, while the IWI failed to achieve T₁₀₀ at all temperatures studied.

The effect of fuels on the properties of the synthesised SCS catalyst reveals that changing the fuel resulted in a catalyst with different physical and chemical properties which were related to the nature of combustion during the synthesis procedure. The fuels having a high enthalpy of combustion (citric acid and ODH) were observed to result in voluminous gas production, and rapid combustion in comparison to the fuels having a lower enthalpy of combustion. Thus, these fuels were found to give catalysts which have similar physical and chemical properties. The H₂-TPR and XPS studies revealed that these catalysts contained supported PdO over the Pd_xCe_{1-x}O_{2-δ} support.

The XRD and HRTEM studies of the citric acid synthesized catalyst provided further evidence that this catalyst contained PdO supported on Pd_xCe_{1-x}O_{2-δ}. However, these techniques did not reveal any supported PdO for the ODH synthesized catalyst. From the XPS studies, however, it was observed that the amount of the supported PdO is minimal in the ODH catalyst in comparison to the citric acid catalyst.

The N₂-Physisorption studies revealed that the ODH and citric acid synthesized catalysts have low surface areas and larger pore volumes due to the voluminous nature of the combustion during the synthesis. Furthermore, these catalysts were observed to have a larger crystallite size which was also observed by the XRD studies. From the Raman spectroscopy studies, the ODH and citric acid catalysts were observed to be very defective and thus contained a high amount of oxygen vacancies in comparison to the other SC synthesized catalysts.

Table 5.1 Summary of the physical and chemical properties of the solution combustion synthesised catalysts.

Catalysts	Fuel	Surface area (m ² . g ⁻¹)	Oxygen vacancy	Crystallite size (nm)	T ₅₀ (°C)	T ₁₀₀ (°C)
Pd _{0.03} Ce _{0.97} O _{2-δ}	Tartaric acid	35	0.175	14.36	532	-
Pd _{0.03} Ce _{0.97} O _{2-δ}	Urea	65	0.035	10.49	515	525
Pd _{0.03} Ce _{0.97} O _{2-δ}	Alanine	12	0.194	12.81	510	550
Pd _{0.03} Ce _{0.97} O _{2-δ}	Citric acid	7	0.495	26.40	440	500
Pd _{0.03} Ce _{0.97} O _{2-δ}	ODH	4	0.328	24.49	498	535

The XRD and Raman studies did not show any major differences between the urea, alanine and tartaric acid synthesized catalysts. These catalysts were synthesized via a smooth and controllable combustion process. The XPS studies also revealed no major differences between these catalysts. However, from the N₂-Physisorption studies, these catalysts were observed to have different surface areas. The urea synthesized catalyst was observed to have the highest surface area, followed by the tartaric acid synthesized catalyst and lastly the alanine synthesized catalyst, as shown in Table 5.1. The SEM studies further revealed that these catalysts have different microstructures with the tartaric acid observed to have a sponge-like surface morphology. Furthermore, the urea synthesized catalyst was observed to have a spherical morphology, while the alanine catalyst was observed to have a foam-like morphology. From the H₂-TPR studies, it was observed that the urea and alanine catalysts had a similar amount of PdO available for the reaction. However, the tartaric acid synthesized catalyst was observed to have a minimum amount of the PdO available in comparison to the urea and alanine synthesized catalysts. These results presented an insight on the position of the incorporated Pd in the lattice structure of ceria.

The methane combustion studies revealed that there are several factors that affect the catalyst activity. These factors were found to be temperature dependent. At temperatures below 350 °C, it was observed that the catalyst activity depended on the crystallite size, with the citric acid and ODH synthesized catalysts exhibiting a high methane conversion. From 350 °C to 600 °C, several factors such as the surface area, oxygen vacancies and the positioning of the Pd in the lattice structure of ceria, were seen to significantly affect the catalyst activity. The PdO supported catalysts were observed to be highly active in this temperature range due to the presence of the supported PdO. Furthermore, the supported PdO resulted in the formation of PdO₂ which is highly active for methane combustion at low temperatures. Thus, the citric acid synthesized catalyst was found to be the best catalyst. The ODH catalyst was also noted to be highly active at low-temperatures due to supported PdO being present.

