

Effect of H₂O on CH₄ Oxidation over PdO/Al₂O₃ and CeO_x/PdO/Al₂O₃

Catalysts

by

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Abstract

Natural gas is a promising alternative fuel for transportation systems because of reduced CO, CO₂, SO₂, and NO_x emissions into the environment, and its abundance and low cost compared with gasoline and diesel. A significant obstacle in the use of NG for vehicle fuels is that CH₄ is difficult to oxidize in the presence of CO₂ and H₂O and at the low exhaust gas temperature (500-550°C) of natural gas vehicles (NGV). Although Pd is the most active catalyst for CH₄ oxidation, the presence of H₂O suppresses the catalyst activity.

The effect of H₂O on the activity of Pd/Al₂O₃ catalysts with Pd loadings of 0.3, 2.6 and 6.5Pd (wt.%) and corresponding dispersions of 57%, 48%, and 33%, was well described by a kinetic model that accounted for the effect of H₂O. Langmuir adsorption was assumed to determine the amount of H₂O adsorbed on active sites for the catalysts with different Pd dispersions under wet and dry reaction conditions. The estimated kinetic parameters of apparent activation energy, E_a of 60.6±11.5 kJ.mol⁻¹ and heat of H₂O adsorption, ΔH_{H_2O} of -81.5±9.1 kJ.mol⁻¹ indicate that CH₄ oxidation is independent of Pd dispersion.

Using different preparation methods and varying Ce:Pd ratios, it was found that sequential impregnation of the Al₂O₃ support by Ce and Pd, with Ce:Pd ratio of 5, yielded a catalyst that had the least inhibition by H₂O. H₂O adsorption is the dominant mechanism for activity loss, although some sintering of the support may also occur. In a Time-on-Stream (TOS) study with extra H₂O added to the feed gas, the chemical and physical properties of the catalysts showed only small changes before and after use. The less negative effect of H₂O at higher temperature and at lower H₂O concentration was also confirmed by the kinetic study.

The kinetic model is consistent with a Langmuir mechanism in which H_2O adsorption suppresses C-H bond activation on the active sites. The kinetic analysis shows that the Ce added to the $\text{PdO}/\text{Al}_2\text{O}_3$ catalyst suppresses the amount of H_2O adsorbed onto the catalyst, thereby reducing the H_2O inhibition effect in the presence of Ce.

Preface

This PhD thesis consists of eight chapters that was conducted by Mina Alyani under the supervision of Professor Kevin J. Smith in the Department of Chemical and Biological Engineering at UBC. A version of Chapter 2 has been published in a reviewed journal and a version of Chapters 5 and 7 has been submitted for publication. Chapters 4 and 6 are in preparation to be submitted for publication. The preparation of this dissertation and the papers were all done by Mina Alyani with the final approval of Professor Kevin J. Smith in the Department of Chemical and Biological Engineering at UBC.

The literature review, reactor set-up, catalyst preparation, catalyst characterization, catalyst testing, reaction modeling, kinetics study, and data analysis were done by Mina Alyani under the direct supervision of Professor Kevin J. Smith. Some parts of the catalyst preparation, catalyst characterization, catalyst testing, and collecting data reported in Appendix I were done by Christoph Heinz.

The publications and conference papers included in this thesis are shown below:

Mina Alyani, Kevin J. Smith, A kinetic analysis of the inhibition of CH₄ oxidation by H₂O on PdO/Al₂O₃ and CeO₂/PdO/Al₂O₃ catalysts. Ind. Eng. Chem. Res. (2016). DOI: 10.1021/acs.iecr.6b01881; Publication Date (Web): July 7, 2016

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This paper was published in Catalysts journal. Sections 2.3 and 3 were prepared and written by Mina Alyani under revision and final approval of Professor Kevin J. Smith. These sections were included in Chapter 2 and Appendix J. Sections 2, 2.1, 2.2, 2.4, and 4 of this paper were prepared and written by Rahman Gholami Shahrestani under revision and final approval of Professor Kevin J. Smith. Sections 1, 5, and Abstract of this paper were a joint contribution of all authors.

Mina Alyani, Kevin J. Smith, Effect of Pd loading on the activity and stability of Pd/Al₂O₃ catalysts in the presence of H₂O. 24th Canadian Symposium on Catalysis, Ottawa, ON (2016).

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Mina Alyani, Kevin J. Smith, Effect of Water on the Deactivation of Pd-based Catalysts during Methane Oxidation at Low Temperature. 23rd Canadian Symposium on Catalysis, Edmonton, AB (2014).

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Nomenclature

A	Cross sectional area of the reactor (m^2)
Al_s	Al surface composition (at.%)
C	BET Constant (-)
C_T	Total number of active site ($\text{mol}_{\text{site}} \cdot \text{g}_{\text{cat}}^{-1}$)
C_{CH_4}	Bulk concentration of CH_4 ($\text{mol} \cdot \text{m}^{-3}$)
$C_{\text{CH}_4}^b$	Bulk concentration of CH_4 ($\text{mol} \cdot \text{m}^{-3}$)
$C_{\text{CH}_4}^s$	Concentration of CH_4 on the catalyst surface ($\text{mol} \cdot \text{m}^{-3}$)
C_M	Mears criterion factor (-)
$(\text{Ce}/\text{Al})_b$	Ce:Al bulk atom ratio ($\frac{\text{at.}\%}{\text{at.}\%}$)
Ce_s	Ce surface composition (at.%)
d	Distance between two planes of atoms in X-ray diffraction analysis (d-spacing) (nm)
d_p	Particle diameter (m)
d_{bed}	Internal diameter of bed (cm)
d_{pore}	Pore size (nm)
D_{ij}	Binary bulk diffusivity of components i and j ($\text{m}^2 \cdot \text{s}^{-1}$)
D_{ij}^{eff}	Bulk effective diffusivity of components i and j ($\text{m}^2 \cdot \text{s}^{-1}$)
D_K	Knudsen diffusivity ($\text{m}^2 \cdot \text{s}^{-1}$)
D_K^{eff}	Effective Knudsen diffusivity ($\text{m}^2 \cdot \text{s}^{-1}$)
D_{eff}^0	Effective diffusivity at $T_0=330^\circ\text{C}$ ($\text{m}^2 \cdot \text{s}^{-1}$)
D_{eff}	Effective diffusivity ($\text{m}^2 \cdot \text{s}^{-1}$)
dW_{cat}	Differential mass (g)
E_a	Apparent activation energy ($\text{kJ} \cdot \text{mol}^{-1}$)
E_B	Binding energy (eV)
E_k	Kinetic energy (eV)
F_{CH_4}	Molar flow rate of CH_4 ($\text{mol} \cdot \text{s}^{-1}$)
$F_{\text{CH}_4}^0$	Molar flow rate of CH_4 at the inlet ($\text{mol} \cdot \text{s}^{-1}$)

$F_{CH_4 W_{cat}}$	Molar flow rate of CH ₄ at W _{cat} (mol.s ⁻¹)
g	Gram(s)
G	Superficial mass velocity (kg.m ⁻² .s ⁻¹)
h	Hour(s)
h _v	Energy of X-ray photon in XPS analysis (eV)
I _{re_i}	Relative intensity of component i based on He (-)
j _D	j _D factor (-)
k	CH ₄ reaction rate constant (s ⁻¹)
k _c	External mass transfer coefficient (m.s ⁻¹)
k _s ⁰	Pre-exponential factor for CH ₄ reaction rate constant (mol.g _{cat} .mol _{site} ⁻² .s ⁻¹ .Pa ⁻¹)
k _s	CH ₄ reaction rate constant (mol.g _{cat} .mol _{site} ⁻² .s ⁻¹ .Pa ⁻¹)
k _d	Rate of catalyst deactivation (min ⁻¹)
k _{d,d}	Rate of catalyst deactivation under dry reaction condition (min ⁻¹)
k _{d,w}	Rate of catalyst deactivation under wet reaction condition (min ⁻¹)
k _f	Rate constant H ₂ O adsorption (Pa ⁻¹ .s ⁻¹)
k _r	Rate constant for H ₂ O desorption (s ⁻¹)
K _{H₂O} ⁰	Pre-exponential factor for equilibrium constant of H ₂ O adsorption (Pa ⁻¹)
K _{H₂O}	Equilibrium constant for H ₂ O adsorption (Pa ⁻¹)
L	Crystallite size measured by X-ray diffraction (nm)
L _{bed}	Length of catalyst bed (cm)
m	Total mass of catalyst bed (g)
Mw _i	Molecular weight of component i (g.mol ⁻¹)
n	number of active sites involved in the dissociative adsorption of the CH ₄ (-)
n	Order of CH ₄ oxidation reaction (-)
n	Order of diffracted beam in X-ray diffraction (-)
N _A	Avogadro constant (mol ⁻¹)
O*-O*	Two adsorbed oxygen site pair (-)
O*-*	Adsorbed oxygen and a vacancy site pair (-)
P	Total pressure (Pa)

P	Partial pressure of N ₂ in surface area measurement (mmHg)
P ₀	Saturation pressure in surface area measurement (mmHg)
P _i	Partial pressure of component i=CH ₄ , O ₂ , H ₂ O (Pa)
P _c	Critical pressure of component i (kPa)
Pd _s	Pd surface composition (at.%)
Pd-*	Pd vacant site (-)
Pd-OH	Covered active site by OH group (-)
R	Ideal gas constant, 8.3144 (Pa.m ³ .mol ⁻¹ .K ⁻¹)
Re	Reynolds number
r _{CH₄}	CH ₄ reaction rate (mol.(cm ³ .s) ⁻¹)
r _{CH₄} ^m	CH ₄ reaction rate (mol.g _{cat} ⁻¹ .s ⁻¹)
r _{CH₄} ^s	CH ₄ reaction rate (mol.mol _{site} ⁻¹ .s ⁻¹)
s	Second(s)
Sc	Schmidt Number (-)
Sh	Sherwood Number (-)
S _{BET}	BET surface area (m ² .g ⁻¹)
t	Time (s)
T ₀	Reference temperature (603K)
T _c	Critical temperature of component i (K)
T	Temperature (°C, K)
T ₁₀ , T ₅₀ , T ₉₀	Light-off temperatures at 10%, 50%, and 90% CH ₄ conversion (°C)
u _s	Superficial gas velocity (m.s ⁻¹)
V	Volume of adsorbed gas at a constant pressure P (cm ³ (STP).g _{cat} ⁻¹)
V _m	Volume adsorbed at monolayer coverage (cm ³ (STP).g _{cat} ⁻¹)
V _{bed}	Volume of bed (cm ³)
V ₀	Molar volume of gas (22414 cm ³ .mol ⁻¹)
V ₀	Catalyst pore volume (cm ³ .g ⁻¹)
W _{cat}	Catalyst mass (g)
W _{SiC}	Mass of SiC (g)
X _{CH₄}	CH ₄ conversion (mol.%)

X_s	CH ₄ conversion at infinite time (mol.%)
y_{Ar}	Ar volume fraction (-)
y_{CH_4}	CH ₄ volume fraction (-)
y_{He}	He volume fraction (-)
y_{O_2}	O ₂ volume fraction (-)
Y_{re_i}	Relative volume fraction of component i based on He (-)

Greek Letters

ρ_{bed}	Catalyst density (g.cm ⁻³)
ρ_{SiC}	SiC density (g.cm ⁻³)
ρ_{cat}	Catalyst density (g.cm ⁻³)
ρ_{bSiC}	Catalyst bed (g.cm ⁻³) density of both catalyst and SiC
ρ_g	Gas density (kg.m ³)
ρ_s	Density of solid (g.cm ⁻³)
ϵ_{bSiC}	Bed porosity (-)
ϵ_p	Particle porosity (-)
$(\epsilon/k)_i$	Lennard-Jones energy/Boltzmann's constant for component i (-)
ΔH_{H_2O}	Enthalpy of H ₂ O adsorption (kJ.mol ⁻¹)
$\Delta X_{dry-wet}$	The difference between CH ₄ conversion in dry feed gas after 24h and wet feed gas after removing water
ΔX_s	The difference between X_s for the dry and wet feed
η	Internal effectiveness factor (-)
φ	Thiele modulus (-)
θ	Angle of reflection in XRD (°)
θ_v	Vacant active site (-)
θ_{H_2O}	Fraction of active sites covered by H ₂ O (-)
β	Full Width at Half Maximum, FWHM (Radians)
v_0	Total volumetric flow rate (cm ³ .s ⁻¹)

$\alpha_{\text{H}_2\text{O}}$	Initial partial pressure of H ₂ O per initial partial pressure of CH ₄ (-)
λ	X-ray wavelength for XRD analysis (Å)
τ	Tortuosity factor (-)
σ	The occupied area by adsorption of a single molecule of N ₂ (Å ²)
σ	Constriction factor (-)
σ_i	Lennard-Jones characteristic length for component i (i=He or CH ₄)
Ω_D	Collision integral (-)
μ	Gas dynamic viscosity (kg.m ⁻¹ .s ⁻¹)

List of Abbreviations

AAS	Atomic absorption spectroscopy
A/F	Air/fuel
B.E.	Binding energy (eV)
BET	Brunauer-Emmett-Teller
BET SA	BET surface area ($\text{m}^2 \cdot \text{g}_{\text{cat}}^{-1}$)
BJH	Barrett-Joyner-Halenda
CeO _x	Cerium oxide
CNG	Compressed natural gas
co-xCe/yPd/Al ₂ O ₃	A catalyst consists of x wt.%Ce and y wt.%Pd over Al ₂ O ₃ prepared by co-impregnation method
DFT	Density Functional Theory
GHG	Greenhouse gas
GHSV	Gas hourly space velocity ($\text{cm}^3 \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$)
LEV	Low emission vehicle
LNG	Liquefied natural gas
MBtu	Million British thermal units
MMT	Million metric tons
MFC	Mass flow controller
MVK	Mars-van Krevelen model
MS	Mass spectrometer
NG	Natural gas
NGV	Natural gas vehicle
NO _x	Nitrogen oxides
ODE	Ordinary differential equation
OSC	Oxygen storage capacity
PDE	Partial differential equation
PdO	Palladium oxide
QMS	Quadrupole mass spectrometer
RDS	Rate determining step

seq-xCe/yPd/Al ₂ O ₃	A catalyst consists of x wt.%Ce and y wt.%Pd over Al ₂ O ₃ prepared by sequential impregnation method
sccm	cm ³ (STP).min ⁻¹
SO _x	Sulfur oxides
TLEV	Transitional low emission vehicle
TOF	Turn-over frequency (s ⁻¹)
TOS	Time on stream (h)
TPO	Temperature-programmed oxidation of CH ₄
TWC	Three-way catalytic converter
ULEV	Ultra low emission vehicle
vol.	Volume
(v/v)	Volume basis
wt.	Weight basis
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

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my parents

Chapter 1: Introduction

1.1 Background

Natural gas (NG) is a hydrocarbon gas mixture that consists primarily of CH₄ and small amounts of other hydrocarbons and impurities, as shown in Table 1.1 [1]. CH₄ has the highest H:C ratio between all hydrocarbons that results in the lowest CO₂ emissions per unit of energy when compared with gasoline and diesel fuels. The high octane number of natural gas (octane number 130) also improves the combustion efficiency by increasing the compression ratio of the NG engine. Based on the U.S. Energy Information Administration (EIA) report, over 759 million cubic meters of natural gas is consumed in the United States annually [2] and about 150,000 vehicles use natural gas in the U.S. [3].

Table 1.1. Natural gas composition [1]

Component	Vol.%
CH ₄	70-90
C ₂ H ₆ , C ₃ H ₈ , C ₄ H ₁₀	0-20
CO ₂	0-8.0
O ₂	0-0.2
N ₂	0-5.0
H ₂ S	0-5.0
He, Ne, Xe	trace

Natural gas can be used as a fuel in the form of compressed natural gas (CNG) or liquefied natural gas (LNG) [3]. The advantages of using natural gas as a fuel in the transportation sector is its low cost and high availability [3]. Figure 1.1 compares natural gas, gasoline, and diesel fuel prices in the U.S over the past years.

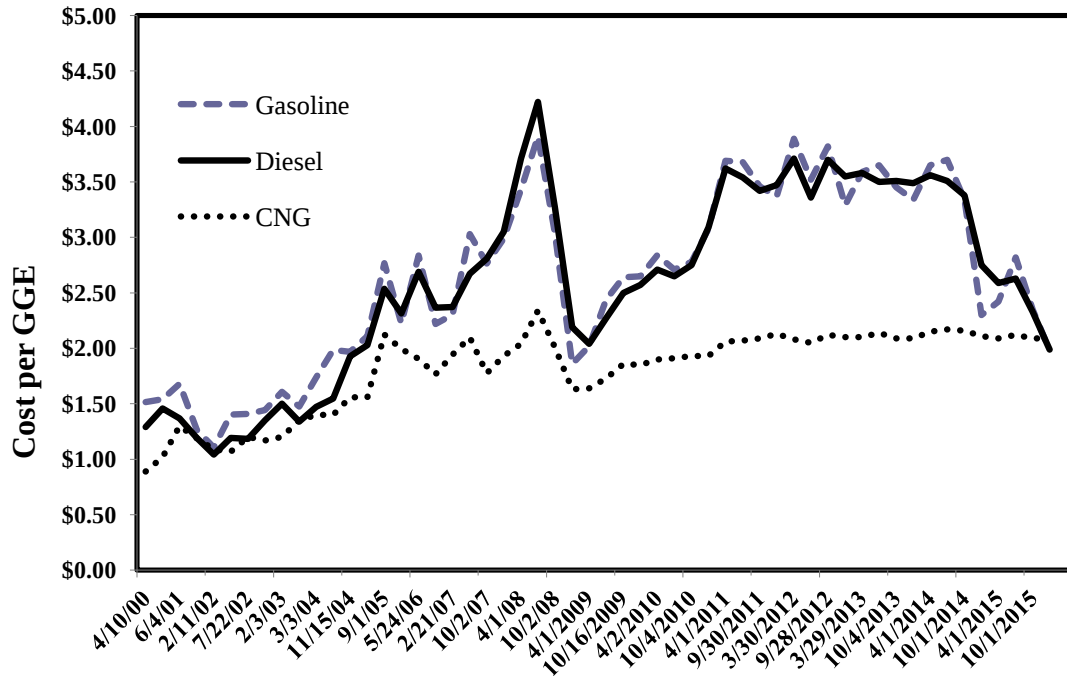


Figure 1.1. Average prices for gasoline, diesel, and CNG over time (Adopted from [3])

The CO₂ equivalent emissions from fossil fuel combustion in the U.S. is about 5,157.7 MMT/yr and 33.3% is from the transportation sector [4]. Emissions from the transport sector are limited by regulations and Table 1.2 reports the exhaust emission limits for light-duty vehicles in the U.S. in 2016. Note that there is no limit legislated for CH₄ emission.

Table 1.2. Exhaust emission limits for Light-Duty vehicles (Adopted from [5])

Vehicle Type	Emissions Category	Useful Life Standard	NMOG ^b g.mi ⁻¹	NO _x g.mi ⁻¹	CO g.mi ⁻¹	Formaldehyde g.mi ⁻¹	PM ^c g.mi ⁻¹
LDVs ^a	TLEV	Intermediate	0.125	0.4	3.4	0.015	-
	LEV		0.075	0.2	3.4	0.015	-
	ULEV		0.040	0.2	1.7	0.008	-
	TLEV	Full	0.156	0.6	4.2	0.018	0.08
	LEV		0.090	0.3	4.2	0.018	0.08
	ULEV		0.055	0.3	2.1	0.011	0.04

^a Light-Duty Vehicles, ^b Non-Methane Organic Gases, ^c Particulate Matter

In 2013 approximately 2.1 MMT CO₂ emissions equivalent of CH₄ was emitted from natural gas transportation systems [4]. The low H₂S concentration in natural gas means that it also has the lowest SO₂ emissions from combustion when compared to other fossil fuels. Table 1.3 compares the exhaust emissions using CNG and gasoline fuels and clearly shows the lower emissions associated with CNG.

Table 1.3. Fuel economy and exhaust gas compositions using CNG and gasoline (Adopted from [3])

Vehicle Type	Fuel Economy mi.gal ⁻¹	CO g.mi ⁻¹	CO ₂ g.mi ⁻¹	NMOG g.mi ⁻¹	NO _x g.mi ⁻¹
CNG	11.54	1.99	563.54	0.05	0.54
Gasoline	13.10	5.83	666.85	0.29	0.78

The greenhouse effect or global warming is one of the critical issues facing our environment. The principal greenhouse gases are CH₄, CO₂, and N₂O which serve to retain heat close to the earth by absorbing infrared radiation and slowing down its emitting rate [6]. Increasing the heat trapping potential of the atmosphere by increasing the concentration of greenhouse gases causes harmful effects on human life. The Global Warming Potential (GWP) is an index used to compare the greenhouse gas effect of different gases [7]. The index calculates the ratio of absorbed energy caused by the emission of one ton of a gas such as CH₄ or N₂O to the absorbed energy caused by CO₂ over a specified time period. The GWP value of CH₄ and N₂O are reported as 28-36 and 265-298, respectively, for a 100 year time horizon, indicating that CH₄ and N₂O absorb 28 times and 265 times more energy than CO₂, regardless of their lifetime [7].

A significant barrier for using natural gas vehicles (NGVs) is the unburned CH_4 emitted to the atmosphere from the vehicle exhaust gas. Since CH_4 has a higher GWP than CO_2 , the complete combustion of unburned CH_4 by a catalytic converter is the main challenge.

Three-way catalytic converters (TWC) were developed to control vehicle emissions using gasoline. As shown in Figure 1.2, a TWC consists of a washcoated ceramic or metal monolith in a honeycomb structure with 1 mm^2 channels that permit a high flow rate of exhaust gas with minimal pressure drop [8]. The washcoat is made of high surface area Al_2O_3 combined with CeO_2 and ZrO_2 in order to increase the oxygen storage capacity and thermal stability of the monolith [8]. The washcoated monolith is impregnated with active metals such as Pt and Rh. The typical amount of noble metal is 1-2 wt.% of the washcoated monolith with a ratio of Pt:Rh=17:1 [9]. Oxidation of CO and HC to CO_2 occurs in the presence of Pt and Rh is used to reduce NO_x to N_2 [8,10].