In this study, there was no major correlation between the activity and surface area as shown in Table 6.1. However, the urea synthesized catalyst was observed to reach T₁₀₀ at lower temperatures in comparison to the ODH synthesized catalyst. This was attributed to the difference in surface areas, since the reaction above 350 °C is known to be affected by mass transfer limitations.

From this work, the citric acid synthesized catalyst was shown to be the most active catalyst and, thus, the citric acid synthesized catalyst was further tested under various conditions to establish the catalyst stability, and to determine if there were any further structural changes. To evaluate these effects, several studies were conducted, including time on stream, influence of heating and cooling, and the effect of removing lattice oxygen. This catalyst showed no deactivation at various temperatures and GHSVs. Furthermore, the heating and cooling curve revealed that upon heating, the PdO₂ is transformed to PdO and, thus, lower methane conversions were observed in comparison to the cooling cycle. During the cooling cycle, the PdO was re-oxidized to form highly active PdO₂ which resulted in higher methane conversion. The lattice oxygen studies revealed the participation of lattice oxygen in the reaction, however, more studies are required to establish the significance of this oxygen species.

Chapter 6

Additional remarks and recommendation for future research

The combustion synthesised $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{\delta-2}$ catalyst prepared using citric acid as a fuel has shown remarkable activity and thermal stability for methane combustion, which are some of the main requirements for fuel cell and emission control applications. However, to determine if these advantages of the SCS catalyst can be utilised for fuel cell and emission control, the catalyst is required to be loaded into the respective reactor configurations. Emission control studies have been known to use feeds that also contain impurities such as NO_x and CO_x ^{1, 2} and, thus, further studies are required to establish the effect of these impurities on methane combustion activity.

Several studies have shown the benefits of the solution combustion synthesised catalysts, however, there is still a lot that is not known about the parameters affecting the solution combustion synthesis method. In this study, the effect of fuels was evaluated, and concluded that each fuel used affected the physical and chemical properties of the synthesised catalyst.³ However, the effect of SCS parameters such as flame temperature, amount of water and fuel to oxidant ratio needs to be evaluated since these parameters will give an insight on the properties of the solution combustion method. Conversely, other synthesis techniques such as co-precipitation and co-shell may need to be evaluated, as these methods will give an insight into the benefits of the solution combustion synthesis method. Also, the possibility of doping these catalysts with cheaper transition metals e.g. Cu, may prove useful.

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Appendix A

Test units design and Components



Figure A-1 The custom built fix-bed reactor used in this study.

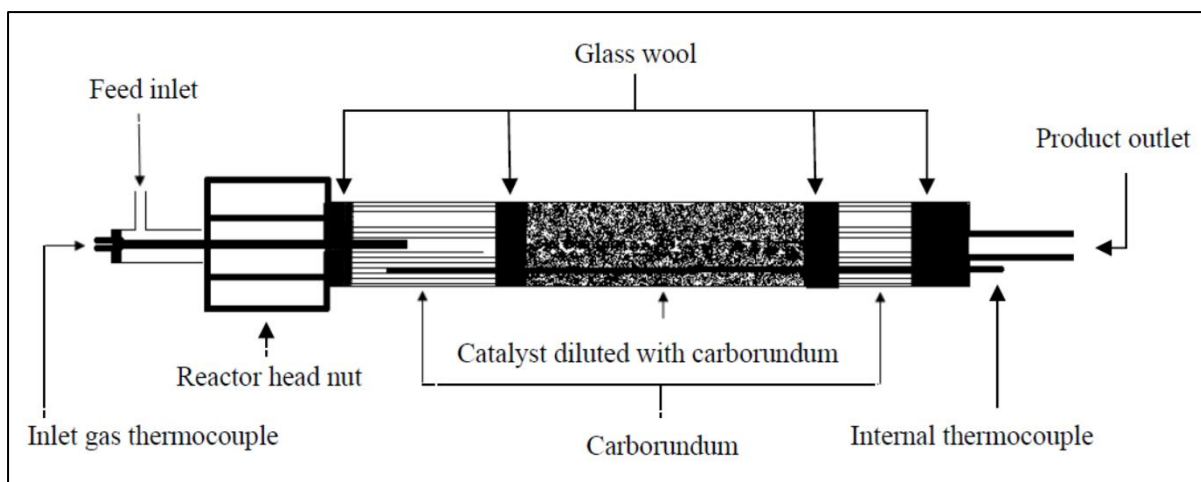


Figure A-2 An illustration of a packed reactor tube.

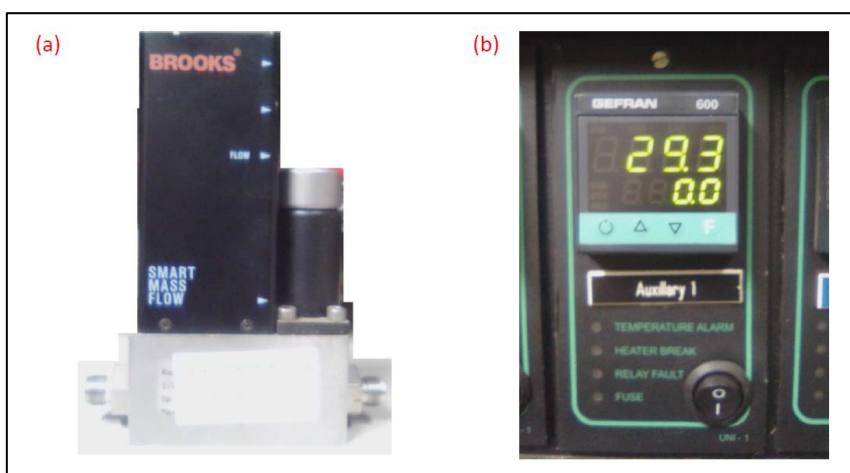


Figure A-3 (a) Bronkhorst MFC and (b) GEFRAN temperature control unit.

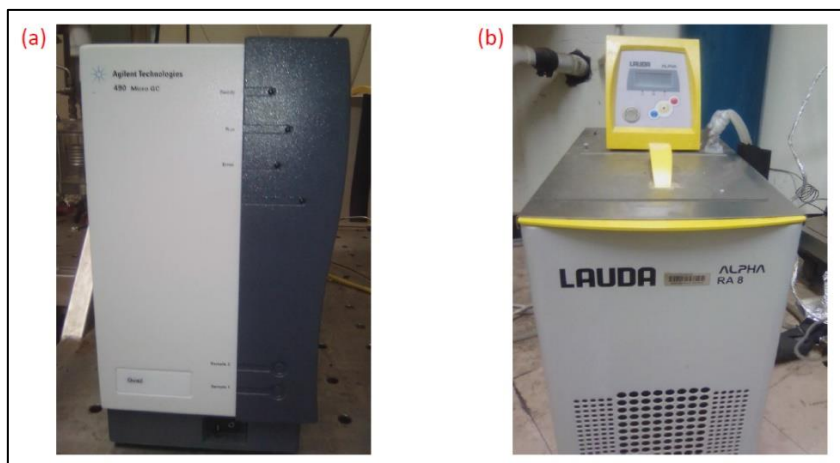


Figure A-4 (a) Aligent Technologies 490 Micro GC and (b) Lauda-Brinkmann chiller, LAUDA Alpha.