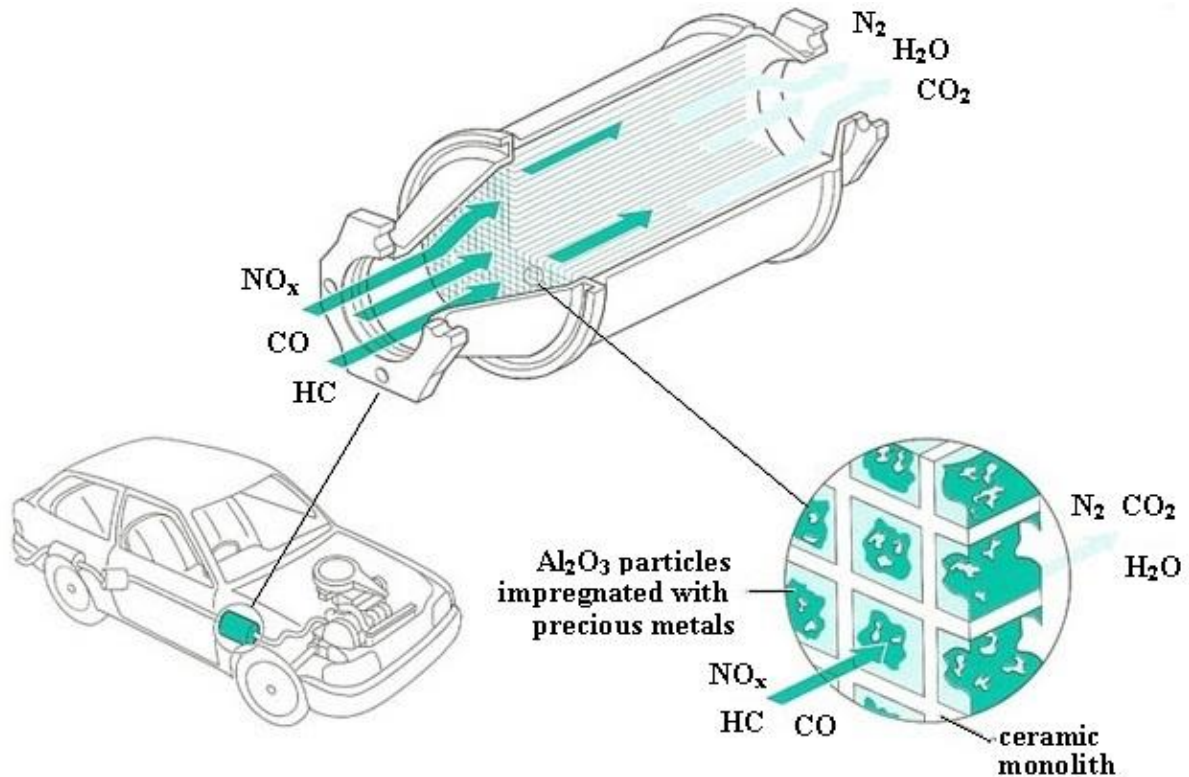


Figure 1.2. The three-way catalytic converter installed in the exhaust gas emitted from gasoline engines

[11]

A high conversion for both oxidation and reduction reactions in a TWC is obtained by controlling the air to fuel ratio (A/F) in an engine operating using gasoline fuel. Figure 1.3 shows the HC, CO, and NO_x concentration as a function of A/F. If the engine is operated under rich burn conditions (a lack of air), CO and HC oxidation is unlikely, however, the reduction of NO_x is highest as a result of high CO concentration. At stoichiometric conditions in an engine operating using gasoline fuel (A/F=14.6), the CO and HC combustion occurs faster than rich burn conditions because of higher O₂ concentration, on the other hand, the increase in temperature and low CO concentration as a result of combustion suppresses NO_x reduction ($\text{NO} + \text{CO} \rightarrow \frac{1}{2}\text{N}_2 + \text{CO}_2$). Under lean burn conditions (A/F > 14.6), the concentration of CO and NO_x decreases, while the HC concentration

becomes higher than that under the stoichiometric conditions, as the combustion process is unstable at high A/F ratio [8].

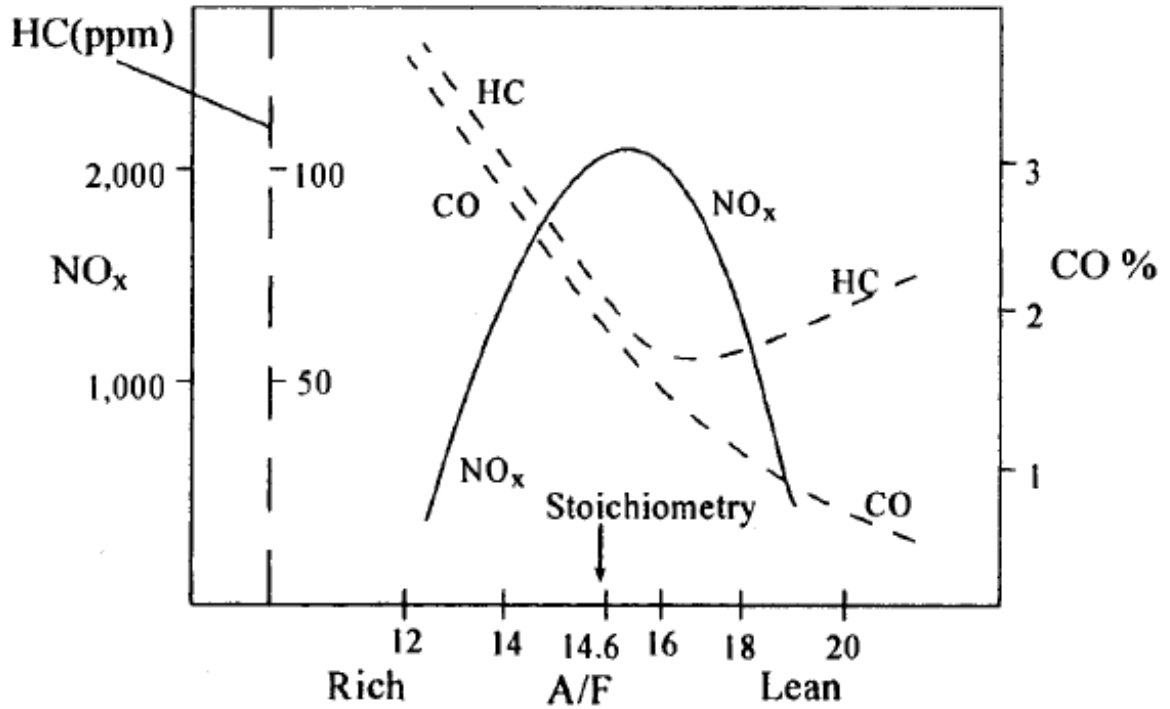


Figure 1.3. The concentration of NO_x, CO, and HCs as a function of air /fuel ratio operating in gasoline engines [8] (Copyright © 2010 John Wiley and Sons)

As the exhaust temperature in natural gas vehicles (500-550°C) is lower than gasoline or diesel vehicles, CH₄ is not burned completely in NGVs and around 500-1500 ppm of CH₄ remains unreacted in the exhaust gas [12]. The unburned CH₄ along with 10-15vol.% H₂O and 15vol.% CO₂ pass through the catalytic converters [12]. Typical TWCs used for gasoline engines are not able to completely oxidize CH₄ at the low exhaust gas temperature of NGVs in the presence of high H₂O concentrations. CH₄ is difficult to oxidize because of the high C-H bond strength (~415 kJ.mol⁻¹) which makes it resistant to oxidation [13,14]. Typical

catalytic converters for NGVs use Pd as catalyst, a more affordable option than Pt or Rh and the most active metal for CH₄/CO combustion [15,16].

Complete oxidation of CH₄ has been widely studied in recent decades [12,16–28] mainly focusing on the effect of different supports (Al₂O₃, SiO₂, ZrO₂, and CeO₂) and different metals, such as noble metals, rare earth metals, transition metals, and lanthanides. In most studies the loading of Pd was in the range of 0.5-5wt.% in order to simulate the Pd loading in washcoated monolith catalysts of commercial spark ignition natural gas engines [18]. The main focus has been on developing a catalyst that can operate at low temperature (< 400°C) and oxidize CH₄ completely ($\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$). Although Pd-based catalysts are active for CH₄ oxidation, they lose their activity during reaction. Possible causes of the loss in activity during CH₄ oxidation include a reversible loss caused by H₂O adsorption (Figure 1.4(a)) or an irreversible loss, caused by, for example, sintering that affects the physical and chemical properties of the catalysts permanently or formation of inactive sites such as Pd(OH)₂ (Figure 1.4(b)).

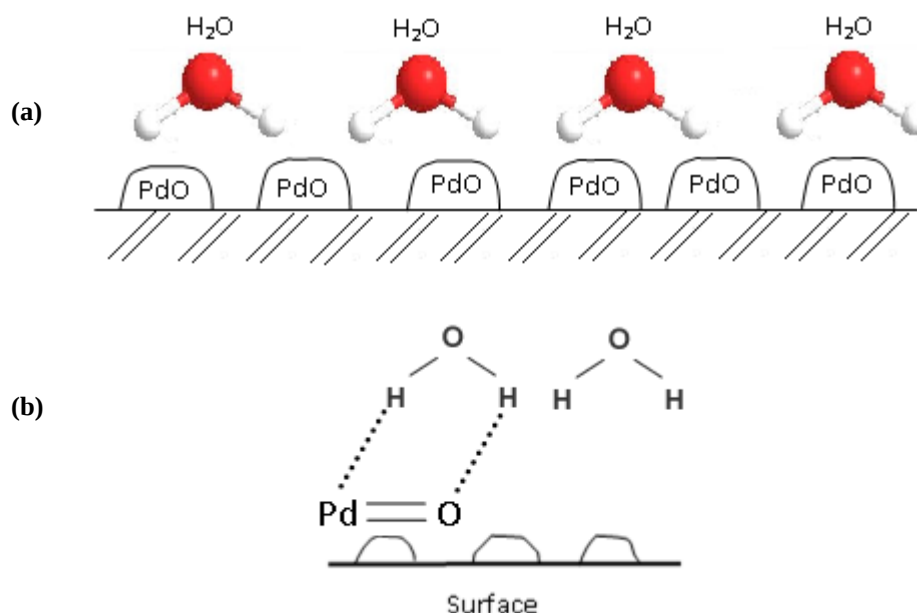


Figure 1.4. Possible mechanisms of catalyst activity loss by H₂O: (a) H₂O adsorption on PdO active sites, (b) formation of inactive Pd(OH)₂

H₂O plays a crucial role in terms of catalyst activity during CH₄ oxidation and is the main product of the complete oxidation of CH₄ in addition to CO₂. At low temperatures the activity of Pd-based catalysts is mainly affected by H₂O. As more H₂O is produced during the reaction, the catalytic activity decreases as does the life time of the catalysts [29].

The rate limiting step in CH₄ oxidation depends on the H₂O concentration and the reaction temperature [17]. At a reaction temperature higher than 500°C along with the H₂O produced from the CH₄ oxidation reaction (dry feed), the H₂O effect is negligible and the rate determining step is C-H bond activation. Therefore, the reaction order with respect to H₂O is zero [30]. However, at low reaction temperature (< 500°C) and 3.5vol.% H₂O concentration in the wet feed, slow desorption of H₂O from the catalyst surface means that the rate limiting step is H₂O desorption from the catalyst surface [30]. At conditions where H₂O desorption is the rate determining step, the concentration of H₂O must be considered in order to calculate

the activation energy [17,31]. Proposed reaction steps for the CH₄-O₂ reaction on Pd-based catalysts assume that CH₄ dissociation occurs by the interaction of CH₄ on a PdO/Pd-* site pair, where Pd-* refers to an O vacancy [17,32]. Following several surface oxidation reactions, CO₂ and Pd-OH species result [17,32]. OH desorption (2Pd-OH→PdO+Pd-*+H₂O) leads to the formation of oxygen vacancies on the catalyst surface. These vacancies can be re-oxidized by the oxygen from PdO, oxygen from the support or O₂ from the gas phase. However, in the presence of H₂O, slower OH migration and consequently slower H₂O desorption from the catalyst surface, leads to the suppression of oxygen exchange between the support and the vacant sites [32–34]. In the case of a support with high oxygen storage capacity (OSC) such as CeO₂, the oxygen exchange from the support to the oxygen vacancies can be improved. However, the negative effect of H₂O is not completely reversed in the presence of high OSC supports. Studies emphasizing the effect of supports with high OSC [33,34], preparation method [35], temperature and H₂O concentration [30] on activity suppression by H₂O are available. However, a clear comparison between the long term stability of Pd based catalysts with/without a high OSC species (e.g. Pd/Al₂O₃ vs. Pd/CeO₂/Al₂O₃) in the presence of high H₂O concentrations during CH₄ oxidation at low temperature as a function of time, has not been reported. Furthermore, the kinetics of the CH₄ oxidation reaction in relation to the effect of H₂O and the presence of high OSC species has not been reported.

1.2 Objectives of the Thesis

Since H₂O has a significant impact on active sites by adsorption and by suppressing the oxygen exchange between Pd vacant sites and the oxide supports, the objectives of this study

are formed as below.

- To determine the structure sensitivity of Pd based catalysts during CH₄ oxidation by investigating the effect of Pd loading on reaction kinetics.
- To understand the effect of different preparation methods and various Ce:Pd ratios on the inhibiting effect of H₂O during CH₄ oxidation at temperatures < 400°C.
- To determine the reversible and irreversible effects of H₂O on the physical and chemical properties of the catalysts after extended reaction periods.
- To develop a unifying kinetic model that quantifies the role of H₂O in the inhibition of catalyst activity, with and without CeO₂ over a wide range of H₂O concentrations. The kinetic model parameters will also be used to quantify the effect of adding CeO₂ to the support.

1.3 Approach of the Thesis

In order to meet the stated objectives, a series of experiments along with a kinetic study that accounts for the effect of H₂O has been performed. As a first step, a general introduction regarding the negative effects of CH₄ as a GHG, removal of unburned CH₄ in the exhaust gas of NGVs in the presence of H₂O, and the importance of an active catalyst that remains stable at low temperatures (< 500°C), is explained in Chapter 1.

In Chapter 2, a literature review is presented in order to provide a comprehensive review of the effect of H₂O on CH₄ oxidation over Pd catalysts at low temperatures, as well as to identify knowledge gaps in the mechanism of H₂O inhibition.

Chapter 3 includes details regarding catalyst preparation with different Pd loadings, Ce:Pd ratios, as well as different preparation methods used in this study. The thermal pre-treatments applied to the catalysts, the experimental equipment, the Temperature Programmed Oxidation (TPO) and Time-on-Stream (TOS) test methodology to measure both initial activity and stability of the catalysts, as well as various characterization techniques applied to the catalysts are explained in this chapter. The calculations related to the effectiveness factor, carbon balance, and CH₄ conversion during the TPO and TOS tests are also described in this chapter.

In Chapter 4 the effect of Pd loading (0.3wt.%-6.5wt.%) on the physical and chemical properties of the catalysts, as well as their stability in the presence of H₂O is reported. The PdO/Al₂O₃ catalysts with different Pd loadings are compared in initial activity and stability by TPO and TOS tests, respectively. The effect of Pd dispersion on the amount of H₂O adsorbed on active sites is also examined. The values of the rate constant and the equilibrium constant for H₂O adsorption were obtained from the reactor design equation to show the structure insensitivity of the catalysts within the narrow Pd dispersion range of 33-57%.

In Chapter 5, the effect of varying Ce:Pd ratio with a constant 6.5wt.% of Pd loading on the initial activity of the catalysts is presented. Same as Chapter 4, the values of the rate constant and the equilibrium constant for H₂O adsorption were obtained from the reactor design equation for co-2.9Ce/6.5Pd/Al₂O₃ catalyst and compared to those reported in Chapter 4 for the 6.5Pd/Al₂O₃ catalyst in order to show the beneficial effect of CeO₂ in suppressing the negative effect of H₂O. A dynamic study of the loss in the activity of the catalysts by applying an exponential empirical equation to the TOS results is discussed and the rate of

deactivation (k_d) as a function of different temperatures (300-380°C) and different H₂O concentrations (0 and 5vol.%) is obtained.

In Chapter 6, the effect of catalyst preparation using co-impregnation and sequential impregnation methods on the initial activity and stability of the catalysts is reported. Three catalysts using co-impregnation method and five catalysts using sequential impregnation method are prepared and compared in terms of activity at different temperatures and H₂O concentrations. Five xCe/Al₂O₃ supports with the same Ce loadings as the sequentially impregnated catalysts were also prepared and characterized in order to understand the interaction of Pd with CeO₂ and CeO₂ with Al₂O₃. The oxygen exchange mechanism was invoked to emphasize the role of CeO₂ on the oxygen storage capacity (OSC) of the support and on the catalyst activity.

Chapter 7 develops a kinetic model to describe the inhibiting effect of H₂O on TOS tests in a non-steady state system. A linear regression is applied to the experimental results presented in Chapters 4 and 5 and the rate of H₂O desorption (k_r) as a function of temperature are calculated for each individual catalyst in order to explain the role of Ce on the H₂O desorption.

In Chapter 8 conclusions of this study along with recommendations for future work are presented. Supplementary information is included in the appendices. Appendix A provides the details of catalyst preparation, Appendix B explains different characterization techniques used in this study, and Appendix C provides the information about the unit calibration, including mass flow controllers, mass spectrometers, and liquid pump. In Appendices D and E the error analysis and CH₄ conversion calculation procedures are explained. The

repeatability of the TPO and TOS reactions are shown in Appendix F. Appendix G contains some supplementary figures and tables for Chapter 6. Mass transfer calculations are shown in Appendix H. The results for PdO/ZrO_x/Al₂O₃ catalysts are presented in Appendix I since ZrO₂ promoted catalyst was not the main focus of the study. Supplementary information of bimetallic catalysts are presented in Appendix J. Lastly, the details of the kinetic model MATLAB code are provided in Appendix K.

Chapter 2: Literature Review¹

2.1 Introduction

In this chapter the effect of various supports, including metal oxides with high oxygen storage capacity, on the inhibiting effect of H₂O are reviewed. The molecular structures of cerium oxide, such as CeO₂ and Ce₂O₃ will be compared and their ability to transfer O in order to suppress the negative effect of H₂O on the activity of Pd-based catalysts will be explained. In addition, the effect of aging the catalysts with/without extra H₂O and its effect on the structure of the catalysts such as BET surface area, Pd dispersion, and the oxidation state of Pd will be considered. The effect of temperature and partial pressure of both reactants and products on the reaction order and the apparent activation energy in CH₄ combustion will be reviewed. Lastly, the various kinetic models, such as Langmuir-Hinshelwood, Mars-van Krevelen, and Eley-Rideal will be compared in terms of their response to the inhibiting effect of H₂O.

2.2 Effect of the Support on the Inhibiting Effect of H₂O during CH₄ Oxidation

2.2.1 CH₄ Conversion on Different Supports

The data of Table 2.1 show that the inhibition of CH₄ oxidation by H₂O on Pd catalysts is

¹ A version of this chapter was published in "Rahman Gholami, Mina Alyani, Kevin J. Smith, Deactivation of Pd Catalysts by Water during Low Temperature Methane Oxidation Relevant to Natural Gas Vehicle Converters. Catalysts 5 (2015) 561-594."

dependent upon the support. Light-off temperature at 30% CH₄ conversion (T₃₀) of Pd catalysts were compared at a constant Gas Hourly Space Velocity (GHSV) and gas feed composition for different supports. Pd/Al₂O₃ shows significantly more inhibition with 10% H₂O added to the feed than either the Pd/SnO₂ or Pd/Al₂O₃-36NiO catalysts.

Table 2.1. Comparing light-off temperature (T₃₀) for CH₄ oxidation over Pd supported catalysts [23]

(Copyright © 2002 Elsevier)

Catalyst	1.1%Pd/Al ₂ O ₃	1.1%Pd/SnO ₂	1.1%Pd/Al ₂ O ₃ -36NiO
GHSV, h ⁻¹	48,000		
Dry feed gas composition, vol. %	1%CH ₄ /20%O ₂ in N ₂		
	T ₃₀ , °C		
Added H ₂ O, vol. %			
0	345	290	372
1	400	315	372
5	430	335	420
10	460	360	425
20	510	365	445

More detailed data from Kikuchi et al. [23] comparing CH₄ light-off curves for a 1.1wt.%Pd/Al₂O₃ catalyst and a 1.1wt.%Pd/SnO₂ catalyst with H₂O added to the feed over a range of concentrations (1-20 vol.%), are shown in Figures 2.1 and 2.2. By increasing the H₂O concentration, the CH₄ light-off curves for both catalysts shift to higher temperatures. However, the temperature shift is larger over the Pd/Al₂O₃ catalyst than the Pd/SnO₂. The authors completed a simplified kinetic analysis of the CH₄ oxidation rate data to show that the enthalpy of adsorption of H₂O is strongest on the Pd/Al₂O₃ catalyst ($\Delta H_{ad} \sim -49 \text{ kJ.mol}^{-1}$), from which they concluded that the significant loss in activity of the Pd/Al₂O₃ in the presence of H₂O is due to a high coverage of the active sites by H₂O [23]. These results could also be interpreted according to the more recent proposals by Schwartz et al. [33,34], that hydroxyl accumulation on the support hinders oxygen migration and exchange, and

hence CH_4 oxidation. The strong adsorption of H_2O determined by kinetic analysis on the $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst [23] is consistent with a large hydroxyl accumulation on the catalyst surface that could inhibit the O exchange.

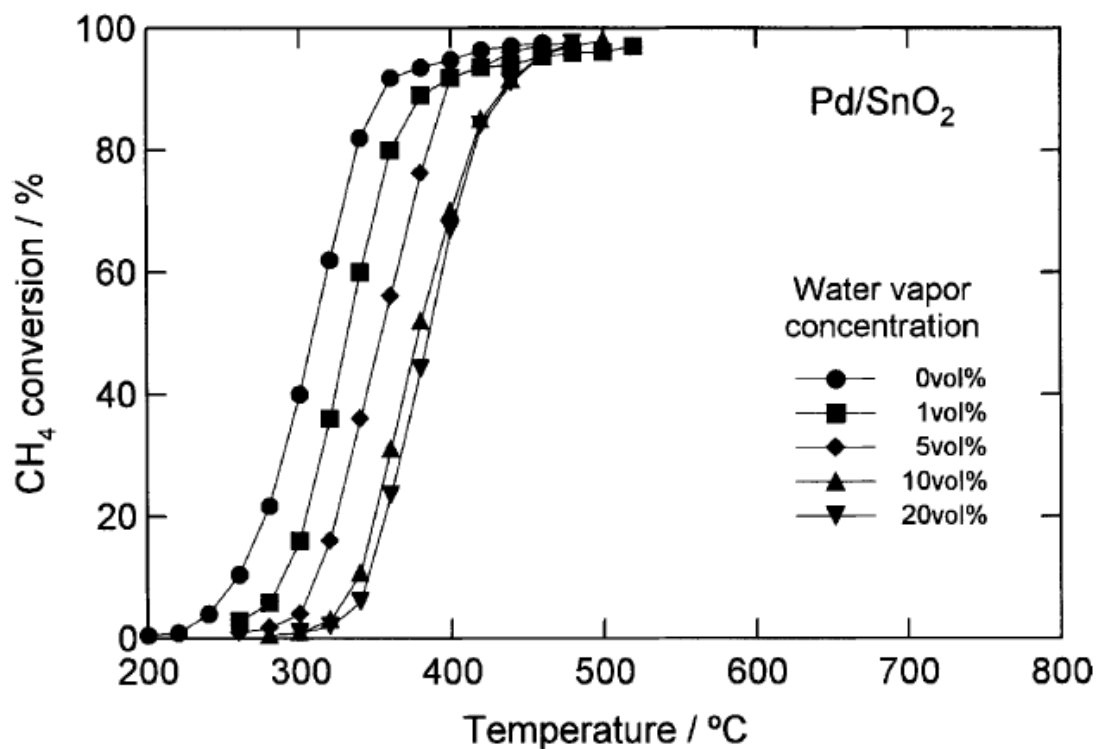


Figure 2.1. Catalytic combustion of CH_4 over 1.1wt.% Pd/SnO_2 with different amounts of H_2O added (vol.%). Reaction conditions: 1vol.% CH_4 , 20vol.% O_2 , 0-20vol.% H_2O , balanced in N_2 .

GHSV=48,000 h^{-1} [23] (Copyright © 2002 Elsevier)

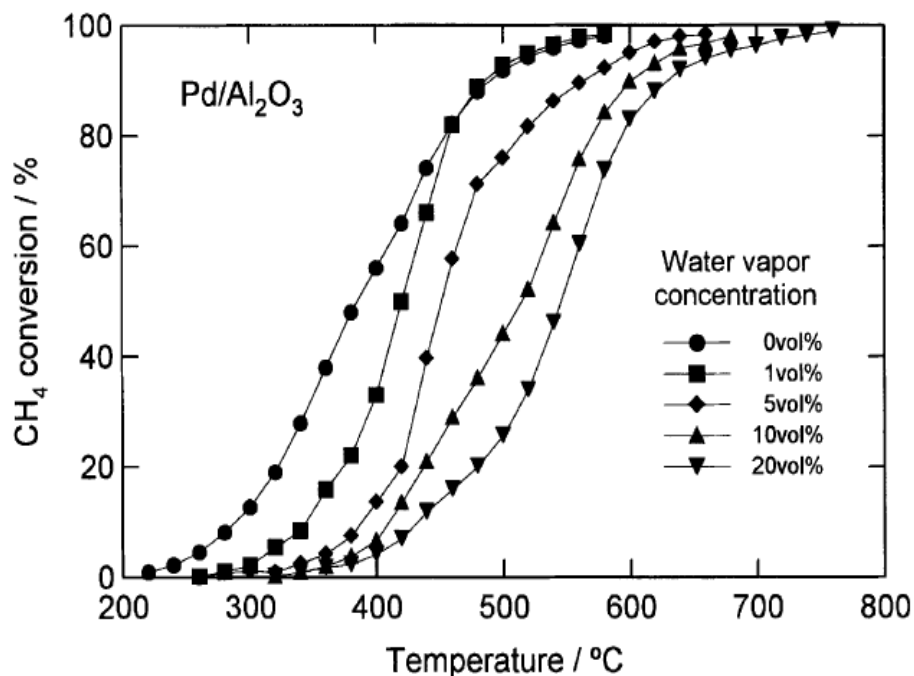


Figure 2.2. Catalytic combustion of CH₄ over 1.1wt.%Pd/Al₂O₃ with different amounts of H₂O added (vol.%). Reaction conditions: 1vol.%CH₄, 20vol.%O₂, 0-20vol.%H₂O, balanced in N₂.

GHSV=48,000h⁻¹ [23] (Copyright © 2002 Elsevier)

2.2.2 High Oxygen Mobility of Support

The rate of deactivation during CH₄ oxidation in the presence of H₂O has been shown to be reduced by using a support with high oxygen surface mobility. At temperatures below 450°C, Ciuparu et al. [36] reported the inhibition effect of H₂O to be dependent upon the oxygen mobility of the support. Comparing PdO supported on oxides with increasing surface oxygen mobility: Al₂O₃ < ZrO₂ < Ce_{0.1}Zr_{0.9}O₂, they showed that the resistance to H₂O inhibition during CH₄ oxidation increased in the same order. The deactivation rate of PdO was also compared over Al₂O₃, MgO, and TiO₂ supports by Schwartz et al. [33,34] at temperatures < 450°C. The deactivation was shown to be a consequence of reduced oxygen mobility due to hydroxyl adsorption. It was also shown that a PdO/MgO catalyst had a

slower deactivation rate compared with Al_2O_3 and TiO_2 supports because of the higher oxygen surface mobility on the MgO [33,34]. However, Pd catalysts dispersed on other supports such as MCM-41 that have high surface area ($1113 \text{ m}^2/\text{g}$) and lower oxygen mobility than MgO and Al_2O_3 , did not deactivate either, suggesting that other factors also play a role, depending on the catalyst and the support. Another study compared the stability of Pd/SiO_2 and Pd/ZrO_2 during CH_4 oxidation using a dry feed gas [37]. Pd/ZrO_2 is stable after 40h TOS, while the CH_4 conversion over Pd/SiO_2 catalyst increases from 13% to 32% in the first 3h, and then decreases to 22% after 96h (see Figure 2.3). Although the Pd/ZrO_2 catalyst is more stable than the Pd/SiO_2 catalyst, its conversion is lower than for the Pd/SiO_2 catalyst. The lower deactivation rate observed on the Pd/ZrO_2 is consistent with the higher oxygen mobility of this catalyst compared to Pd/SiO_2 , as noted above.

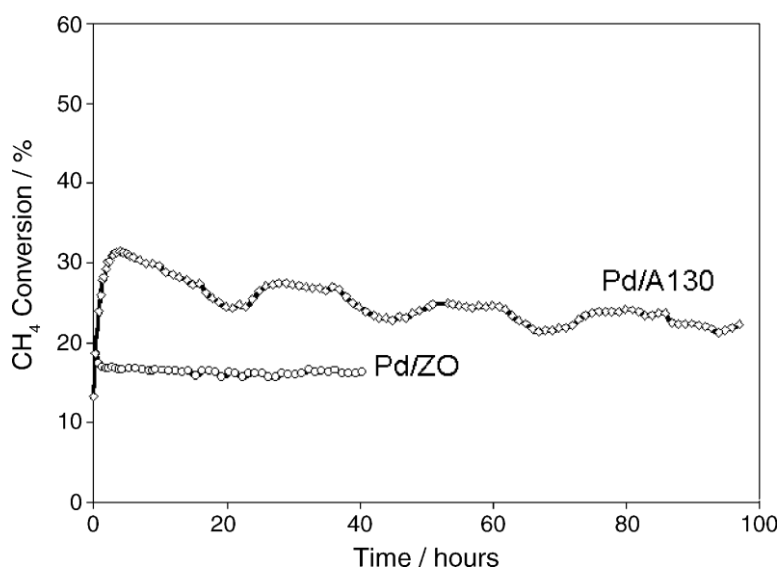


Figure 2.3. Methane conversion for Pd/ZrO_2 and $\text{Pd}/\text{Aerosil130}$ catalysts. Reaction conditions: 1.5% CH_4 ; 6% O_2 ; total flow= $90 \text{ cm}^3 \cdot \text{min}^{-1}$, balanced in He ; temperature= 325°C ; catalyst mass= 0.2g [37] (Copyright

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2.2.3 Effect of Catalyst Structure on Activity

Metal-support interactions, support stability and the tendency of the support to encapsulate Pd, may also play a role in the deactivation of Pd catalysts during CH₄ oxidation. Gannouni et al. [38] compared Pd catalysts supported on silica and mesoporous aluminosilicas and showed that, according to the light-off curves measured with 1% CH₄, 4% O₂ in He, the CH₄ oxidation activity is enhanced on the pure silica support, whereas on the aluminosilica, the beneficial effect of Al³⁺ on metal dispersion and catalytic activity is counterbalanced by partial metal encapsulation. Above 500°C in the presence of H₂O, the structural collapse of the support, metal sintering, and metal encapsulation by the support all occur [38]. Zhu et al. [39] reported the encapsulation of PdO active sites by SiO₂ during CH₄ oxidation at 325°C and during reduction in H₂ at 650°C. The authors suggested that the high temperature, the H₂O formed during reaction, and the formation of Pd silicide during reduction followed by oxidation in O₂, were all important factors promoting the encapsulation of PdO by the SiO₂. Migration of SiO₂ onto the metal crystallites in other catalyst systems containing H₂O has also been reported in the literature [40,41]. Yoshida et al. [42] also examined the effect of various metal oxide supports of Pd on the low temperature oxidation of CH₄ (Table 2.2). The catalytic activity varied with the support, but the support oxides with moderate acid strength (Al₂O₃ and SiO₂) gave maximum CH₄ conversion. For these catalysts higher activity corresponded to a higher oxidation state of Pd (bulk PdO). The lower activity of Pd on basic supports, was attributed to the formation of binary oxides from PdO and the support (such as Pd/MgO_x), in spite of a high Pd oxidation state.

Table 2.2. Effect of support on properties of 5wt.%Pd catalysts and their CH₄ oxidation conversion (Data adapted with permission from [42])

Support	Support Acid Strength	Pd Dispersion		CH ₄ Conversion ^a
	(H ₀)	Fresh	Used	%
MgO	22.3	0.21	0.20	12
ZrO ₂	9.3	0.41	0.12	3
Al ₂ O ₃	3.3	0.35	0.20	59
SiO ₂	-5.6	0.09	0.11	58
SiO ₂ -ZrO ₂	-8.2	0.16	0.13	20
SiO ₂ -Al ₂ O ₃	-11.9	0.12	0.06	10
SO ₄ ²⁻ -ZrO ₂	-13.6	-	0.02	11

^aMeasured at 350°C in 0.25%CH₄/3%O₂ in He at GHSV of 1,200,000 h⁻¹

A comparison of initial CH₄ oxidation activity as a function of temperature for Pd-Pt catalysts on Al₂O₃, ZrO₂, LaMnAl₁₁O₁₉, and Ce-ZrO₂ was reported by Persson et al. [43], with the monolith catalysts tested in a tubular quartz flow reactor at atmospheric pressure in 1.5vol.% CH₄ in dry air and a space velocity of 250,000 h⁻¹. For steady-state experiments, the reaction temperature was set at 470°C and then increased to 720°C stepwise in 50°C increments, with each temperature held for 1h. The Pd-Pt/Al₂O₃ catalyst had the highest activity at lower temperatures, while the Pd-Pt/Ce-ZrO₂ catalyst had the highest activity between 620°C and 800°C [43]. The authors suggested that the higher surface area of the Al₂O₃ compared to the other supports (90 m²/g for Al₂O₃ versus 10 m²/g for Ce-ZrO₂), resulted in a more stable catalyst. The authors also noted that the Ce-ZrO₂ likely enhances the stability of the PdO, similar to the enhanced stability observed on CeO₂ [36]. In addition, ZrO₂ has high oxygen mobility [36] and the ability to re-oxidize metallic Pd into PdO was

observed to vary between the supports. Pd/alumina is re-oxidized very slowly, whereas Pd supported on ceria-stabilised ZrO_2 , is re-oxidized more rapidly.

2.2.4 Hydrophobicity of the Support

Since H_2O adsorption on the Pd and/or the support is an important step in inhibiting CH_4 oxidation over Pd, support hydrophobicity may be expected to impact the inhibition effect of H_2O . Araya et al. [37] studied this effect on the deactivation of Pd-based catalysts by preparing 1wt.% Pd on two different commercial silicas, Aerosil130 and Aerosil R972. The Aerosil R972 is hydrophobic since the OH groups have been replaced by methyl groups. Both 1%Pd/A130 and 1%Pd/R972 were reacted at 325°C with 3% H_2O , 1.5% CH_4 , 6% O_2 at a total flow rate of $90\text{ cm}^3\cdot\text{min}^{-1}$. As shown in Figure 2.4, the effect of H_2O addition to the feed gas is approximately the same for both the hydrophobic silica, Pd/R972 and the Pd/A130. In both cases, a large decrease in CH_4 conversion is observed with the introduction of H_2O to the reactor. The authors reported a reaction order with respect to H_2O of -0.25 for both Pd/A130 and Pd/R972, emphasizing that the hydrophobicity of the support does not affect the extent of H_2O inhibition observed on either catalyst.

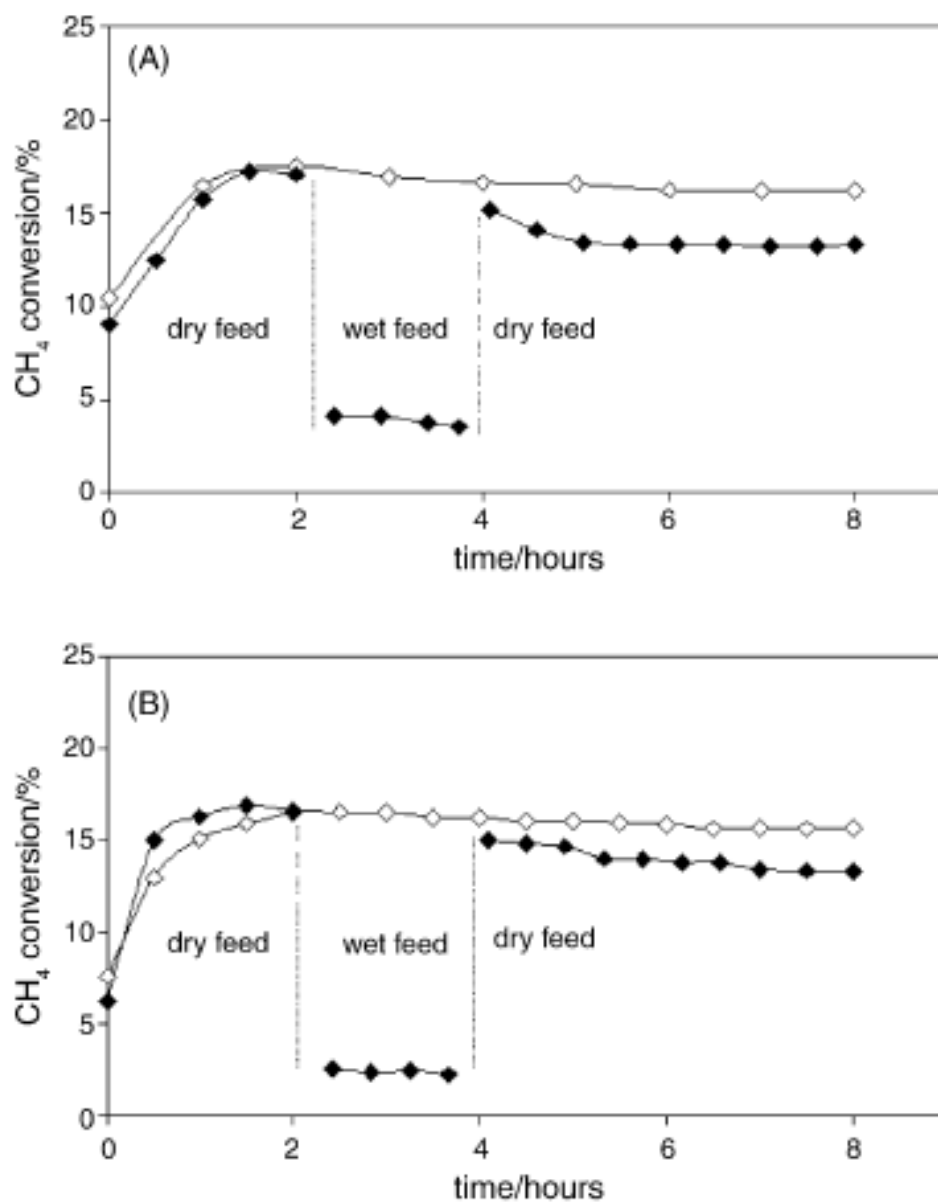


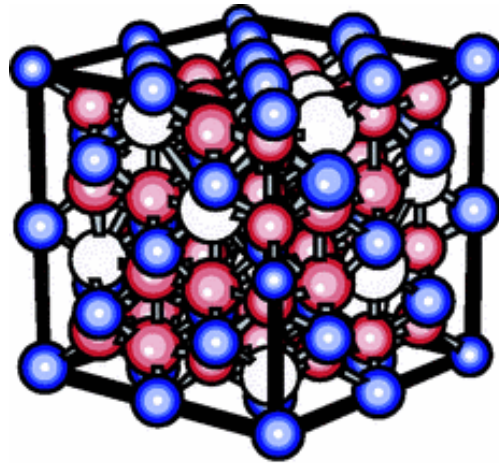
Figure 2.4. A) Pd/Aerosil130 catalyst, B) Pd/R972 catalyst.

Reaction conditions: total flow=90cm³ (STP).min⁻¹, temperature=325°C; catalyst mass=0.2 g.

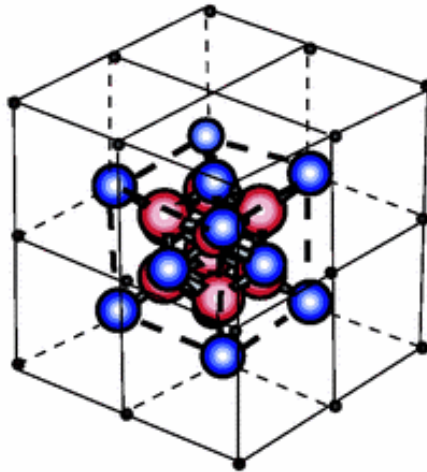
Open symbols: dry feed 1.5%CH₄; 6%O₂ balance He; closed symbol: wet feed 1.5%CH₄; 6%O₂ with 3%H₂O, balance He [37] (Copyright © 2005 Elsevier)

2.3 The Role of CeO₂

The oxygen storage capacity plays an important role in the performance of TWC [44–46]. The reactivity of CeO₂ originates mainly from its redox chemistry, which allows the storage of O₂ under oxidizing conditions (Ce⁴⁺) and the release of O₂ under reducing conditions (Ce³⁺) [46]. Among the elements in the periodic table, Ce is known for its unusual electronic structure with the *f*-orbital partially occupied in Ce [47]. It is also known that the cerium structure remains as face centered cubic, f.c.c during γ - α isostructure transition [47]. However, this structure preservation occurs by a drastic collapse in the volume of the unit cell. The change in volume during the transition is due to delocalization of the 4*f* electrons [47]. Figure 2.5 shows the cubic unit cell structure of Ce₂O₃ and CeO₂. The Ce₂O₃ cells are made up of eight unit cells of CeO₂, however, the volume of each cell is increased by 3% and 25% of the oxygen atoms are removed [47]. Figure 2.5(a) shows the presence of the oxygen vacancies and larger lattice unit cell for Ce₂O₃ compared to the CeO₂ cells.



a)



b)

Figure 2.5. Ce_2O_3 lattice unit cells (a) and CeO_2 (b). Blue spheres represent the cerium, red and white spheres are defined as oxygen atoms and vacancies, respectively [47] (Copyright © 2002 American Physical Society)

In terms of the possibility to form an oxygen vacancy, about 4.55 eV energy is required for the pure CeO_2 (Figure 2.6(a)), however, this number reduces to 0.26 eV if an oxygen vacancy forms next to a pair of Ce^{3+} atoms that are surrounded by the CeO_2 matrix (Figure 2.6(b)) [47] indicating higher possibility of formation of oxygen vacancies in the presence of Ce_2O_3 .

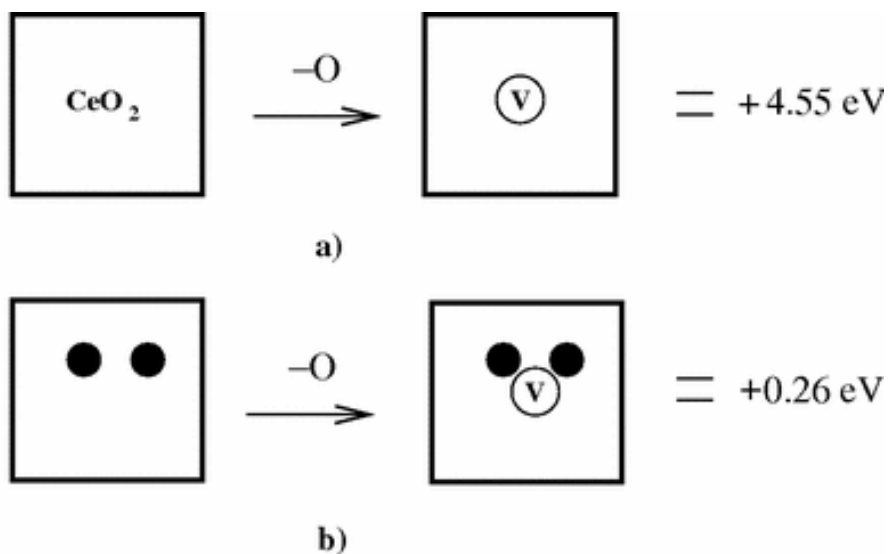


Figure 2.6. The formation of oxygen vacancy for (a) a CeO_2 crystal, (b) a pair of Ce^{3+} . Black spheres indicate the Ce^{3+} and V indicates oxygen vacancy (Reproduced with permission from [47])

Since O transfer in ceria occurs easily, it can be written as CeO_{2-x} with x in the range of 0-0.5 [46]. Tsunekawa et al. [48] showed that for small ceria particles ($\leq 1.5 \text{ nm}$), x is equal to 0.5 and ceria is in a fully reduced form that is presented as cubic Ce_2O_3 [48]. However, Hailstone et al. [46] showed the formation of Ce_2O_3 depends on the crystallite size of ceria. It was shown that even for ceria crystallite size $< 1 \text{ nm}$, no Ce_2O_3 was observed. Ideally, decreasing the ceria crystallite size should lead to an increase the OSC because of increasing the surface area/mol of CeO_2 [46]. However, Hailstone et al. showed the OSC for ceria with the crystallite size of 11.8 nm is $425 \mu\text{mol of O}_2/\text{g}_{\text{CeO}_2}$, and this decreases to $349 \mu\text{mol O}_2/\text{g}_{\text{CeO}_2}$ and $65 \mu\text{mol O}_2/\text{g}_{\text{CeO}_2}$ as the CeO_2 crystallite size decreases to 2.0 nm and 1.1 nm , respectively [46].