Appendix B

List of chemicals, reactor conditioning and data analysis using a micro GC

List of chemicals

Table B-1 The list of chemicals and their chemical formula

Chemical and gases	Chemical formula	Purity
Cerium oxide	CeO ₂	99.5%
Palladium (II) nitrate hydrate	Pd(NO ₃) ₂	99.5%
Ammonium cerium (IV) oxide	(NH ₄) ₂ Ce(NO ₃) ₆	99.0%
Oxalyl hydrazide	NH ₂ NHCOCONHNH ₂	98.0%
Citric acid monohydrate	C ₆ H ₈ O ₇ * H ₂ O	98.0%
β-alanine	NH ₂ CH ₂ CH ₂ COOH	98.0%
Tartaric acid	HO ₂ CCH(OH)CH(OH)CO ₂ H	99.0%
Urea	NH ₂ CONH ₂	99.0%
Concentrated sulphuric acid	H ₂ SO ₄	99.5%
Carborundum (24 grit)	SiC	99.9%

Reactor conditioning:

Isothermal zone determination:

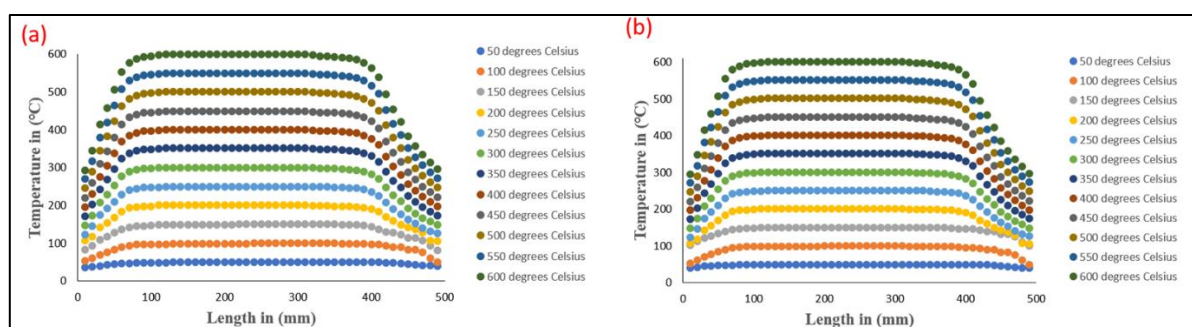


Figure B-1 Isothermal zone determination at various temperatures for a) reactor 1 (LHR) and reactor 2 (RHR)

For both reactors, the isothermal zone was noted to be between the 100 mm and 300 mm from the bottom of the reactor.

Mass flow rate calibration:

Mass controller calibration was performed over the stainless-steel fix-bed reactor. A bubble flow meter was used to calibrate different gasses mass flow controllers (MFC). A graph of the measured flow rate vs the set flow rate was used to check for linearity and offset of the mass flow controllers as shown in figure B-2.

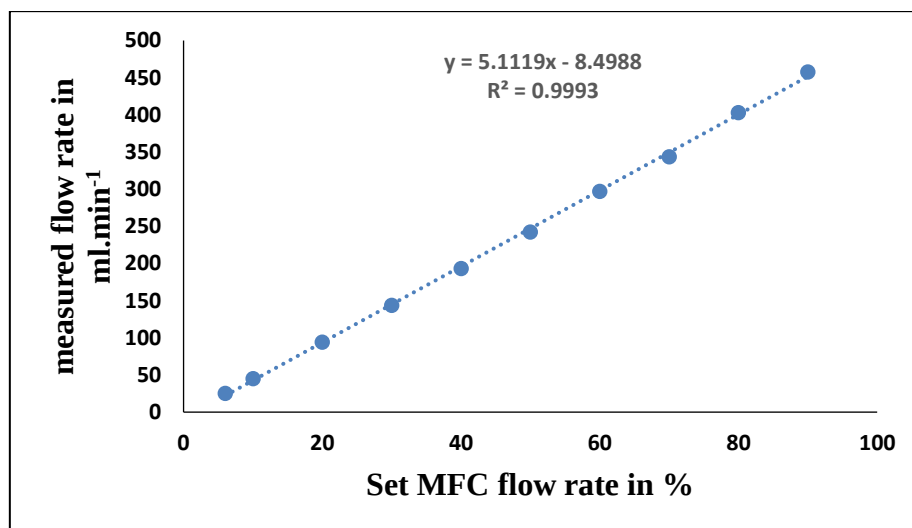


Figure B-2 Nitrogen mass flow controller calibration curve.