Table 2.3. Lattice expansion and oxygen storage capacity of CeO₂ as a function of crystallite size [46]**(Copyright © 2009 American Chemical Society)**

mean diameter nm	Lattice Constant nm	Lattice Expansion %	OSC μmol of O ₂ /g _{CeO₂}
1.1±0.3	0.578	6.8	65
2.0±0.5	0.555	2.6	349
11.8±1.2	0.547	1.1	425

In another study, the f.c.c structure of crystalline ceria was confirmed for three samples with different particle diameter of 6.7 nm, 3.8 nm, and 2.1 nm, while the calculated lattice parameter for the samples with different crystallite size decreased from 5.560 Å to 5.453 Å [48].

The presence of noble metals such as Pd improves the oxygen mobility of CeO₂ [49]. One of the most active CH₄ oxidation catalysts reported in the literature is PdO encapsulated in porous CeO₂ [35]. The authors reported that the high activity was due to the strong interaction/contact between the CeO₂ and the PdO, combined with the high O exchange mobility of CeO₂. Colussi et al. [50,51] showed that only Pd particles in direct contact with the CeO₂ re-oxidize at higher temperature and that the re-oxidation of the oxygen vacant site, Pd-*, is kinetically enhanced when in contact with CeO₂ [51]. Hence the effect of CeO₂ and the optimum loading varies in different studies, depending on the catalyst preparation method [52,53].

Colussi et al. compared the activity of Pd/CeO₂ catalysts prepared by two different methods [54]. The Pd/CeO₂ catalysts using solution combustion synthesis (SCS) were more active than those prepared by incipient impregnation (IWI), with three to five times higher reaction rate in the former case. The higher activity is ascribed to more stable Pd-O active sites. The

ex situ XRD analysis of the fresh and used SCS and IWI catalysts after reaction cycles confirmed the presence of PdO only. However, the in situ XRD analysis revealed a dynamic transformation of PdO→Pd→PdO during heating-cooling cycles for both IWI and SCS catalysts.

The oxygen release and uptake measurements were also performed in order to quantify the PdO→Pd transformation while the catalysts were exposed to 2vol.% O₂ in N₂ upon heating/cooling cycles by varying the temperature from room temperature to 1000°C. The SCS sample had lower O₂ uptake/release than IWI samples indicating the presence of a stable form of Pd-O-Ce sites that do not contribute to the transformation [54]. However, the identical Pd dispersion for both SCS and IWI samples, measured by H₂ chemisorption, confirms that the lower O₂ uptake and release measured for the SCS sample is only a consequence of stable Pd-O, not as a result of Pd encapsulation [54]. Table 2.4 shows the O₂ release and uptake for the catalysts. In another study [55], the presence of Pd²⁺ cations embedded in CeO₂ was observed for the Pd/CeO₂ catalysts prepared using solution-combustion method, however, the palladium was in metallic form (Pd⁰) for the catalyst prepared by the wet impregnation method.

Table 2.4. The amount of oxygen adsorption/desorption on IWI and SCS samples per gram of catalyst
(Reproduced with permission from [54])

Sample	Pd Loading	O ₂ release	O ₂ uptake
	wt. %	($\mu\text{mol/g}_{\text{Pd}}$) $\times 10^{-3}$	($\mu\text{mol/g}_{\text{Pd}}$) $\times 10^{-3}$
IWI	1.71	3.76	3.79
SCS	1.71	3.34	3.28

The preparation method along with the pretreatment of the Pd/CeO₂ catalysts can have a strong impact on the morphology and oxidation state of the catalysts [56]. Stasinska et al. [57] reported no enhancement in the activity of a PdO/Ce-Al₂O₃ catalyst prepared using a sol-gel method, compared to PdO/Al₂O₃, except when operated at low temperature (< 427°C). In contrast, Groppi et al. [58] reported that the temperature of PdO reduction and Pd⁰ re-oxidation increased by about 50-60°C on a 2.5wt.%Pd/11.5wt.%CeO₂/Al₂O₃ catalyst, compared to 2.5wt.%Pd/Al₂O₃ catalyst, in agreement with the observation that the CH₄ combustion was not affected by the CeO₂ except at high temperature. Colussi et al. also reported that the oxygen uptake on 10%Pd/15%CeO₂/Al₂O₃ catalyst was higher than other catalysts without CeO₂ [59]. The optimum amount of CeO₂ varies in different studies [52,53], although high loadings of Ce (50wt.%) are known to suppress catalytic activity [52]. Xiao et al. [60] studied the effect of preparation method on the activity of 2wt.%Pd/CeO₂ catalyst. Using impregnation (IM) and deposition-precipitation (DP) methods, they showed that DP is a favorable method in terms of achieving high activity and stability as 50% CH₄ conversion occurred at 257°C for the Pd-DP catalyst, about 300°C lower than that for Pd-IM catalyst [60]. The highly dispersed Pd along with the high concentration of oxygen vacancies lead to improved catalytic activity of the Pd-DP. The Pd-DP catalyst was aged in the presence of 1vol.% CH₄ and 99vol.% air with a space velocity of 50,000h⁻¹ at 300°C. The catalytic activity decreased slightly from 100% to 93.4% after 16h. However, the deactivation was completely recovered by reducing the catalyst at 300°C in the presence of H₂ for 1h [60]. The same recovery was observed by Bozo et al. [61] as they showed reducing the Pd/Ce_{0.67}Zr_{0.33}O₂ catalyst at 300°C leads to formation of oxygen vacancies [61]. Raman spectroscopy of pure CeO₂, Pd-DP, and Pd-IM showed there is a

main Raman band at 465.5 cm^{-1} indicating the symmetrical Ce-O bond. This Raman band was observed for all three samples, however, the intensity decreased significantly for Pd-IM and Pd-DP catalysts. This decrease was a consequence of high deficiency of CeO_2 due to formation of oxygen vacancies [60]. The Raman spectra of the samples are shown in Figure 2.7.

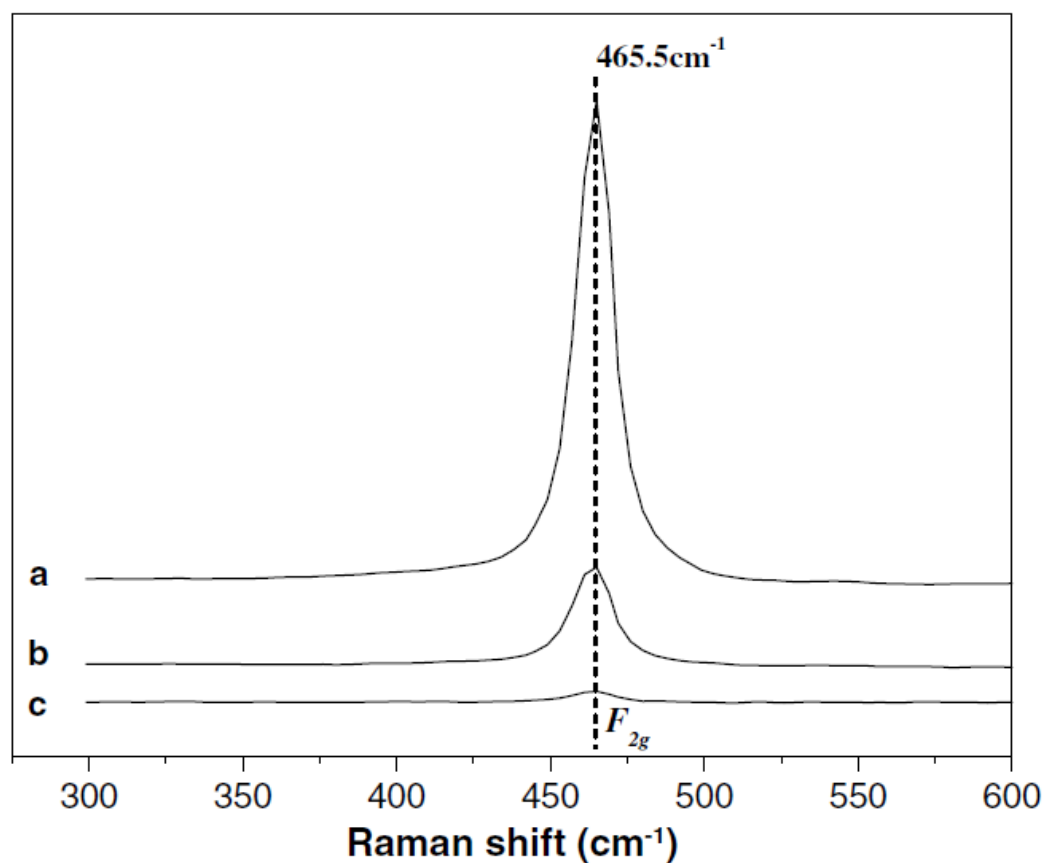


Figure 2.7. Raman spectra for (a) CeO_2 , (b) Pd catalyst prepared by impregnation method, and (c) Pd catalyst prepared by deposition-precipitation method [60] (Copyright © 2005 Elsevier)

Misch et al. [62] investigated the C-H bond activity for partial oxidation of CH_4 in the presence of Pd substituted CeO_2 ($\text{Ce}_{1-x}\text{Pd}_x\text{O}_{2-\delta}$). The catalyst was prepared using ultrasonic spray pyrolysis (USP) with PdO particle size of 10 nm. The presence of Pd substituted in the

lattice cells was proved at $x=0.1$ in $\text{Ce}_{1-x}\text{Pd}_x\text{O}_{2-\delta}$. However, it was shown the catalyst is only active for C-H bond activation after reducing the Pd^{2+} to Pd metal.

A computational density functional theory (DFT) investigation of the complete oxidation of CH_4 over CeO_2 (111), PdO (100), and $\text{Pd}_x\text{Ce}_{1-x}\text{O}_2$ (111) was presented by Mayernick et al. suggesting the lowest reaction barrier occurs for $\text{Pd}_x\text{Ce}_{1-x}\text{O}_2$ (111) surface [56]. It was also shown that the $\text{Pd}_x\text{Ce}_{1-x}\text{O}_2$ (111) surface is more stable than PdO (100) surface [63]. The rate determining step for complete oxidation of CH_4 over Pd/CeO₂ catalysts was considered to be C-H activation that is a function of the oxidation state of palladium, morphology, and also Pd, Ce, and O composition of the surface [56]. Comparing the activation barrier between CeO_2 (111), PdO (100), and $\text{Pd}_x\text{Ce}_{1-x}\text{O}_2$ (111) surface shows a minimum activation barrier obtained for the $\text{Pd}_x\text{Ce}_{1-x}\text{O}_2$ (111) surface at +0.18 eV as it was +1.65 eV and +1.08 eV for the CeO_2 (111) and PdO (100) surface, respectively [56].

2.4 Structure Sensitivity of the Pd Based Catalysts

The structure of Pd-based catalysts is an important factor in determining their activity for CH_4 oxidation. The activity of Pd catalysts is strongly affected by the Pd particle size distribution as reported in some studies [64,65]. Hicks et al. [65] examined the effect of metal dispersion on the catalyst activity. When the catalyst was exposed to reaction conditions, the Pd restructured as it converted to PdO and this led to increasing dispersion. The smaller particle size of PdO with higher dispersion showed higher interaction of active sites with the support, which stabilized the PdO and decreased the activity of the catalyst. Otto et al. [66] also showed that for $\text{Pd}/\text{Al}_2\text{O}_3$ catalysts with Pd loadings $\leq 0.5\text{wt.}\%$, a 1.6 eV increase in the Pd binding energy is observed that indicates the formation of highly dispersed

PdO that leads to stronger chemical interaction of palladium and the support [66]. In another study by Gigola et al. [67,68], the interaction strength of the Pd and Al₂O₃ support was distinguished by the precursor concentration. Lower Pd concentration caused stronger interaction between Pd and the Al₂O₃ support. Ciuparu et al. [30] showed that it is difficult to distinguish the role of PdO particle size and the oxygen mobility of the support on the activity of the catalysts [30]. Castellazzi et al. [69] showed the turn-over frequency (TOF) for the Pd/Al₂O₃ catalysts with 1wt.%, 2wt.%, and 4wt.%Pd varies as $5.6 \times 10^{-3} \text{ s}^{-1}$, $1.7 \times 10^{-2} \text{ s}^{-1}$, and $3.5 \times 10^{-2} \text{ s}^{-1}$, respectively. The 1wt.%Pd catalyst had a higher dispersion of PdO than the 2wt.% and 4wt.% Pd/Al₂O₃ catalysts. However, the higher TOF is not related to the PdO dispersion corresponding to the different Pd loading. Since aging the catalysts caused a negligible decrease in PdO dispersion for the 1wt.%Pd/Al₂O₃ catalyst and it remained constant for the other catalysts, the TOFs increased for all catalysts. They conclude that the TOF is mostly dependent on the Pd-support interaction, not the PdO particle size [69]. In other studies, the change in TOFs was also considered independent of the particle size [70–72]. The activity of 2.7wt.%Pd/ γ -Al₂O₃ catalyst was monitored as a function of particle size. The catalyst was treated under a heating process at 550°C in the presence of air for about 40 days and the activity was measured during this period [71]. The particle size increased significantly from 14 nm to 80 nm, while the activity of the catalyst per gram of palladium remained unaffected by TOS. Ribeiro et al. [72] showed the TOFs for the PdO crystallite size in the range of 2-110 nm changes only from $2 \times 10^{-2} \text{ s}^{-1}$ to $8 \times 10^{-2} \text{ s}^{-1}$. Zhu et al. [73] also showed the reaction order is insensitive to the structure of the catalysts. Comparing the TOFs for Pd (111), Pd (100), and Pd (110) show that regardless of the surface structure of the Pd, the reaction rate is only dependent on the oxygen-oxygen interaction as the Pd surface is

covered by the adsorbed oxygen [73]. Fujimoto et al. [74] showed the structure sensitivity over Al_2O_3 is limited to Pd particle size < 7 nm. Since the structure sensitivity of Pd based catalysts for CH_4 oxidation is still under debate, the effect of Pd dispersion on the amount of H_2O adsorbed on PdO active sites needs to be examined.

2.5 Kinetics of H_2O Inhibition in CH_4 Oxidation

The rate of reaction for CH_4 oxidation is a function of temperature, the CH_4 and O_2 reactant partial pressures, product H_2O and CO_2 partial pressures, the oxidation state of Pd at reaction conditions (PdO , Pd^0), size and morphology of the catalyst [17]. The effect of catalyst pretreatment on the reaction rate was studied by Muto et al. [75]. The 2wt.%Pd/ Al_2O_3 catalyst was pretreated at 450°C in H_2 , O_2 , or N_2 before measuring the activity. It was shown that the rate of CH_4 oxidation was faster for the catalyst pretreated in N_2 rather than O_2 or H_2 . However, the difference in CH_4 oxidation rate decreased as the reaction temperature increased to 450°C . The reaction orders with respect to CH_4 and O_2 were reported by Muto et al. [75] using Equation 2.1.

$$r = kP_{\text{CH}_4}^m P_{\text{O}_2}^n \quad 2.1$$

where r , k , P_{CH_4} , and P_{O_2} are defined as the CH_4 oxidation reaction rate, the reaction rate constant, and partial pressure of CH_4 and O_2 , respectively. The m and n values in Equation 2.1 are compared with other studies in Table 2.5. The low reaction order with respect to O_2 is due to the presence of PdO in the CH_4 combustion reaction [75]. In another study by Zhu et al. [73], it was shown that the reaction order for CH_4 and O_2 is structure insensitive. Pd (111), Pd (100), Pd (110), and Pd foil in both metal or oxide phase have the order of $0.7 < \text{CH}_4 < 1$

and $-0.1 < O_2 < 0.2$ [73], indicating that the large single-crystal Pd catalysts result in the same CH₄ combustion activity regardless of the oxidation state of Pd [73].

Table 2.5. Apparent activation energy and order of CH₄ combustion reaction over Pd catalysts

Catalyst	E _a	Reaction Order			Temperature Range	Refs
	kJ.mol ⁻¹	CH ₄	O ₂	H ₂ O	°C	
Supported Catalysts						
10%Pd/ZrO ₂	174	1.00	0.00	-1.00	232-360	[72]
1.1%Pd/Al ₂ O ₃	81	1.00	0.00	-1.00	290-500	[23]
1%Pd/ZrO ₂	170	1.00	0.00	-1.00	227-441	[37]
1%Pd/SiO ₂	-	1.00	0.00	-0.25	227-441	[37]
7.3%Pd/Al ₂ O ₃	86 (151) ^a	1.00	0.10	-0.80	253-315	[76]
0.5%Pd/Al ₂ O ₃	60	0.90	0.08	-1.3 to -0.9	240-400	[77]
Model Catalysts						
Pd foil	125	0.7	-0.10	0.05	296-360	[73]
Pd(111)	140	0.7	-0.10	0.05	296-360	[73]
Pd(100)	130	0.9	0.01	0.07	296-360	[73]
PdO foil	125	0.7	0.20	-0.90	296-360	[73]
PdO(111)	140	0.8	-0.10	-0.90	296-360	[73]
PdO(100)	125	0.8	0.10	-1.00	296-360	[73]

^a 86 kJ.mol⁻¹ and 151 kJ.mol⁻¹ for the dry and wet conditions, respectively.

The studies of the inhibition effect of the reaction products confirm the strong negative effect of H₂O on CH₄ oxidation [72,76,78,79]. Ribeiro et al. [72] investigated the effect of extra H₂O added to the feed stream on the reaction order. A mixture of 1%CH₄, 0.24%CO₂, and H₂O in the range of 0.03-0.15% in air was used to measure the TOFs as a function of H₂O concentration. The reaction order with respect to H₂O was reported as -0.98 [72]. The reaction orders close to -1 indicate strong competition of H₂O molecules with CH₄ for the surface sites [72]. The inhibiting effect of H₂O was explained by the formation of reversible Pd(OH)₂ at the surface of PdO active sites [72,80]. The reaction rate order for H₂O was determined as a function of temperature by Ciuparu et al. [81]. The H₂O inhibition effect is more dominant at temperatures below 450°C [81]. In another study by Hurtado et al. [77] the reaction order with respect to H₂O varied from -1.3 to -0.9 while the temperature increased

from 300°C to 350°C, indicating the inhibition is the result of H₂O adsorption. The activation energy is strongly affected by the presence of H₂O [17,31]. As shown by Carsten et al. [31], the apparent activation energy for CH₄ combustion over Pd catalysts should be corrected to account for the inhibiting effect of H₂O [31]. In the study by van Giezen et al. [76] an empirical equation was derived to define the order of reaction with respect to H₂O, γ .

$$r = k_1([H_2O])^\gamma \quad 2.2$$

In a differential system assuming a small change in CH₄ and O₂ concentration and a constant temperature, k_1 is defined as:

$$k_1 = k_1^0 [CH_4]^{1.0} [O_2]^{0.1} \exp \left[-\frac{E_a}{RT} \right] \quad 2.3$$

k_1^0 is defined as the pre-exponential factor. Equation 2.4 represents the H₂O concentration at the bottom of the catalyst bed which is a function of both extra H₂O added ($[H_2O]_{in}$) and residence time (τ).

$$[H_2O]_{out} = [H_2O]_{in} + [(1 - \gamma)2k_1\tau]^{1/(1-\gamma)} \quad 2.4$$

By plotting the conversion as a function of residence time, the reaction order of H₂O was found to be -0.76 and -0.74 for a wet and dry feed, respectively. It was also shown that the apparent activation energy is dependent on the H₂O concentration as E_a was estimated at 86 kJ.mol⁻¹ in dry feed and 151 kJ.mol⁻¹ for a feed with 2vol.% H₂O [76]. In spite of the difference in E_a for dry and wet feed, the reaction order was independent of H₂O concentration, i.e. there is no significant difference between the values of -0.76 vs. -0.74.

The apparent activation energy of 174 kJ.mol⁻¹ reported for 10%Pd/ZrO₂ catalyst is in agreement with other studies concerning the effect of H₂O on activation energy [31,71,72,74]. E_a values corrected for the effect of H₂O are shown in Table 2.5.

A kinetic study of the effect of H₂O with respect to CH₄ adsorption as a rate determining step, was investigated by Kikuchi et al. using Equation 2.5 [23].

$$r = k_r[\text{CH}_4]\theta_v \quad 2.5$$

The rate of reaction, r , is a function of CH₄ partial pressure and the fraction of vacant sites, θ_v . k_r is defined in Equation 2.6 and represents the surface rate of CH₄ combustion as a function of apparent activation energy (E_a). It is assumed that adsorption of CH₄ molecules on PdO active sites is irreversible and dissociative, therefore, the PdO site coverage is only affected by H₂O. The fast desorption of CO₂ molecules formed by CH₄ oxidation reaction causes a zero coverage of active sites by CO₂ [23].

$$k_r = k_{r0} \exp\left(\frac{-E_a}{RT}\right) \quad 2.6$$

The fraction of vacant sites, defined in Equation 2.7, shows the dependency of vacant sites on the partial pressure of H₂O ($P_{\text{H}_2\text{O}}$) and the adsorption equilibrium constant, $K_{\text{H}_2\text{O}}$. It is assumed that the H₂O adsorption/desorption is at equilibrium [23].

$$\theta_v = 1 - \theta_{\text{H}_2\text{O}} = \frac{1}{1 + K_{\text{H}_2\text{O}}[\text{H}_2\text{O}]} \quad 2.7$$

By plotting $\ln k_r$ and $\ln K_{\text{H}_2\text{O}}$ versus $1/T$, the values for the apparent activation energy and the enthalpy for H₂O adsorption were estimated for Pd/Al₂O₃, Pd/SnO₂, and Pd/Al₂O₃-36NiO catalysts [23]. Pd/Al₂O₃ catalyst, with the most negative value for the enthalpy of H₂O adsorption, is confirmed to have the highest equilibrium H₂O coverage of PdO active sites compared to Pd/SnO₂ and Pd/Al₂O₃-36NiO catalysts and in agreement with the experimental results reported in [23]. Table 2.6 compares the apparent activation energy and enthalpy of H₂O adsorption reported for the different catalysts.