Data analysis using a micro GC:

The data analysis was performed by sampling the feed and product stream on to the Varian CP-4900 micro GC. This type of micro-GC contains three modules with each module consisting of an injector, column and a thermal conductivity detector (TCD). The conditions of each of these are summarized in the Table B-2 below.

Table B-2 Micro GC settings for methane combustion reactions

Channel	1	2	3
Column	Molsieve 5A	Molsieve 5A	5CB
Column length [m]	10	20	8
Injector temperature [°C]	40	40	40
Oven temperature [°C]	-	50	50
Pressure [kPa]	-	90	70
Carrier gas	Ar	H ₂	H ₂
Gas analysed	H ₂ , He	He, O ₂ , CO, N ₂ , CH ₄	CO ₂ , H ₂ O

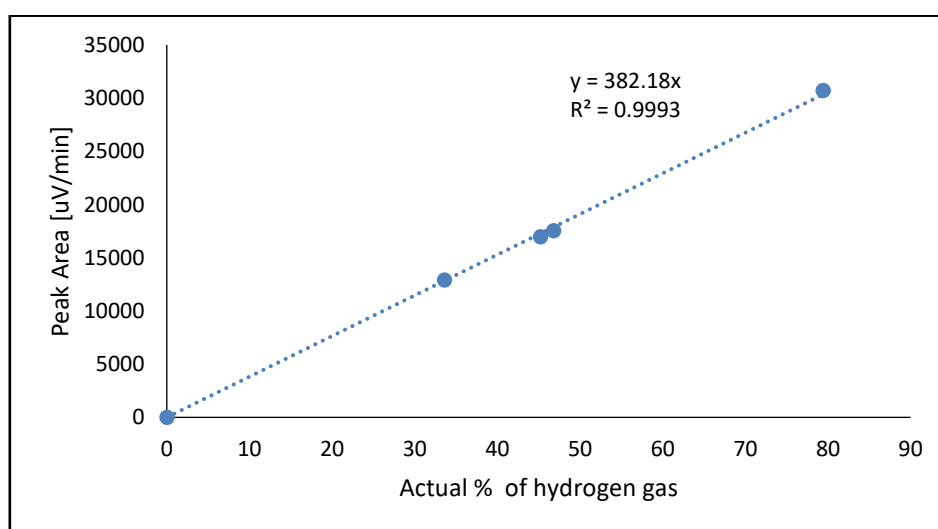
Micro-GC Calibration:

Before calibrating the micro GC, the columns (Channel 1 and 2) were baked for 12 hours at 180 °C to remove absorbed water and other chemicals retained in the column. The retention time of each gas was determined by flowing the individual gases and sampling the reactor by-pass stream on the micro-GC. The retention time of each gas is tabulated in the table B-3 below.

Table B-3 Retention times of the analysed gases in the micro GC channels.

Gas	Retention time [min]		
	Molsieve 5A	Molsieve 5A	5CB
	(10 m)	(20 m)	
H ₂	0.41	-	-
CO ₂	-	-	1.07
O ₂	-	0.56	-
CO	-	1.3	-
N ₂	-	0.7	-
CH ₄	-	2.4	-
H ₂ O*	-	-	1.38

To calibrate the micro-GC, A series of gas mixtures of known concentrations were used. The gases were allowed to mix in the blend pot for approximately two hours before being sampled on the micro GC and an average peak area of each gas was then plotted against the actual percentage of each gas in the mixture as show in the figure B-3 below.

**Figure B-3** The GC calibration curve for Hydrogen gas.

Appendix C

Characterization

Table C-1 The XRD parameters of the PdO observed in the Pd_{0.03}Ce_{0.97}O_{2-δ}Citric acid diffractogram.

Pattern : 00-041-1107		Radiation = 1.788970					Quality : High				
PdO		2th	i	h	k	l					
		34.177	3	1	0	0					
		39.162	22	0	0	2					
		39.501	100	1	0	1					
Palladium Oxide		49.097	14	1	1	0					
Also called: palladinite, Palladinite (NR)		52.934	1	1	0	2					
		64.503	20	1	1	2					
		71.258	15	1	0	3					
		71.956	11	2	0	0					
		84.192	6	0	0	4					
		85.128	15	2	0	2					
		85.391	13	2	1	1					
		104.093	3	1	1	4					
		111.599	5	2	1	3					
		112.355	5	2	2	0					
Lattice : Tetragonal		123.570	2	3	0	0					
S.G. : P42/mmc (131)		125.181	5	1	0	5					
a = 3.04560		126.088	5	2	0	4					
		127.184	5	2	2	2					
		127.555	5	3	0	1					
		136.513	2	3	1	0					
		139.537	1	2	1	4					
		161.048	4	3	1	2					
			1	0	0	6					
			1	3	0	3					
			1	3	1	3					
			2	3	2	0					
			4	2	1	5					
			5	2	2	4					
			4	3	2	1					
			2	1	1	6					
Mol. weight = 122.40											
Volume [CD] = 49.52											
Dx = 8.209											
Z = 2											
Additional Patterns: To replace 00-006-0515. Color: Black. General Comments: Average relative standard deviation in intensity of the ten strongest reflections for three specimen mounts = 4%. Validated by a calculated pattern. Sample Source or Locality: Sample obtained from ROC/RIC. Data collection flag: Ambient.											
Welton-Holzer, J., McCarthy, G., North Dakota State University, Fargo, North Dakota, USA., ICDD Grant-in-Aid (1989)											
Radiation : CuKα		Filter : Monochromator crystal									
Lambda : 1.54184		d-sp : Diffractometer									
SS/FOM : F30= 43(0.0180,39)											