Table 2.6. Estimated values of E_a and ΔH_{ads} (Reproduced with permission from [23])

Catalyst	E_a kJ.mol ⁻¹	ΔH_{ads} for H ₂ O kJ.mol ⁻¹
1.1%Pd/Al ₂ O ₃	81	-49
1.1%Pd/SnO ₂	111	-31
1.1%Pd/Al ₂ O ₃ -36NiO	90	-30

Cullis et al. [78] studied the effect of a large quantity of H₂O in the range of $0-5.5 \times 10^{-5}$ mol (sic) added to a system with a mixture of 1.8×10^{-6} mol (sic) CH₄ and 3.6×10^{-6} mol (sic) O₂ at 352°C in the presence of 2.7%Pd/Al₂O₃ catalyst. The conversion of CH₄ decreased by increasing the H₂O content, emphasizing the inhibiting effect of H₂O, however, the H₂O produced from the CH₄ oxidation reaction is not found to have any significant effect on the activity of the catalyst [78]. van Giezen et al. [76] showed the reaction order for H₂O remains constant at -0.8 ± 0.2 independent of different H₂O concentrations. However, as shown by Ciuparu et al. the reaction order with respect to H₂O is zero in a dry feed stream [30]. At a constant reaction temperature, the order of reaction with respect to H₂O varies between 0 and -1 as a function of CH₄ conversion [30]. Since a higher H₂O content occurs at higher CH₄ conversion (it is a product of reaction), the order of reaction has higher negative values with increased conversion.

CH₄ oxidation over PdO active sites may occur at different conditions such that either CH₄ activation or H₂O desorption is the rate determining step [17,82]. During the CH₄ oxidation reaction, CH₄ and ¹⁶O on the PdO surface interact with each other, causing the adsorption of CH₄ and the production of CO₂ and OH on the surface of the catalyst [17,32]. The oxygen vacancy is rapidly replaced by the diffusion of ¹⁸O₂ from bulk to the surface of the catalyst.

Figure 2.8 shows the schematic of the oxygen exchange during the CH₄ oxidation reaction reported by Ciuparu et al. [32].

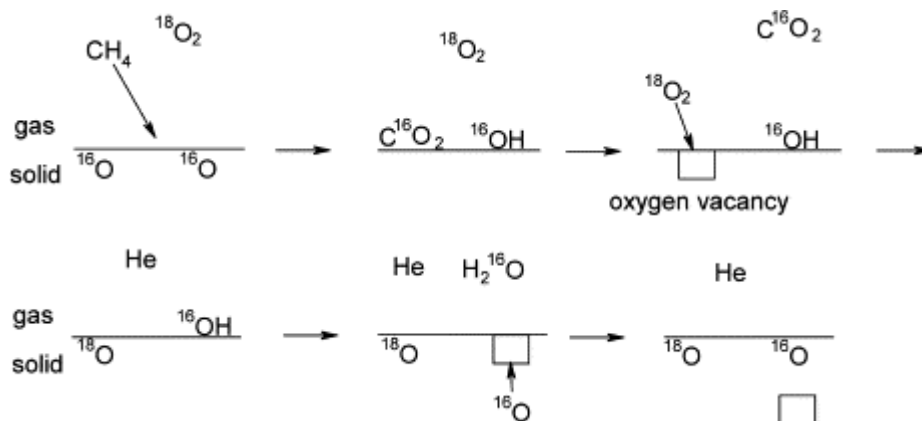
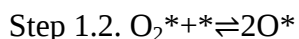
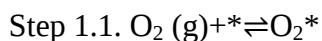


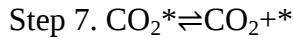
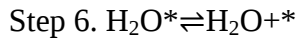
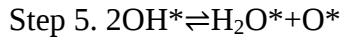
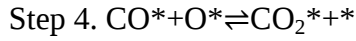
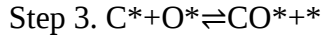
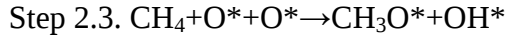
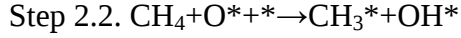
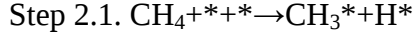
Figure 2.8. Oxygen exchange mechanism for CH₄ oxidation using labeled (¹⁸O¹⁶O) pulsed experiments

[32] (Copyright © 2002 Elsevier)

In another study by Schwartz et al. [34] the oxygen exchange from the gas phase, ¹⁸O₂, and the oxide support, ¹⁶O, to the catalyst surface was studied over a 3wt.%PdO/Al₂O₃. It was shown that the oxygen exchange in the absence of CH₄ becomes significant at temperatures higher than 380°C. The authors suggested that the rate determining step at low temperature (< 500°C) and high H₂O content is water desorption from the surface of the catalyst and that the reaction order with respect to H₂O is -1. However, at a high temperature and low H₂O concentration, the rate determining step is CH₄ activation and the reaction order with respect to H₂O will be zero [30].

The kinetic mechanism of the CH₄-O₂ reaction on supported Pd clusters proposed by Chin et al. [82] is given below.





In this mechanism * and O* correspond to Pd-* and PdO, respectively, as used in the present study.

This schematic indicates the dissociation of both CH₄ and O₂ molecules on the Pd/Al₂O₃ catalyst surface and reaction of CH₄ with O* species that results in the formation of OH* and CO* species. Steps 5-8 are quasi-equilibrated steps that indicate desorption of the produced species. The activation of C-H bond (steps 2.1 to 2.3) is more favorable on the O*-O* than O*-O*. Since the oxygen chemical potential, O*-O* (an adsorbed oxygen and a vacancy site pair) or O*-O* (two adsorbed oxygen site pair), are influenced by the Pd cluster size and O₂ pressure, the C-H bond activation and consequently the TOF are a function of the Pd cluster size and O₂ pressure [82].

As shown in Figure 2.9 the CH₄ oxidation 1st-order rate constant is higher at lower O₂ pressure [82]. For the CH₄ combustion reaction occurring over a 0.2wt.%Pd/Al₂O₃ catalyst at 873K with 4.85 kPa CH₄, the O₂ pressure varied between 0.3-1.7 kPa. The higher CH₄ oxidation rate constant was obtained at an O₂ pressure less than 1.2 kPa and 0.7 kPa for catalysts with 21.3 nm and 4.8 nm Pd cluster size, respectively. However, the reactivity of the Pd with 4.8 nm cluster size is lower than those with 21.3 nm and decreasing the O₂ pressure caused an increase in the rate constant for both 4.8 nm and 21.3 nm Pd clusters. At a constant O₂ pressure, the larger Pd clusters have weaker O* binding that leads to higher vacant site densities which are more effective for C-H bond activation.

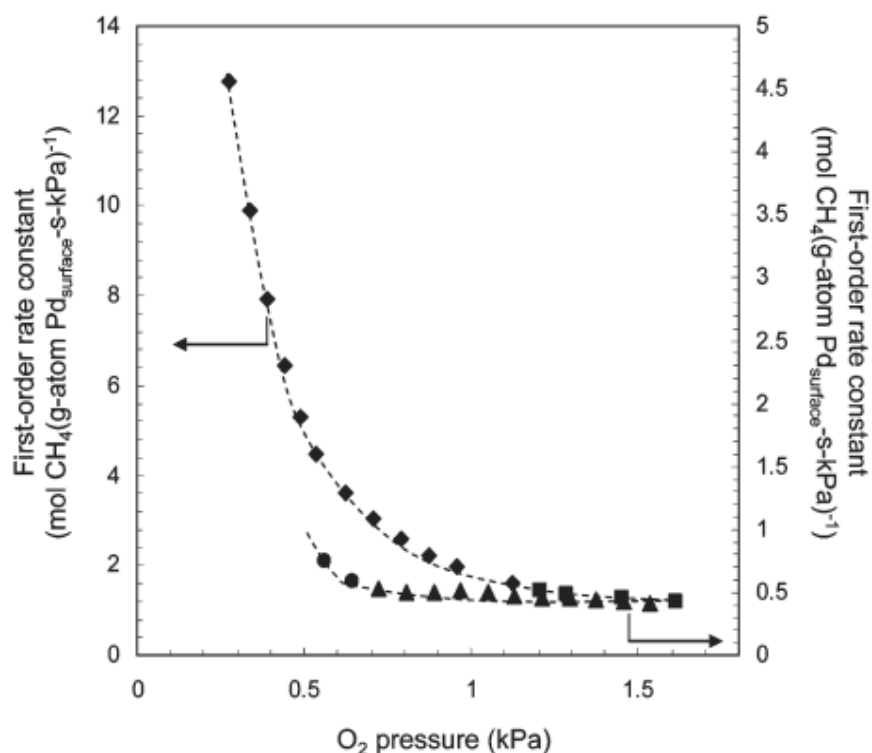


Figure 2.9. Effect of O₂ pressure on the CH₄ oxidation rate constant over 0.2wt.%Pd/Al₂O₃ catalyst at 873K (4.8 nm (●, ▲) and 21.3 nm (◆, ■) Pd cluster diameter) [82] (Copyright © 2011 American Chemical Society)

The transition of C-H bond activation (step 2.1 to 2.3) from less reactive O*-O* sites to more active O*-* sites by decreasing O₂ pressure, leads to a higher CH₄ oxidation rate constant. The same transition mechanism leads to the higher catalyst activity with larger Pd cluster size [82]. Different types of kinetic mechanisms were proposed to model the effect of temperature, H₂O concentration, and partial pressure of the reactants and products on the activity of the Pd-based catalysts. Using Langmuir-Hinshelwood [23,30,77,83–86], and Mars-van Krevelen [77] mechanisms it was proposed that the rate limiting step is either the activation of C-H bond [20] or H₂O desorption [30], depending on temperature and H₂O concentration. However, in the presence of H₂O, there is an agreement that OH group adsorption on the catalyst surface is the main cause of loss in catalyst activity [23,77,86]. Cortes et al. [86] defined the decay function that is expressed as Equation 2.8.

$$A(t) = R_{CO_2}(t)/R_{max} \quad 2.8$$

$R_{CO_2}(t)$ is the reaction rate at time t and R_{max} is the maximum reaction rate achieved at the initial reactivation. $A(t)$, the decay fraction, was functionalized versus TOS using a linear form, a hyperbolic form representing sintering, an exponential equation corresponding to the poisoning of the catalyst surface by chemisorption, and an equation describing coking or fouling of the catalyst surface. The best fit to the experimental results was obtained by the latter equation, indicating that the loss in activity during TOS is related to OH groups on the surface of the catalyst [86].

In another study by Hurtado et al. [77] the kinetics of the CH₄-O₂ reaction was studied for a 0.5%Pd/Al₂O₃ catalyst. Eley-Rideal, Langmuir Hinshelwood, and Mars-van Krevelen

models were applied to the experimental results. Among these models, the Mars-van Krevelen model that describes the slow desorption of H₂O was found to have the best fit. In a modified version of MVK that contains an additional term in order to provide the dependency of reaction rate on the excess amount of H₂O, the adsorption of H₂O on the oxidized Pd active sites was considered as the inhibiting effect of H₂O [77].

$$r = \frac{k_1 k_2 P_{CH_4} P_{O_2}}{k_1 P_{O_2} (1 + K_{H_2O} P_{H_2O}) + 2k_2 P_{CH_4} + (k_1 k_2 / k_3) P_{CH_4} P_{O_2}} \quad 2.9$$

The parameters are defined as the rate constant for the irreversible adsorbed oxygen (k_1), rate constant for the CH₄ reaction on the surface (k_2), and rate constant for the desorption of products (k_3), and K_{H_2O} as the equilibrium constant for the adsorption of H₂O. The estimated value of ΔH_{H_2O} for K_{H_2O} in Equation 2.9 for reduced and oxidized 0.5%Pd/Al₂O₃ catalyst were obtained as -66.1 kJ.mol⁻¹ and -54.5 kJ.mol⁻¹, showing the more inhibiting effect of H₂O adsorption on the reduced catalyst.

2.6 Summary

The effect of H₂O on the CH₄ oxidation reaction using different catalyst supports shows more inhibition by H₂O on Pd/Al₂O₃ than Pd/SnO₂ or Pd/ZrO₂ catalysts, reflecting the stronger H₂O adsorption and consequently less O exchange on the Pd/Al₂O₃ catalyst than the Pd/SnO₂ or Pd/ZrO₂ catalysts. Supports with higher oxygen surface mobility, such as CeO₂ and ZrO₂, show slower deactivation rate compared to Al₂O₃. Accumulation and slow desorption of OH groups from the support may hinder oxygen exchange with the Pd/PdO, leading to activity loss. The preparation method along with the pretreatment of the Pd/CeO₂ catalysts may have an impact on the oxidation state of CeO₂ as it was shown that the OSC of

CeO₂ increases with increasing crystallite size. There is a complex relationship between the role of Pd and the oxygen mobility of the support on the activity of the catalysts. Some studies confirm the high deficiency of CeO₂ in the presence of Pd by formation of Ce₂O₃.

The RDS in the CH₄-O₂ reaction is considered to be C-H bond activation in most studies. The order of CH₄ oxidation reaction with respect to H₂O has a negative value, indicating the inhibiting effect of H₂O. The negative value has been reported in the literature in the range of 0 to -1, depending on the H₂O concentration, type of support, and temperature. The effect of H₂O is more dominant at temperatures below 500°C. A Langmuir-Hinshelwood mechanism is assumed in several kinetic studies of CH₄-O₂ combustion. The slow desorption of H₂O inhibits catalyst activity. The accumulation of OH groups and their low tendency to desorb from the catalyst surface suppress the oxygen exchange between the oxide support and the Pd-* vacant sites, causing a loss in the activity of the catalysts. The supports with high OSC such as CeO₂, can suppress the negative effect of H₂O as CeO₂ facilitates oxygen transfer from the oxide support to the vacant sites.

In spite of a broad study in terms of the effect of high OSC species (CeO₂) on the activity of Pd supported Al₂O₃ catalysts, a clear comparison between the long term stability of catalysts with/without CeO₂ has not been reported. In addition, the inhibiting effect of H₂O during CH₄ oxidation at low temperature (< 400°C) on Pd based catalysts with/without CeO₂ needs to be studied. The structure sensitivity of Pd based catalysts is still under debate. To understand the effect of Pd loading on the activity and stability, catalysts with different Pd loadings need to be examined for CH₄ oxidation reaction in the presence and absence of

H₂O. Also, the reversible and irreversible effects of H₂O need to be investigated quantitatively.

The kinetics of H₂O inhibition for different supports are well described in the literature, however, a study of the dynamic response of the catalyst to H₂O addition that accounts for the effect of high OSC of the oxide supports and the inhibiting effect of H₂O, is not available.

Chapter 3: Experimental

This chapter describes the experimental methods and procedures applied in this study and includes catalyst preparation, catalyst characterization, and catalyst activity tests for the CH₄ oxidation reaction done with and without H₂O added to the feed gas. The catalyst tests were done either by temperature programmed oxidation (TPO) of CH₄ and time-on-stream (TOS) tests at fixed reaction conditions using PdO/Al₂O₃ and PdO/CeO_x/Al₂O₃ catalysts in a fixed bed reactor. The descriptions that follow are augmented with additional details provided in Appendices A, B, and E. Note that a preliminary study of a PdO/ZrO_x/Al₂O₃ catalyst was also completed, but since this catalyst was not the main focus of the study, the results are reported in Appendix I.

3.1 Catalyst Preparation

All of the catalysts studied in this thesis contain Pd, Ce, or Zr on the γ -Al₂O₃ support. The catalysts are calcined before use and are operated in O₂ rich atmospheres so that the metal elements of the catalysts are present in the form of metal oxides. Throughout the thesis, the composition of the catalysts is reported in terms of the metal content (Pd, Ce, and Zr) as a weight % of the calcined catalyst. For example, the 6.5Pd/Al₂O₃ catalyst has a Pd content of 6.5wt.%, equivalent to a 8.0wt.% PdO.

A typical TWC has a monolith structure, washcoated with a porous material such as γ -Al₂O₃, and impregnated by a mixture of noble metals such as Pt, Pd, and Rh that provide the active sites for reaction [9]. The total amount of noble metals is 1-2wt.% of the washcoated γ -Al₂O₃. If Pd is the only noble metal used in the catalytic converter, the loading is typically 5

times higher than that used for Pt and Rh based catalysts [9]. Hence, in most studies using Pd supported on Al_2O_3 , the Pd loading is approximately 5wt.%.

In the present study all the catalysts are Pd-based catalysts using $\gamma\text{-Al}_2\text{O}_3$ as the support. Since some characterization techniques such as XRD are not effective at low Pd loading (e.g. <2wt.%), a higher Pd loading was used to assist in the characterization of the catalysts. Hence, in this study Pd loading was varied from 0.3wt.% to 6.5wt.%.

All of the Pd catalysts studied in this thesis were prepared using incipient wetness impregnation. Generally, a commercial granular $\gamma\text{-Al}_2\text{O}_3$ (Sasol North America, alumina spheres 2.5/210) was crushed manually using mortar and pestle and sieved to obtain an alumina powder with particle size in the range 90-354 μm to be used as the oxide support of the catalysts. The alumina powder was dried at 120°C for 24h in ambient air. The $\gamma\text{-Al}_2\text{O}_3$ had a specific surface area of 224 m^2/g , a pore volume of 0.53 cm^3/g , and 9.4 nm average pore size.

For the Pd/ Al_2O_3 catalysts (reported in Chapter 4), approximately 2.7 g of the support was impregnated with an aqueous solution of Pd obtained from 0.1N HNO_3 and $\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (Aldrich $\geq 99\%$ purity) in order to yield the desired loading of Pd (0.3wt.%, 2.6wt.%, and 6.5wt.% Pd). The impregnated catalysts were left at room temperature for 48h and then dried in an oven at 100°C for 8h. The dried catalysts were sieved again in order to obtain the mesh size in the range of 90-354 μm . Finally, the catalysts were calcined in situ in 100 $\text{cm}^3(\text{STP}) \cdot \text{min}^{-1}$ air (Praxair extra dry air) while heating from room temperature at 10°C.min⁻¹ to 450°C, with the final temperature held for 15h. The calcined catalysts are identified as xPd/ Al_2O_3 , where x is the wt.% of Pd present in the PdO/ Al_2O_3 calcined catalysts. The

purpose of the calcination is to remove undesired components originating from the precursors and also to stabilize the PdO phase. The catalysts were subsequently cooled to room temperature before testing.

For the Ce/Pd/Al₂O₃ catalysts reported in Chapter 5, approximately 2.7 g of the support was co-impregnated with an aqueous premixed solution of Pd and Ce, obtained from 0.1N HNO₃, Pd(NO₃)₂.xH₂O (Aldrich $\leq$ 100% purity) and Ce(NO₃)₃.6H₂O (Aldrich 99% purity) in order to yield the desired loading of Pd and Ce. The thermal treatment of the impregnated Al₂O₃ was the same as that stated above. The catalysts prepared by this method are identified as co-xCe/yPd/Al₂O₃ catalysts where "co" stands for co-impregnation, x is the wt.% of Ce with 0.94wt.%, 2.9wt.%, 4.8wt.%, and 9.5wt.% Ce loadings and y is the wt.% of Pd which is fixed at 6.5wt.% loading.

The catalysts investigated in Chapter 6 were prepared by co-impregnation and sequential impregnation methods. The co-impregnation catalyst followed the same procedure as for the catalysts reported in Chapter 5, however, the Ce loadings were higher (2wt.%, 14wt.% and 47wt.%) and the Pd loading was kept constant at 3.4wt.%. For sequential impregnation, the Al₂O₃ support was first impregnated with an aqueous solution of Ce obtained from 0.1N HNO₃, Ce(NO₃)₃.6H₂O (Aldrich 99% purity) in order to yield the desired loading of Ce. The impregnated supports were left at room temperature for 48h and then dried in an oven at 100°C for 8h and calcined in atmospheric air while heating from room temperature at 10°C.min⁻¹ to 450°C, with the final temperature held for 15h. The new calcined CeO₂-Al₂O₃ supports were impregnated with an aqueous solution of Pd obtained from 0.1N HNO₃, Pd(NO₃)₂.xH₂O (Aldrich $\leq$ 100% purity) then left at room temperature for 48h, dried in an

oven at 100°C for 8h and calcined in situ in 100 cm³(STP).min⁻¹ air (Praxair extra dry air) while heating from room temperature at 10°C.min⁻¹ to 450°C, with the final temperature held for 15h. The catalysts were cooled to room temperature before the activity test. The catalysts prepared by this method are identified as seq-xCe/yPd/Al₂O₃ catalysts where "seq" stands for sequential impregnation, x is the wt.% of Ce with 2wt.%, 6wt.%, 17wt.%, 28wt.%, and 57wt.% Ce loadings and y is the wt.% of Pd which is fixed at 3.4wt.% loading.

The amount of solvent used to prepare the Pd and Ce solutions was selected based on the solubility of each precursor and also the pore volume of γ -Al₂O₃ support. As the required volume of solvent to dissolve the Ce salt in the co-47Ce/3.4Pd/Al₂O₃ catalyst was higher than the pore volume of 1.35 g of γ -alumina support [87], the premixed solution of Pd and Ce salts were added to the support in three steps. Between each step, the catalyst was left at room temperature for 48h in order to complete the impregnation. Then the catalyst was dried in an oven at 100°C for 8h and calcined in air at 450°C for 15h. The same method was applied in order to prepare the seq-57Ce/3.4Pd/Al₂O₃ catalyst.

The details of the calculations of the required amount of chemicals and solvent needed to prepare the catalysts with different Pd and Ce loadings are reported in Appendix A. Repeatability of the preparation method was confirmed using atomic absorption spectroscopy to determine the Pd content present in a xPd/Al₂O₃ catalyst prepared in two different batches. The standard deviation of the catalyst preparation is reported in Appendix D.

3.2 Catalyst Characterization

Several characterization techniques such as atomic absorption spectroscopy, ICP analysis, N₂

adsorption-desorption, XRD, XPS, ToF-SIMS, and CO chemisorption were used in order to identify the properties of the fresh and aged catalysts. Details of these techniques are provided in the following sections.

3.2.1 Atomic Absorption Spectroscopy

The Pd content of the prepared catalysts was determined by Atomic Absorption Spectroscopy (AAS; GBC 904) using an air-acetylene flame with 5.0 mA current, 247.6 nm wavelength, slit width of 0.2 nm, 0.08 $\mu\text{g/mL}$ sensitivity and optimum working range of 4-15 $\mu\text{g/mL}$ of the Pd solution. For the analysis, 10 mg of each catalyst was digested in 2 mL HCl (50wt.%), 2 mL HNO_3 (20wt.%) and 2 mL H_2SO_4 (96wt.%). The resulting solution was diluted with deionized water to obtain approximately 10 $\mu\text{g/mL}$ Pd prior to AAS analysis. Various Pd solutions with different Pd concentrations (0-15 $\mu\text{g/mL}$) were also prepared using a 1000 $\mu\text{g/mL}$ Pd solution diluted with deionized water. All Pd loadings reported in this thesis are actual loadings after being analyzed by AAS.