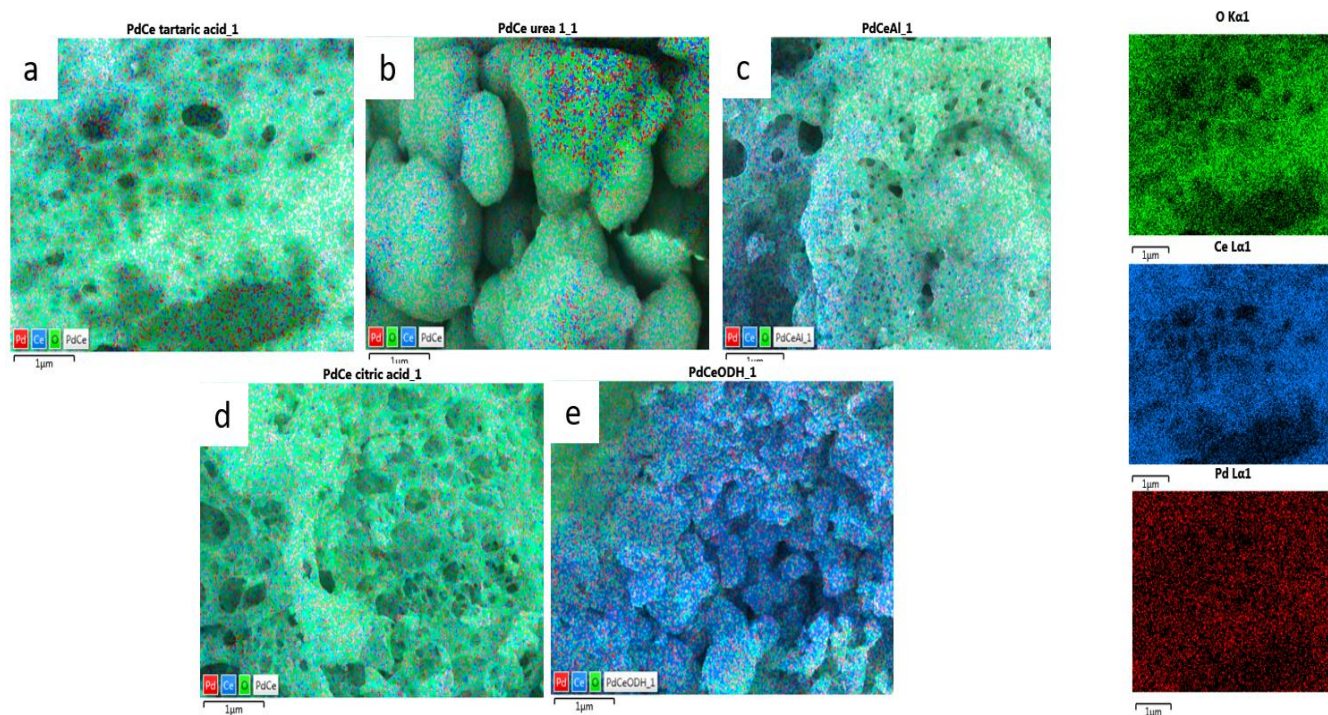


Figure C-1 SEM-EDX images of a) $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Tartaric acid, b) $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Urea, c) $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Alanine, d) $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ Citric acid and e) $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ ODH.

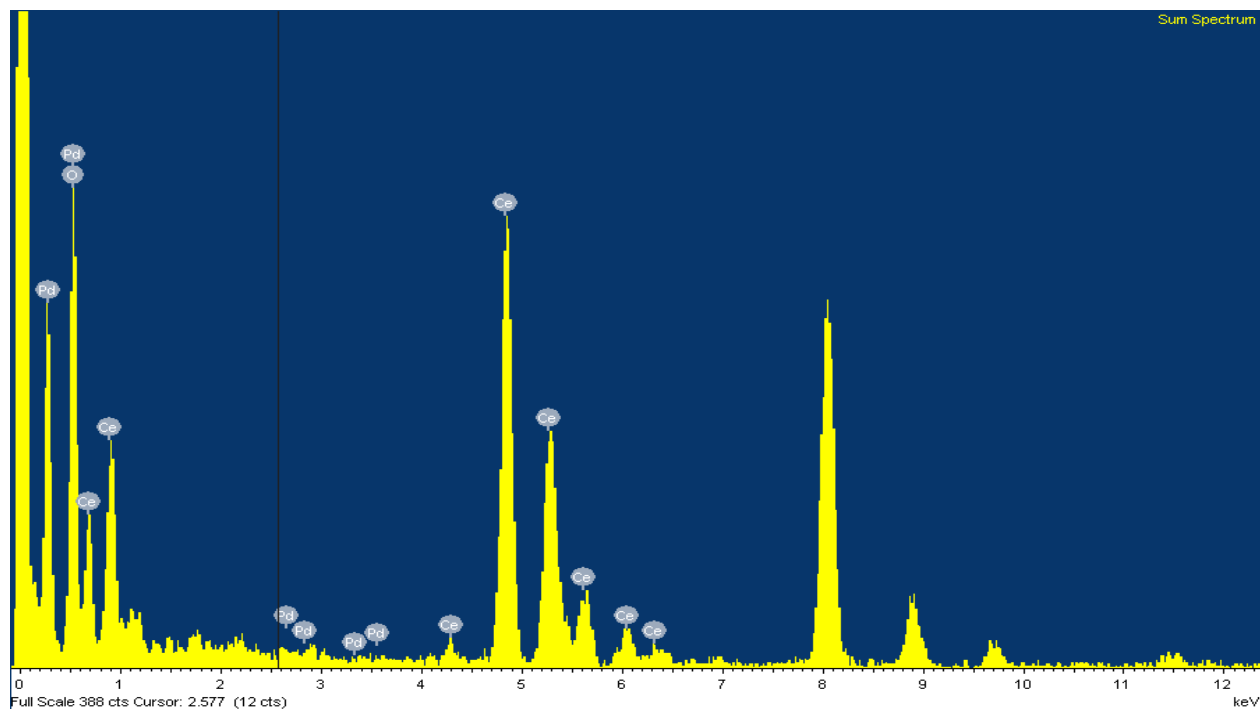


Figure C-2 HRTEM-EDX images of $\text{Pd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ catalysts.