3.2.2 ICP Analysis

The Ce content was measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using a Thermo Scientific X-Series II with a Cetac ASX-520 autosampler. The samples were digested in 1 mL concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ and diluted to 50 mL with deionized water. All Ce loadings reported in this thesis are actual loadings after being analyzed by ICP.

3.2.3 N_2 Adsorption-desorption

Brunauer-Emmett-Teller (BET) surface area, pore volume, and pore size of the catalysts were determined from N_2 adsorption isotherms measured at 77K using a Micromeritics

ASAP 2020 analyzer. Approximately 0.1g of the catalyst sample was loaded inside a glass tube and sealed with a plastic frit and degassed at 250°C for 12h in vacuum in order to remove moisture. Then a N₂ adsorption-desorption isotherm was obtained as a function of relative pressure at 77K. The BET surface area was calculated using the BET isotherm. The Barrett–Joyner–Halenda (BJH) method was used to estimate the average pore size and the total volume of adsorbed N₂ at the relative pressure of P/P^0 of 0.995 was used to calculate the pore volume of the catalyst. Details are provided in Appendix B.1.

3.2.4 X-ray Diffraction

X-ray diffraction patterns were collected using a Bruker D8 Focus (LynxEye detector) diffractometer with a CoK α source operating at 40 kV and 40 mA and X-ray wavelength of 1.7902 Å. The analysis was performed using a scan range of 10-80° with a step size of 0.04° and step time of 4 s. The Scherrer equation was used to calculate the crystallite size [8]. Details of the XRD analysis are provided in Appendix B.2.

3.2.5 X-ray Photoelectron Spectroscopy

A Leybold MAX200 X-ray photoelectron spectrometer (XPS) with Al K α achromatic X-ray source and a survey pass energy of 192 eV and narrow pass energy of 48 eV was used to determine the Pd, Ce, and Zr oxidation states, the Pd/Al atomic ratio as well as the catalyst surface composition. XPSPEAK41 was used to analyze the spectra after background subtraction by the nonlinear Shirley method. Details of XPS analysis are provided in Appendix B.3.

3.2.6 Time-of-Flight Secondary Ion Mass Spectrometry

A Physical Electronics TRIFT V nanoTOF instrument was used for ToF-SIMS analysis in order to detect the surface composition of Pd, Al, and Ce. The approximate depth of analysis in ToF-SIMS is 2 nm with the source of 30 keV Au^+ pulsed primary ion source in bunched mode. The area of analysis is $400\mu\text{m}\times 400\mu\text{m}$ using the total ion dose of about 10^{12} ions/ cm^2 . The mass spectra were collected in the range of 0-1850 m/z (mass-to-charge) for positive polarity.

3.2.7 CO Chemisorption

A Micromeritics AutoChemII 2920 analyzer was used for CO pulse chemisorption of the reduced catalysts in order to determine the dispersion of PdO active sites. In the analysis, the oxidized catalyst was purged in a $50\text{ cm}^3(\text{STP}).\text{min}^{-1}$ flow rate of Ar (Praxair, UHP) at 200°C for 2h in order to remove moisture. The catalyst was then cooled to 100°C and held for 1h. After degas, a $50\text{ cc}.\text{min}^{-1}$ flow rate of 9.5(v/v)% H_2/Ar (Praxair) at 100°C was fed to the catalyst for 1h, and then cooled to 25°C in He [88]. The purpose of flowing H_2/Ar is to partially reduce the catalyst so that a thin layer of PdO is transformed to Pd^0 that is able to adsorb CO, without affecting the size of the supported PdO particle [74]. The CO uptake was measured by passing pulses of 9.93 (v/v)% CO/He (Praxair) at 25°C over the partially reduced catalyst. The CO pulse injection continued until no additional chemisorption was observed. The CO uptake was measured using a thermal conductivity detector (TCD). Linear CO chemisorption is assumed, so that each surface site (Pd surface atom) is occupied by one CO molecule (stoichiometric factor of 1). Details of the CO uptake and the calculated Pd dispersion is provided in Appendix B.4.

Details of the calculations to determine the standard deviations of the BET, XRD, XPS, and CO chemisorption analyses are reported in Appendix D.

3.3 Catalyst Testing

3.3.1 Experimental Setup

The catalyst CH_4 oxidation activity was measured in a fixed-bed micro-reactor, operating at atmospheric pressure as shown in Figure 3.1. The stainless steel reactor, with 7.0 mm inner diameter, was placed inside an electric tube furnace with a PID temperature controller. The catalyst (90-354 μm mesh size) was diluted with inert SiC of the same size to ensure isothermal operation through the 4.2 cm length of the catalyst bed. The temperature of the bed was monitored using a K-type thermocouple, located in the middle of the catalyst bed. The desired flow rates of each gas in the inlet feed were controlled using electric mass flow controllers (Brooks 5850 TR). The desired inlet gas mixture was obtained using CH_4 (9.93(v/v)% CH_4/He , certified purity or 0.76(v/v)% CH_4/Ar , certified purity), O_2 (Praxair, UHP), He (Praxair, UHP), Ar (Praxair, UHP), and air (Praxair, Extra dry air). He and Ar were used as inert gases to dilute the CH_4/O_2 mixture and obtain the desired flow rate and CH_4 concentration in the inlet gas. Air was used for in situ calcination before the experiment. The outlet gas flow entered a quadrupole mass spectrometer (QMS) to quantify the conversion of CH_4 .

In cases where water was added to the reactant feed gas, liquid water was pumped into the dry feed gas using a Harvard Apparatus Syringe Pump (Model 44). To ensure the water converts to vapor phase, the feed gas mixture with water passed through a pre-heater held at

120°C before entering the reactor. All the feed gas and product lines were heated to the same temperature as the pre-heater in order to ensure that the water remained in the vapor phase. Finally, the outlet gas flow from the reactor passed through a cold-trap followed by a silica gel absorber to remove water before continuous analysis by the mass spectrometer.

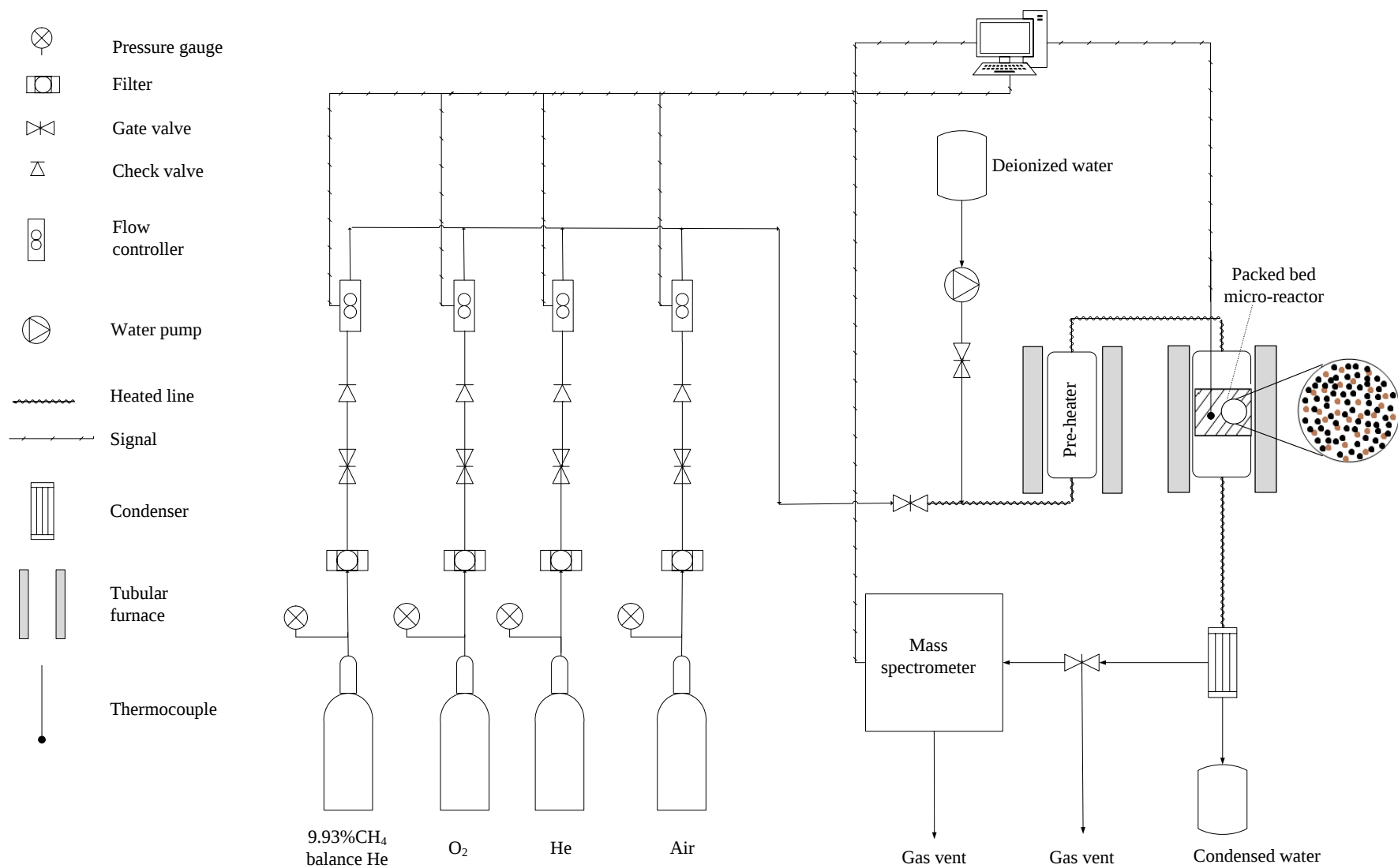


Figure 3.1. Schematic diagram of CH₄ oxidation setup

The outlet gas flow including the reactants and products were analyzed by a VG ProLab quadrupole mass spectrometer (ThermoFisher Scientific) and a RGA-200 quadrupole mass spectrometer (Stanford Research Systems). The outlet gas was continuously monitored by the mass spectrometer. The signal intensity of the mass peaks for CH₄, O₂, CO₂, He, Ar, and H₂O were recorded (see Appendix E.1). The mass spectrometer was calibrated for CH₄, CO₂ (0.5(v/v)% CO₂/Ar or 0.1859(v/v)%CO₂/Ar), and O₂ in the same concentration range as the CH₄ oxidation reaction (see Appendix C.2) and this calibration was used to determine the product gas compositions.

3.3.2 Temperature Programmed Oxidation

Temperature Programmed Oxidation (TPO) tests were done to measure the initial activity of the catalysts. 0.1 g of the dried xCe/yPd/Al₂O₃ catalyst with 90-354 µm mesh size was diluted with 2.5 g inert SiC with the same mesh size as the dried catalyst and loaded into the reactor. Then the mixture was calcined in situ in 100 cm³(STP).min⁻¹ of dry air heating to 450°C at 10°C.min⁻¹ and holding at this temperature for 15h before cooling to room temperature. Then the gas feed, with a total flow rate of 300 cm³(STP).min⁻¹ and GHSV of 180,000 cm³(STP).g_{cat}⁻¹.h⁻¹, consisting of 0.1(v/v)% CH₄, 20(v/v)% O₂ balanced with He and Ar was fed over the calcined catalyst. The reactor temperature was increased from room temperature to 450°C at 5°C.min⁻¹ and the outlet gas was continuously monitored by the VG ProLab quadrupole mass spectrometer to measure the CH₄ conversion as a function of temperature.

3.3.3 Time-on-Stream Experiments

The stability of the catalysts was measured using Time-on-Stream tests in which the CH₄ conversion was measured over a 24h period at a constant temperature and H₂O concentration. The TOS results reported in Chapters 4 and 5 were generated using 0.0833 g of dried catalyst diluted with 2.1g inert SiC. Similar to the TPO experiment, the catalyst was calcined in situ with 100 cm³(STP).min⁻¹ of dry air at 450°C (10°C.min⁻¹) for 15h and cooled to room temperature. Then the total feed gas flow rate of 250 cm³(STP).min⁻¹ corresponding to a GHSV of 180,000 cm³(STP).g_{cat}⁻¹.h⁻¹ with 0.5(v/v)% CH₄, 20(v/v)% O₂, 0 or 5vol.% H₂O balanced with He was fed to the calcined catalyst. Two different water concentrations (0 and 5vol.% water) in the feed gas are referred to as "dry-TOS" and "wet-TOS" tests, respectively. In the dry-TOS experiments, the temperature was increased from room temperature to the desired temperature (300°C, 330°C, 350°C, 380°C, or 400°C) at 5°C.min⁻¹ in the presence of the reactants. The temperature was then held constant as the reaction proceeded for a period of 24h. A similar heat-up procedure was followed for the wet-TOS experiments, except that water was added to the dry feed using a Harvard Apparatus Syringe pump (model 44) to obtain a 5vol.% H₂O in the feed gas once the reaction temperature had stabilized at the desired reaction temperature. The conversion of CH₄ at a constant temperature and constant feed gas flow rate was measured and the variation in CH₄ conversion with TOS was determined using the RGA-200 quadrupole mass spectrometer. After 24h wet-TOS the syringe pump conveying water to the system was stopped and the experiment was followed by a dry-TOS for 2h. The rate of increase in CH₄ conversion upon removing water and conversion in dry-TOS was monitored by the RGA-200 quadrupole

mass spectrometer. Once the experiment was completed, the condensate water collected in the cold trap was measured.

The Time-on-Stream was chosen as 24h to ensure enough time to observe loss in CH₄ conversion and stability. The temperature and reactant concentrations were chosen based on the NGV exhaust conditions (temperature $\leq 400^{\circ}\text{C}$ and CH₄ concentration < 5000 ppm) and water concentration was set at 5vol.% (lower than the water concentration in NGV exhaust gas) to be able to observe the loss in the activity of the catalysts.

The TOS results reported in Chapter 6 were examined using 0.1g of dried catalyst diluted with 2.5g inert SiC. Similar to the TPO experiment, the catalyst was calcined in situ. Then the total feed gas flow rate of $300\text{ cm}^3(\text{STP}).\text{min}^{-1}$ corresponding to a GHSV of $180,000\text{ cm}^3(\text{STP}).\text{g}_{\text{cat}}^{-1}.\text{h}^{-1}$ containing 0.1(v/v)% CH₄, 20(v/v)% O₂, 0, 1, 2, or 5vol.% H₂O balanced with Ar and He was fed to the calcined catalyst. Similar to the TOS experiments in Chapters 4 and 5, the 0vol.% water in the feed gas is referred as "dry" test and 1, 2, and 5vol.% water in the feed gas is referred as "wet" test. Once the reaction temperature reached the desired temperature (310° , 330°C , 350°C , or 370°C) by heating at $5^{\circ}\text{C}.\text{min}^{-1}$ the water was added to the dry feed gas and then held for 24h. The CH₄ conversion was measured using the VG ProLab quadrupole mass spectrometer. Similar to the wet-TOS in Chapters 4 and 5, the syringe pump was stopped after 24h wet-TOS and a 2h dry-TOS experiment was run. The rate of increase in CH₄ conversion upon removing water and conversion in dry-TOS was monitored by the VG ProLab quadrupole mass spectrometer. Once the experiment was completed, the condensate water collected in the cold trap was measured.

Table 3.1 summarizes the choice of conditions for the CH₄ oxidation tests used in this study. In most cases, the tests have been done at conditions close to those that would be encountered in a real NGV exhaust, except for the O₂ content of the feed gas. However, as noted in Chapter 4, the kinetics of the CH₄ oxidation reaction is known to be approximately zero order in O₂ partial pressure, so this deviation is not expected to have a significant impact on the conclusions drawn from this study.

Table 3.1. A comparison of the reaction conditions used in the present study and real NGV operating condition

Parameter	Definition	This study	NGV operating condition [12]
T	Reaction temperature range (°C)	310-400	500-550
P	Total pressure (kPa)	101.325	101.325
y _{CH4}	CH ₄ concentration (ppm)	1000, 5000	500-1500
y _{O2}	O ₂ concentration (vol.%)	20	2-12
GHSV	Gas hourly space velocity (cm ³ .g _{cat} ⁻¹ .h ⁻¹)	180,000	200,000
y _{H2O}	H ₂ O concentration range (vol.%)	0-5	10-15
X _{Pd}	Pd loading range (wt.%)	0.3-6.5	0.5-5
y _{CO2}	CO ₂ concentration (vol.%)	-	15
y _{NOx}	N ₂ concentration (vol.%)	-	Trace
y _{SOx}	SO _x concentration (ppm)	-	1

3.4 Catalyst Activity Calculation

3.4.1 CH₄ Conversion Calculation

CH₄ conversion is calculated based on the mole balance of carbon at the exit of the reactor. Assuming a complete oxidation of CH₄ occurring in the reactor, CO₂ and H₂O are produced according to the reaction: CH₄ + 2O₂ → CO₂ + 2H₂O. The total moles of carbon is constant through the reactor and can be calculated from the measured composition of the reactor exit gas:

$$\sum n_c = n_{CH_4} + n_{CO_2} \quad 3.1$$

Analyzing the reactor exit gas by the mass spectrometer confirmed the formation of CO₂ as a product of CH₄ oxidation (no CO signal was observed by mass spectrometer). In addition, some preliminary CHNS elemental analyses for the used catalysts confirmed no coke deposition on the catalysts, indicating no remaining C during CH₄ oxidation reaction. These observations verify the validity of Equation 3.1. Knowing the total carbon and CH₄ content exiting the reactor, the CH₄ conversion is readily calculated by Equation 3.2.

$$X_{CH_4} = \frac{\sum n_c - n_{CH_4}}{\sum n_c} \times 100 \quad 3.2$$

Further details of the calculations are given in Appendix E.

The properties of the fresh catalysts were determined prior to the CH₄ oxidation reaction using various characterization techniques described in this chapter. The same characterization techniques were used for the used catalysts in order to verify the effect of aging and H₂O adsorption on the properties of the catalysts. Initial activity of the catalysts was determined by Temperature Programmed Oxidation (TPO) tests, while the stability of the catalysts was determined using Time-on-Stream (TOS) tests with/without extra H₂O. A reactor design equation combined with the kinetic model were applied to the experimental data obtained from the TOS experiments in order to calculate the apparent activation energy (E_a), ΔH_{H_2O} , and k_r for PdO/Al₂O₃ and CeO_x/PdO/Al₂O₃ catalysts.

Chapter 4: Effect of Pd Loading on the Activity and Stability of Pd/Al₂O₃ Catalysts in the Presence of H₂O

4.1 Introduction

In this chapter, the effect of different Pd loadings on the activity and stability of the catalysts during CH₄ oxidation was investigated. The Pd loading increased from 0.3wt.% to 6.5wt.%. The goal was to study the effect of Pd loading on the physical and chemical properties of the catalysts as well as their initial activity and stability in the presence of H₂O. In addition, the effect of Pd dispersion on the amount of H₂O adsorbed on active sites was examined in this chapter.

4.2 Results

The effect of varying Pd loading on the properties of the catalysts such as BET surface area, XRD crystallite size, Pd dispersion, Pd oxidation states along with the effect of Pd loading on the catalyst activity for CH₄ oxidation reaction are presented in this section.

4.2.1 Catalyst Properties

The properties of the catalysts with 0.3wt.%, 2.6wt.% and 6.5wt.%Pd loadings are summarized in Table 4.1. The BET surface areas of the catalysts show a small increase from 207 m²/g to 218 m²/g by increasing the amount of Pd from 0.3% to 6.5%. The BET surface area of the 6.5Pd/Al₂O₃ catalyst is close to that of the Al₂O₃ support (224 m²/g), and the pore volume and pore size decrease with increased Pd loading. The CO uptake results show

higher amounts for CO adsorption at higher loadings of Pd. The Pd dispersion obtained by CO chemisorption was 57.0% for the 0.3Pd/Al₂O₃ catalyst decreasing to 48.0% for the 2.6Pd/Al₂O₃ and 33.5% for the 6.5Pd/Al₂O₃ catalyst, indicating lower Pd dispersion obtained at higher Pd loading.

Table 4.1. Properties of PdO catalysts with different loadings of Pd over Al₂O₃

Catalyst	BET SA ^a m ² .g _{cat} ⁻¹	Pore Volume ^a cm ³ .g _{cat} ⁻¹	Pore Size ^a nm	CO Uptake ^b μmol.g _{cat} ⁻¹	Pd Dispersion ^b %	PdO C. Size ^c nm
0.3Pd/Al ₂ O ₃	207	0.47	9.1	35	57.0	-
2.6Pd/Al ₂ O ₃	215	0.45	8.3	119	48.0	6
6.5Pd/Al ₂ O ₃	218	0.43	7.9	204	33.5	6

^a Determined by BET

^b Obtained by CO chemisorption

^c PdO (101) crystallite size obtained by XRD

Figure 4.1(a) shows the XRD analysis for 0.3Pd/Al₂O₃ catalyst. The main peak for PdO (101) appeared at 2θ=39.59°. This peak is also observed at the same 2θ for 2.6Pd/Al₂O₃ and 6.5Pd/Al₂O₃ catalysts in Figure 4.1(b) and 4.1(c). As a result of higher loadings of Pd, a new peak at 2θ=64.50° appears for 2.6Pd/Al₂O₃ and 6.5Pd/Al₂O₃ catalysts that corresponds to PdO (112). The PdO (101) crystallite size was calculated by the Scherrer equation and is reported in Table 4.1. Because of the low concentration of the Pd in the 0.3Pd/Al₂O₃ catalyst, it was not possible to calculate the PdO crystallite size for this catalyst. The crystallite size calculated for the 2.6Pd/Al₂O₃ and 6.5Pd/Al₂O₃ catalysts were the same at 6 nm.

Figure 4.2 presents the XPS Pd 3d spectral analysis for the 0.3Pd/Al₂O₃, 2.6Pd/Al₂O₃,

and 6.5Pd/Al₂O₃ catalysts. The binding energy (B.E.) of the Pd 3d_{5/2} and 3d_{3/2} electrons, the surface compositions of Pd, Al, and O, as well as the Pd/Al ratio on the surface of each catalyst is reported in Table 4.2. The B.E.s for Pd 3d_{5/2} and Pd 3d_{3/2} remain almost the same for 0.3Pd/Al₂O₃, 2.6Pd/Al₂O₃ and 6.5Pd/Al₂O₃ catalysts.

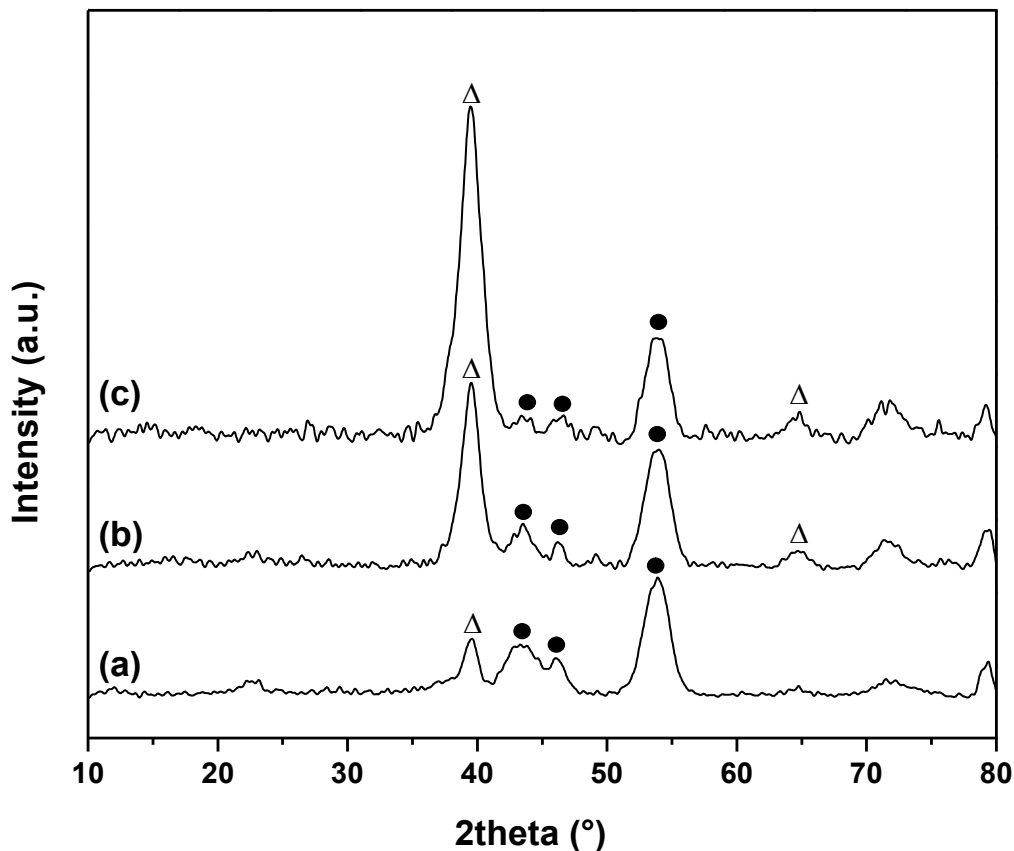


Figure 4.1. XRD patterns for (a) 0.3Pd/Al₂O₃, (b) 2.6Pd/Al₂O₃, and (c) 6.5Pd/Al₂O₃. Δ PdO, $\bullet$ Al₂O₃

Comparing the surface compositions indicates higher amounts of Pd at higher loadings of Pd and the Pd/Al ratio obtained by XPS analysis also shows an increase from 0.4% to 2.3% with increasing Pd loading from 0.3% to 6.5%. The higher Pd/Al ratio on the surface of the catalysts is a consequence of higher Pd loading. Note that the Pd/Al (%) is calculated from the normalized values of surface concentration, excluded C content, as measured by XPS.

Table 4.2. Pd 3d spectra for catalysts with different loadings of Pd

Catalyst	Binding Energy		Surface Composition			Surface
	eV		(at.%)			Pd/Al
	Pd 3d _{5/2}	Pd 3d _{3/2}	Pd	Al	O	%
0.3Pd/Al ₂ O ₃	337.0	342.3	0.16	36.69	63.15	0.4
2.6Pd/Al ₂ O ₃	336.9	342.1	0.53	35.61	63.86	1.5
6.5Pd/Al ₂ O ₃	336.8	342.1	0.85	37.30	61.84	2.3

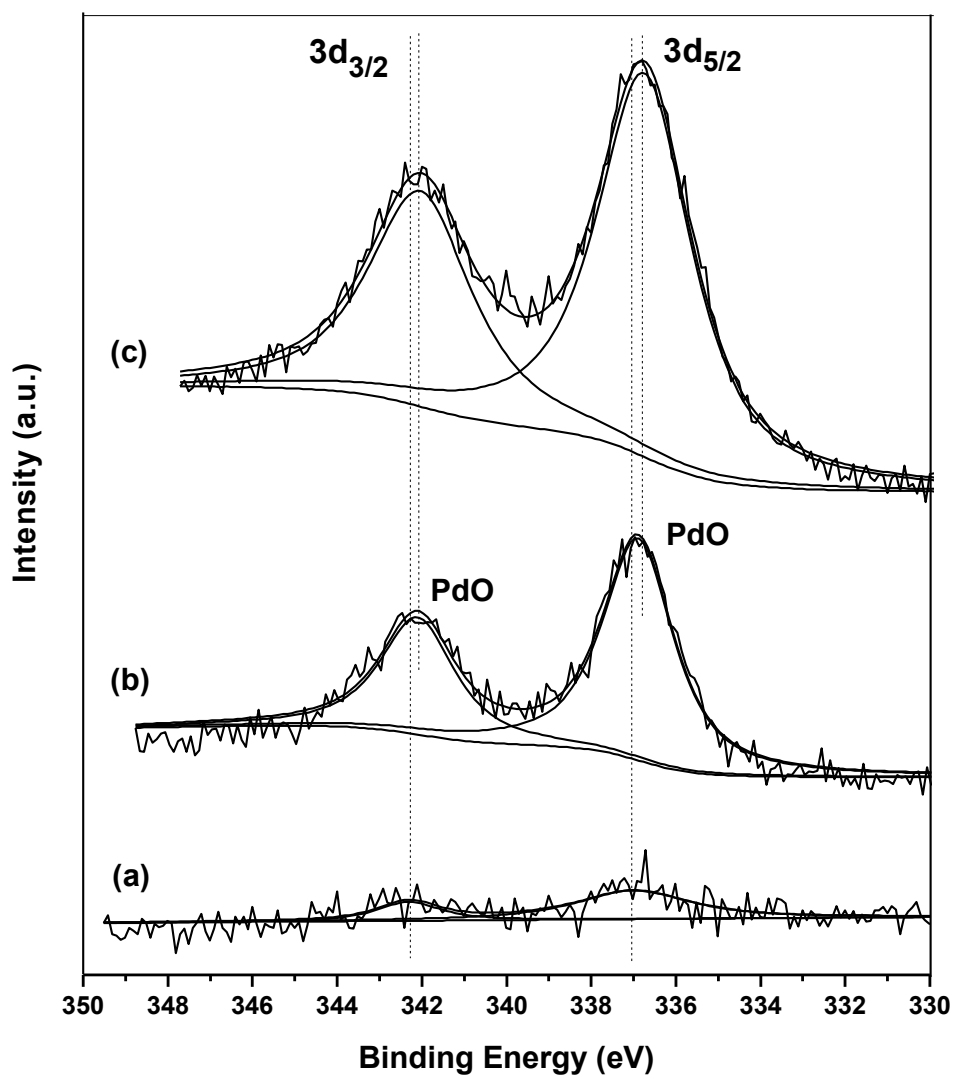


Figure 4.2. XPS Pd 3d spectra measured for (a) 0.3Pd/Al₂O₃, (b) 2.6Pd/Al₂O₃, and (c) 6.5Pd/Al₂O₃

4.2.2 Catalyst Activities

Figure 4.3 reports the initial activity of the calcined 0.3Pd/Al₂O₃, 2.6Pd/Al₂O₃, and 6.5Pd/Al₂O₃ catalysts using a dry feed consisting of 1000 ppmv CH₄ in TPO tests. Higher conversion was obtained for the catalysts with higher Pd loading due to a higher number of active sites within the reactor. Table 4.3 presents T₁₀, T₅₀, and T₉₀ corresponding to the temperature required for 10%, 50%, and 90% CH₄ conversion.

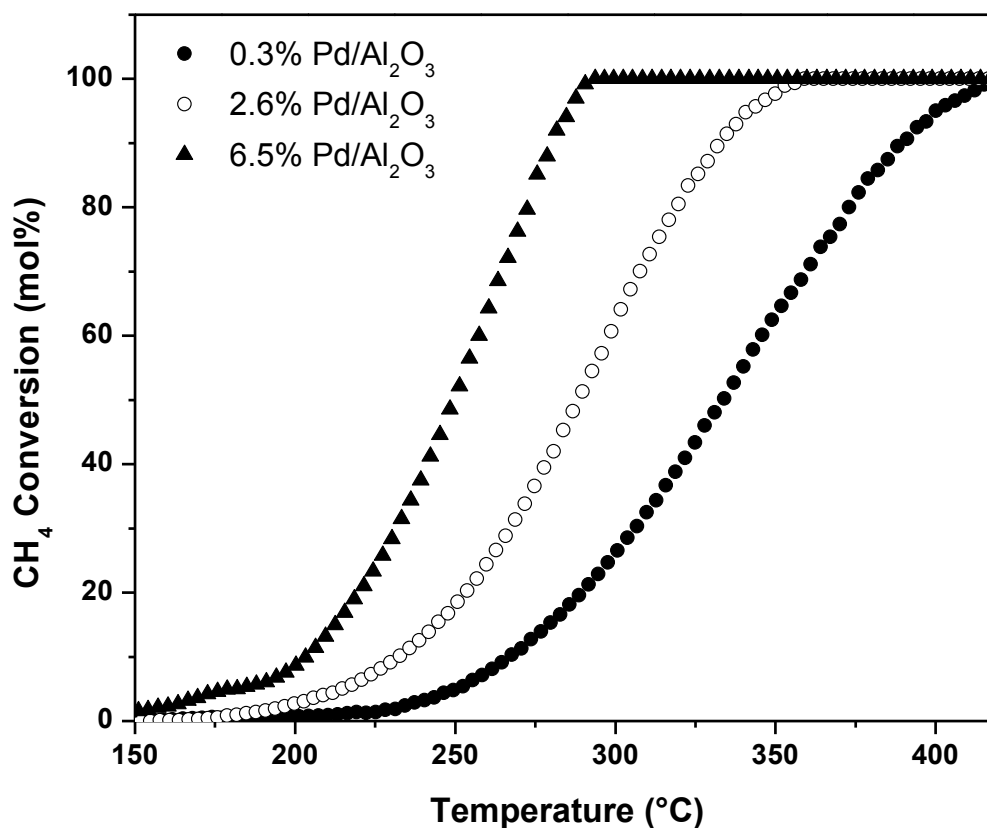


Figure 4.3. Temperature Programmed Oxidation profile. GHSV=180,000 cm³(STP).g_{cat}⁻¹.h⁻¹, 1000 ppmv CH₄, 20(v/v)% O₂, and the balance He and Ar

Table 4.3. Light-off temperatures for 0.3Pd/Al₂O₃, 2.6Pd/Al₂O₃, and 6.5Pd/Al₂O₃ catalysts

Catalyst	T ₁₀ °C	T ₅₀ °C	T ₉₀ °C
0.3Pd/Al ₂ O ₃	267±6	333±4	391±6
2.6Pd/Al ₂ O ₃	232±6	289±4	332±6
6.5Pd/Al ₂ O ₃	203±6	249±4	280±6

The catalysts were tested for CH₄ oxidation to assess their stability in the presence of extra H₂O. Figures 4.4 and 4.5 show the TOS results for a "dry" and "wet" feed gas with 5vol.% extra H₂O over a 24h period at temperatures 330°C and 350°C. All catalysts show a slow loss of activity with TOS in the dry feed gas at 330°C, however, the loss is slower for lower Pd loadings. In wet feed gas with 5vol.% extra H₂O all catalysts showed a much faster loss of activity than the dry feed gas. An exponential loss in activity occurred immediately after the 5vol.% extra H₂O was added for all three catalysts. The exponential loss continued for about 3h, 4h, and 5h for the 0.3Pd/Al₂O₃, 2.6Pd/Al₂O₃, and 6.5Pd/Al₂O₃ catalysts, respectively, followed by a linear loss up to TOS=24h. The shorter exponential loss in activity that occurred for the 0.3Pd/Al₂O₃ catalyst, suggesting that the H₂O adsorption reaches equilibrium faster in the case of 0.3Pd/Al₂O₃ catalyst. This is a result of lower Pd/Al on the catalyst surface, indicating a higher possibility of active site coverage by H₂O on the 0.3Pd/Al₂O₃ catalyst than the other catalysts. Once the active sites coverage by H₂O reaches equilibrium, the minimum CH₄ conversion value is obtained and then stabilizes at that value. The TOS results at 350°C show higher CH₄ conversion and less loss in activity of the catalysts compared with those at 330°C. For instance, after 24h TOS at 350°C the CH₄ conversion for the 0.3Pd/Al₂O₃ catalyst decreased from 56.2% to 38.8% in the dry feed gas and to 3.8% in the wet feed gas, comparing the data at 330°C and 350°C shows higher CH₄

conversion after 24h TOS at 350°C than 330°C for 0.3Pd/Al₂O₃ catalyst. This observation indicates less H₂O adsorption at higher temperatures for all 0.3Pd/Al₂O₃, 2.6Pd/Al₂O₃, and 6.5Pd/Al₂O₃ catalysts.

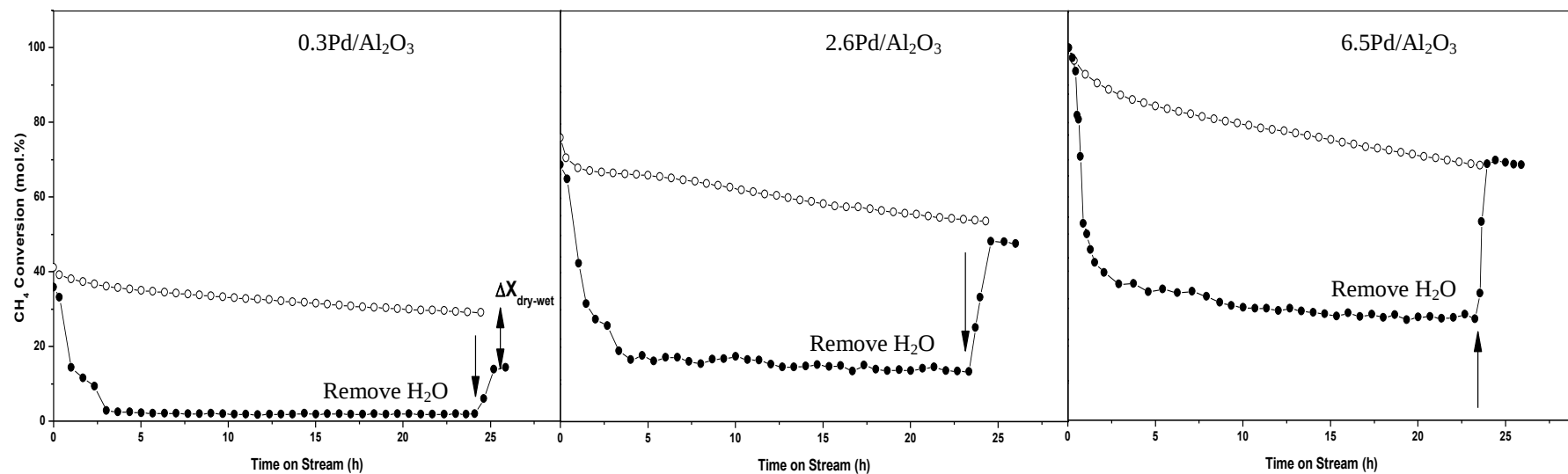


Figure 4.4. TOS results for (a) 0.3Pd/Al₂O₃, (b) 2.6Pd/Al₂O₃, (c) 6.5Pd/Al₂O₃ at T=330°C for dry (open symbol) and wet (closed symbol) conditions.

GHSV=180,000 cm³(STP).g_{cat}⁻¹.h⁻¹, 5000 ppmv CH₄, 20(v/v)% O₂, and the balance He

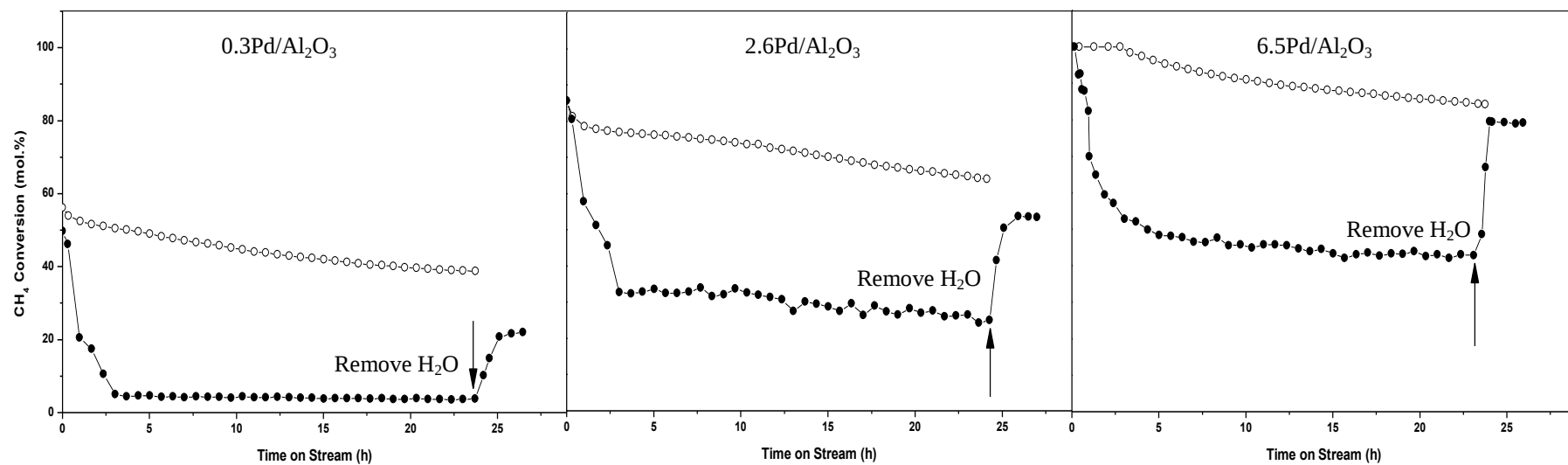


Figure 4.5. TOS results for (a) 0.3Pd/Al₂O₃, (b) 2.6Pd/Al₂O₃, (c) 6.5Pd/Al₂O₃ at T=350°C for dry (open symbol) and wet (closed symbol) conditions.

GHSV=180,000 cm³(STP).g_{cat}⁻¹.h⁻¹, 5000 ppmv CH₄, 20(v/v)% O₂, and the balance He

4.3 Kinetic Model

To quantify the effect of different Pd loadings on the activity and stability of the catalysts, a kinetic analysis of the activity data has been completed. As noted in Chapter 2, the negative effect of H₂O on CH₄ oxidation has been investigated in several studies [72,76,78,79]. In a study by Ribeiro et al. [72] it was confirmed that the order of the CH₄ oxidation reaction is affected by extra H₂O added to the feed gas. The reaction order with respect to H₂O ranges from -1.3 to -0.9 at low temperatures varying from 300°C to 350°C [77] and the activation energy needs to be corrected in order to account for the inhibiting effect of H₂O [31]. van Giezen et al. [76] reported activation energies of 86 kJ.mol⁻¹ and 151 kJ.mol⁻¹ for 7.3%Pd/Al₂O₃ catalyst in dry feed and wet feed, respectively [76].

The fixed-bed micro-reactor was modeled for the reaction conditions with an inlet feed stream of 5000 ppmv CH₄ and 0-5vol.%H₂O entering the catalyst bed at a fixed temperature. For a single component (CH₄ only), the overall mole balance equation in the reactor is $\epsilon_{bSIC} \frac{\partial C_{CH_4}}{\partial t} + \nabla \cdot C_{CH_4} u + \nabla \cdot J = \eta r_{CH_4}$ [89]. $\epsilon_{bSIC} \frac{\partial C_{CH_4}}{\partial t}$ represents the CH₄ accumulation per unit volume, ϵ_{bSIC} is the porosity of the catalyst bed, $\nabla \cdot C_{CH_4} u$ and $\nabla \cdot J$ are the net rate of CH₄ addition per unit volume caused by convection and diffusion, respectively, r_{CH_4} is the actual overall rate of CH₄ oxidation reaction with the unit of mol.(cm³.s)⁻¹, η is the internal effectiveness factor, and C_{CH_4} is the gas molar density or concentration in mol/cm³. A one dimensional packed bed reactor model can be assumed given the high ratio of catalytic bed length to catalyst particle diameter, $\frac{L_{bed}}{d_p} = 203$. Generally, in a packed bed reactor the gas velocity is higher near the wall because of the lower density of the catalyst bed [90,91].

Therefore, the CH_4 concentration gradient in the radial direction can be critical. The ratio of the bed diameter to the catalyst particle diameter, $\frac{d_{\text{bed}}}{d_p}$, higher than 10 can reduce the radial direction effect. In the present study, this ratio is 32. Therefore, the radial direction is neglected. In addition, the $\nabla \cdot \mathbf{J}$ term (diffusion transport) is negligible compared to $\nabla \cdot C_{\text{CH}_4} \mathbf{u}$ (convective transport) as a result of the high superficial velocity ($u=0.24 \text{ m.s}^{-1}$) of the gas through the reactor, therefore the mole balance for CH_4 is simplified as Equation 4.1:

$$\epsilon_{\text{bSiC}} \frac{\partial C_{\text{CH}_4}}{\partial t} + u \frac{\partial C_{\text{CH}_4}}{\partial L} = \eta r_{\text{CH}_4} \quad 4.1$$

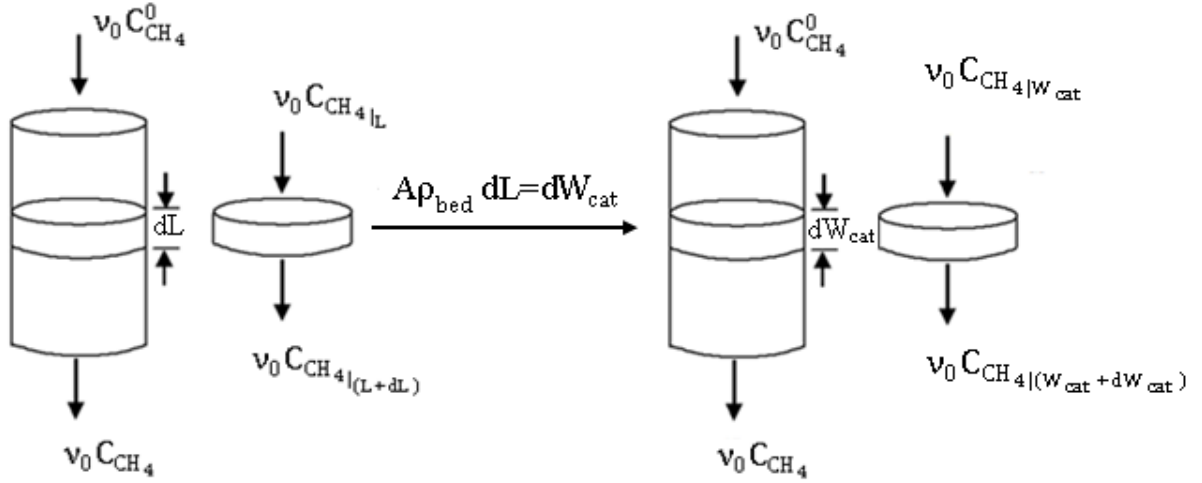


Figure 4.6. Schematic of the reactor used in the CH_4 oxidation process

Since the CH_4 oxidation reaction occurs in the catalyst bed, Equation 4.1 is transformed to Equation 4.2 where the mole balance is a function of mass of catalyst (W_{cat}).

$$\frac{\epsilon_{\text{bSiC}}}{\rho_{\text{bed}}} \frac{\partial C_{\text{CH}_4}}{\partial t} + Au \frac{\partial C_{\text{CH}_4}}{\partial W_{\text{cat}}} = \frac{\eta}{\rho_{\text{bed}}} r_{\text{CH}_4} \quad 4.2$$

W_{cat} and ρ_{bed} represent the mass and density of the catalyst as explained in Appendix H.1.

Au in Equation 4.2 represents the total volumetric flowrate written as $v_0 \text{ (cm}^3 \cdot \text{s}^{-1}\text{)}$.

Equation 4.2 is re-written as:

$$\frac{\varepsilon_{bSiC}}{\rho_{bed}} \frac{\partial C_{CH_4}}{\partial t} = -v_0 \frac{\partial C_{CH_4}}{\partial W_{cat}} + \eta r_{CH_4}^m \quad 4.3$$

where t is the time-on-stream (s), $-v_0 \frac{\partial C_{CH_4}}{\partial W_{cat}}$ represents the net (inlet-outlet) molar flow rate, $r_{CH_4}^m$ is the CH_4 oxidation reaction rate on a mass basis ($\text{mol.g}_{cat}^{-1}.\text{s}^{-1}$) and $\frac{\varepsilon_{bSiC}}{\rho_{bed}} \frac{\partial C_{CH_4}}{\partial t}$ is the accumulation term. The constant values of v_0 , ε_{bSiC} , and ρ_{bed} of Equation 4.3 are reported in Table 4.4. The calculation procedure for ε_{bSiC} and ρ_{bed} are presented in Appendix H.1.

Table 4.4. The constant values of v_0 , ε_{bSiC} , and ρ_{bed} used in Equation 4.3

v_0 $\text{cm}^3(\text{STP}).\text{s}^{-1}$	ε_{bSiC}	ρ_{bed} $\text{g}_{cat}.\text{(cm}^3\text{)}^{-1}$
4.17	0.57	0.051

The calculations for Mears criterion given in Appendix H.2 confirm a negligible external mass transfer effect for the porous catalyst bed emphasizing a rapid mass transfer from the bulk to the catalyst surface, i.e. $C_{CH_4}^b \cong C_{CH_4}^s$, where $C_{CH_4}^b$ and $C_{CH_4}^s$ represent the CH_4 concentration in the bulk phase and on the catalyst surface, respectively. The internal mass transfer effect is considered using the effectiveness factor calculated by Equations 4.4-4.6:

$$\eta = \frac{\text{actual overall rate of reaction}}{\text{rate of reaction with no internal diffusion limitation}} \quad 4.4$$

The internal effectiveness factor was calculated based on the 1st-order reaction rate assumption as follows [92]:

$$\eta = \frac{3}{\varphi} \left(\frac{1}{\tanh \varphi} - \frac{1}{\varphi} \right) \quad 4.5$$

where φ is Thiele modulus defined as:

$$\varphi = \frac{d_p}{2} \sqrt{\frac{k}{D_{\text{eff}}}} \quad 4.6$$

d_p , k , and D_{eff} are the catalyst particle diameter (m), CH_4 oxidation reaction rate constant (s^{-1}), and effective diffusivity ($\text{m}^2.\text{s}^{-1}$), respectively. The rate constant, k , used in Equation 4.6 is calculated from the rate of CH_4 oxidation reaction:

$$-r_{\text{CH}_4} = kC_{\text{CH}_4} \quad 4.7$$

where $-r_{\text{CH}_4}$ is the CH_4 reaction rate on a volumetric basis ($\text{mol}.\text{cm}^3.\text{s}^{-1}$), so that:

$$-r_{\text{CH}_4} = C_T \rho_{\text{cat}} (-r_{\text{CH}_4}^s) \quad 4.8$$

Hence we assume that:

$$k = k_s C_T^2 \rho_{\text{cat}} RT \quad 4.9$$

By substituting Equation 4.9 in Equation 4.6, φ and η can be calculated provided k_s is known. Note that the rate constant in Equation 4.9 is considered to be a function of temperature only. Details of the calculations for effective diffusivity, D_{eff} , are provided in Appendix H.1.

In the present study, following the report by Kikuchi et al. [22], the rate of CH_4 oxidation was assumed 1st-order in CH_4 and dependent on the number of active sites as follows:

$$-r_{\text{CH}_4}^s = k_s P_{\text{CH}_4} C_T \theta_V \quad 4.10$$

where $-r_{\text{CH}_4}^s$ is the CH_4 oxidation reaction rate per mole of active sites as measured by CO uptake ($\text{mol}.\text{mol}_{\text{site}}^{-1}.\text{s}^{-1}$), k_s is the rate constant ($\text{mol}.\text{g}_{\text{cat}}.\text{mol}_{\text{site}}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$), P_{CH_4} is the partial

pressure of CH₄ (Pa) defined as $P_{CH_4} = P(1 - X_{CH_4})y_{CH_4}^0$, C_T is the total number of active sites ($\text{mol}_{\text{site}} \cdot \text{g}_{\text{cat}}^{-1}$), and θ_V is the fraction of vacant site pairs (both PdO and Pd-*). On a mass basis the rate ($\text{mol} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{s}^{-1}$) is given by Equation 4.11 as:

$$-r_{CH_4}^m = k_s P_{CH_4} C_T^2 \theta_V \quad 4.11$$

The rate equation follows from several studies that report the order of reaction with respect to CH₄ and O₂ as 1 and 0, respectively [71,76,93] This implies that the O₂ content of the feed gas does not impact the reaction rate significantly and consequently, the relatively high O₂ content of the present study (20%) should not impact the kinetic analysis. High O₂ partial pressure ensures that the re-oxidation of the catalyst by gas phase O₂ is not O₂ limited. The reaction order for CO₂ is also assumed to be zero, as reported in the literature [76,78] Since the adsorption of CH₄ on the active sites is irreversible, as explained by Kikuchi et al. [23] and Ciuparu and Pfefferle [30] CH₄ is rapidly consumed, indicating a near zero coverage of active sites by CH₄ [30]. In addition, rapid CO₂ desorption implies very low coverage of the active sites by CO₂ [30]. As discussed by Ciuparu and Pfefferle [30], at low temperatures (< 500°C), and moderate to high H₂O content (3.5vol.%), the surface blockage caused by hydroxyl formation is significant. Therefore, the fraction of vacant sites, θ_V , is given by Equation 4.12:

$$\theta_V = 1 - \theta_{H_2O} \quad 4.12$$

Since the reactor is not at steady state, we further assume that the adsorption-desorption of the hydroxyl/H₂O molecules on the catalyst surface is not at equilibrium initially [17] The

accumulation of hydroxyl/H₂O on the active site pair can be described by Equations 4.13 and 4.14.



$$\frac{d\theta_{\text{H}_2\text{O}}}{dt} = k_f P_{\text{H}_2\text{O}} \theta_v - k_r \theta_{\text{H}_2\text{O}} \quad 4.14$$

k_f and k_r are the rate constants for H₂O adsorption and H₂O desorption, respectively. $P_{\text{H}_2\text{O}}$ is determined by stoichiometry as $P(\alpha_{\text{H}_2\text{O}} + 2X_{\text{CH}_4})y_{\text{CH}_4}^0$ and $\alpha_{\text{H}_2\text{O}}$ is defined as $\frac{P_{\text{H}_2\text{O}}^0}{P_{\text{CH}_4}^0}$ at the inlet of the reactor. Substituting Equation 4.12 into Equation 4.14 and integrating, assuming that at $t = 0$, $\theta_{\text{H}_2\text{O}} = 0$, results in Equation 4.15:

$$\theta_{\text{H}_2\text{O}} = \frac{K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}}{1 + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}} [1 - \exp(-k_r(1 + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}})t)] \quad 4.15$$

where $K_{\text{H}_2\text{O}}$ is the H₂O adsorption equilibrium constant, defined as k_f/k_r .

Solving a PDE (Equation 4.3) which is a function of both W_{cat} and t is readily achieved using the Method of Characteristics [94]. Accordingly, for a PDE such as $a \frac{\partial u}{\partial x} + b \frac{\partial u}{\partial y} = c$ with u is defined as $u = f(x, y)$, and a , b , and c are functions of x , y , and u only ($a, b, c \neq f(\frac{\partial u}{\partial x})$ nor $\neq f(\frac{\partial u}{\partial y})$), the PDE can be re-written as below:

$$du = \frac{c}{a} dx = \frac{c}{b} dy \quad 4.16$$

Applying the Method of Characteristics [94] to Equation 4.3 results in Equations 4.17 and 4.18:

$$\frac{dC_{\text{CH}_4}}{dW_{\text{cat}}} = \frac{\eta}{v_0} r_{\text{CH}_4}^m \quad 4.17$$

$$\frac{dC_{CH_4}}{dt} = \frac{\eta}{\frac{\varepsilon_{bSiC}}{\rho_{bSiC}}} r_{CH_4}^m \quad 4.18$$

After substituting Equations 4.11, 4.12, and 4.15 into Equation 4.17, and writing $C_{CH_4} = C_{CH_4}^0 (1 - X_{CH_4})$, where X_{CH_4} is the CH_4 conversion, yields Equation 4.19:

$$\frac{dX_{CH_4}}{d(W_{cat}/F_{CH_4}^0)} = \eta k_s C_T^2 P_{CH_4} \left[1 - \frac{K_{H_2O} P_{H_2O}}{1 + K_{H_2O} P_{H_2O}} (1 - \exp(-k_r (1 + K_{H_2O} P_{H_2O}) t)) \right] \quad 4.19$$

where $F_{CH_4}^0 = \nu_0 C_{CH_4}^0$ (mol.s⁻¹) is the molar flow rate of CH_4 in the inlet of the reactor.

Note that as the TOS increases, i.e. $t \rightarrow \infty$, which for most of the data reported in the present study corresponds to $t \geq 5h$, Equation 4.19 reduces to Equation 4.20 when written in terms of X_{CH_4} :

$$\frac{dX_{CH_4}}{d(W_{cat}/F_{CH_4}^0)} = \eta \frac{k_s C_T^2 P (1 - X_{CH_4}) y_{CH_4}^0}{1 + K_{H_2O} P (\alpha_{H_2O} + 2X_{CH_4}) y_{CH_4}^0} \quad 4.20$$

The temperature dependence of the three unknown parameters of Equations 4.19 and 4.20 are given by:

$$k_s = k_s^0 \exp \left[\frac{-E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad 4.21$$

$$K_{H_2O} = K_{H_2O}^0 \exp \left[\frac{-\Delta H_{H_2O}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad 4.22$$

$$k_r = k_r^0 \exp \left[\frac{-E_r}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad 4.23$$

Note that Equation 4.20 represents the steady-state mole balance equation for the reactor system.

The TOS results presented in Figures 4.4 and 4.5 were used to estimate the model parameters k_s^0 , E_a , $K_{H_2O}^0$, ΔH_{H_2O} associated with Equation 4.20. Accordingly, the steady-state conversions, taken as X_s (the stable CH_4 conversion at $t=5h$ since the CH_4 conversion does not change significantly after this time), were regressed onto Equation 4.20 using the Levenberg-Marquardt non-linear regression algorithm [95] combined with a numerical integration of Equation 4.20 using a 4th-order Runge-Kutta algorithm. The Matlab code used to complete these numerical calculations is reported in Appendix K.

The model parameters were estimated from data obtained at different temperatures and different H_2O concentrations for all $0.3Pd/Al_2O_3$, $2.6Pd/Al_2O_3$, and $6.5Pd/Al_2O_3$ catalysts. The different dispersions of the catalysts are accounted for in the model through the measured CO uptakes (C_T). The inherent assumption of this approach is that the reaction is not PdO structure sensitive in the narrow range of dispersion since we assume that the same kinetic parameters apply to all three catalysts, despite their varying dispersions. Table 4.5 reports the constant parameters used in Equations 4.6 and 4.20 to estimate η , k_s and K_{H_2O} . Note that the effective diffusivity at different temperatures was calculated assuming that D_{eff} varied at $T^{0.5}$. Figure 4.7 shows the estimated X_{CH_4} values from the model versus the measured X_{CH_4} values from Figures 4.4 and 4.5 at $t=5h$ with the adjusted $R^2=0.98$.

Table 4.5. Constant values for 6.5Pd/Al₂O₃ catalyst at T=330°C used in Equation 4.20

W_{cat} (g)	8.33×10^{-2}
Pd (wt.%)	6.5
$F_{CH_4}^0$ (mol.s ⁻¹)	373.6
$y_{CH_4}^0$	0.005
P (Pa)	101325
GHSV (mol.g _{cat} ⁻¹ .s ⁻¹)	2.23×10^{-3}
C_T (mol _{site} .g _{cat} ⁻¹)	2.04×10^{-4}
D_{eff}^0 at 330°C (m ² .s ⁻¹)	1.00×10^{-6}
ρ_{cat} (g.cc ⁻¹)	1.49
d_p (cm)	2.22×10^{-2}
α_{H_2O}	0 and 10

The values of effectiveness factor, rate constant, equilibrium constant for H₂O adsorption were estimated from the kinetic model, and the reaction rate values ($-r_{CH_4}^m$) were calculated by replacing the estimated k_s values in Equation 4.11. The values at different temperatures for the 6.5Pd/Al₂O₃ catalyst are presented in Table 4.6. By increasing the temperature from 300°C to 380°C, the reaction rate shows an order of magnitude increase. Decreasing η with increased temperature reflects the faster increase in intrinsic reaction rate versus actual reaction rate at higher reaction temperatures.

Table 4.6. Estimated values of η , rate constant, equilibrium constant for H₂O adsorption, and reaction rate at different temperatures for 6.5Pd/Al₂O₃ catalyst

T °C	η	k_s mol.g _{cat} .mol _{site} ⁻² .Pa ⁻¹ .s ⁻¹	K_{H_2O} Pa ⁻¹	$-r_{CH_4}^m$ mol.(g _{cat} .s) ⁻¹
300	0.47	7.2	1.25×10^{-2}	1.84×10^{-6}
330	0.36	13.5	5.32×10^{-3}	6.21×10^{-6}
350	0.30	19.9	3.16×10^{-3}	1.17×10^{-5}
380	0.24	34.1	1.53×10^{-3}	1.58×10^{-5}

The estimated parameters of Equations 4.21 and 4.22 are reported in Table 4.7.

Table 4.7. Estimated values obtained from the design equation for CH₄ oxidation over Pd/Al₂O₃ catalysts with different Pd loadings

E_a kJ.mol ⁻¹	k_s^0 mol.g _{cat} ⁻¹ .mol _{site} ⁻² .Pa ⁻¹ .s ⁻¹	ΔH_{H_2O} kJ.mol ⁻¹	$K_{H_2O}^0$ Pa ⁻¹
60.6±11.5	13.5±1.7	-81.5±9.1	5.3×10 ⁻³ ±4.3×10 ⁻⁴

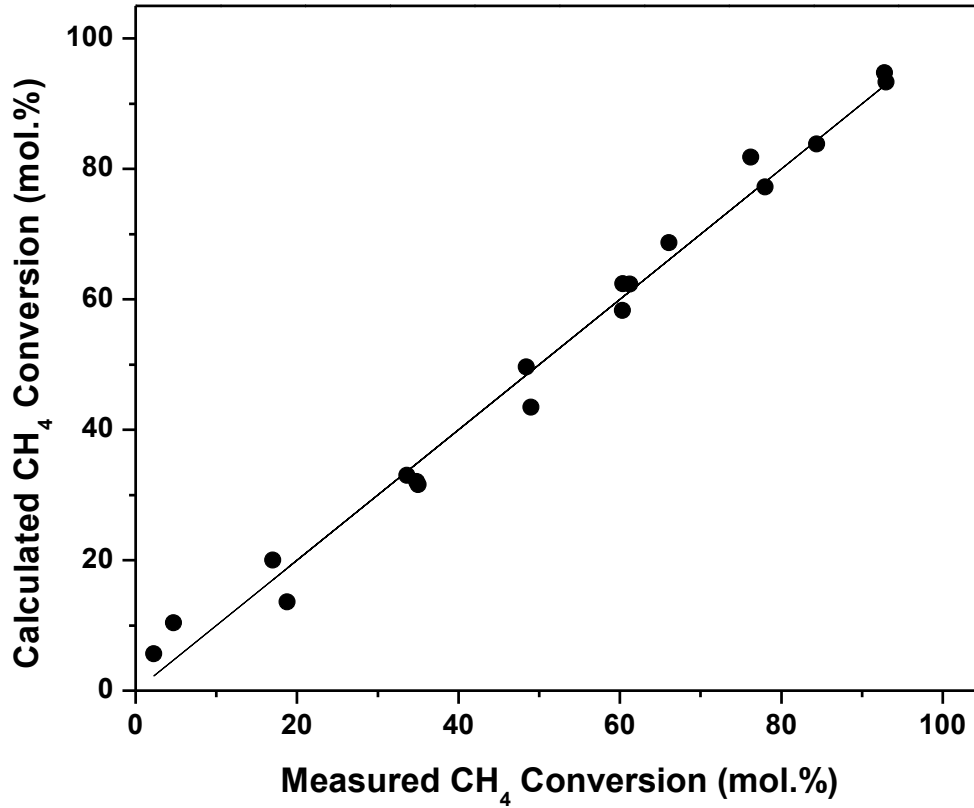


Figure 4.7. Calculated X_{CH_4} values from the kinetic model versus measured X_{CH_4} values from the experiments for xPd/Al₂O₃ catalysts

The value obtained for the apparent activation energy for CH₄ conversion, 60.6±11.5 kJ.mol⁻¹ is lower than the 151 kJ.mol⁻¹ reported in the literature [76] for a 7.3wt%Pd/Al₂O₃ catalyst. Since the value of -81.5±9.1 kJ.mol⁻¹ was estimated for ΔH_{H_2O} , the apparent activation energy considering the H₂O effect is calculated as:

$$E_{a1} = E_a + |\Delta H_{H_2O}| \quad 4.24$$

Hence, the value of $142.1 \text{ kJ.mol}^{-1}$ is obtained which is consistent with other studies [76]. Since the same model parameter values provided a good fit to all the data, regardless of PdO dispersion and H_2O content, we conclude that the CH_4 oxidation reaction is not structure sensitive.

Upon removing the 5vol.% extra H_2O after 24h TOS at both 330°C and 350°C , the CH_4 conversion increased to values close to the conversion measured after 24h TOS in the dry feed gas (See Figures 4.4 and 4.5). This observation confirms a partially reversible effect of H_2O on the catalyst activity. The $\frac{P_{\text{H}_2\text{O}}}{C_T}$ ratio is defined as the H_2O concentration at the reactor exit per total number of active sites with units of $\text{Pa.g}_{\text{cat}}.\mu\text{mol}_{\text{site}}^{-1}$ with high values implying more coverage of the available active sites by H_2O . The amount of H_2O results from both $P_{\text{H}_2\text{O}}^0$ in the inlet of the reactor (0 and 5066.25 Pa for dry and wet feed, respectively) and the amount of H_2O produced during the reaction, which varies with CH_4 conversion and temperature.

Table 4.8. Concentration of H₂O per number of active sites as a function of temperature for catalysts with different Pd loadings

T=330°C		Dry feed		5vol.% extra H ₂ O	
Catalyst	C _T ^a	X ^b	P _{H₂O} /C _T	X ^b	P _{H₂O} /C _T
	μmol _{site} ·g _{cat} ⁻¹	mol.%	Pa·g _{cat} ·μmol _{site} ⁻¹	mol.%	Pa·g _{cat} ·μmol _{site} ⁻¹
0.3Pd/Al ₂ O ₃	35	29.1	8.4	1.9	145.3
2.6Pd/Al ₂ O ₃	119	53.9	4.6	13.4	43.7
6.5Pd/Al ₂ O ₃	204	68.5	3.4	27.2	26.2

T=350°C		Dry feed		5vol.% extra H ₂ O	
Catalyst	C _T ^a	X ^b	P _{H₂O} /C _T	X ^b	P _{H₂O} /C _T
	μmol _{site} ·g _{cat} ⁻¹	mol.%	Pa·g _{cat} ·μmol _{site} ⁻¹	mol.%	Pa·g _{cat} ·μmol _{site} ⁻¹
0.3Pd/Al ₂ O ₃	35	38.8	11.2	3.8	145.9
2.6Pd/Al ₂ O ₃	119	64.1	5.5	25.0	44.7
6.5Pd/Al ₂ O ₃	204	84.3	4.2	42.8	27.8

^a Number of active sites

^b Conversion measured at t=24h

Comparing the $\frac{P_{H_2O}}{C_T}$ ratio as a function of Pd loading at a constant temperature and H₂O concentration shows higher values of $\frac{P_{H_2O}}{C_T}$ at lower Pd loadings. The significant decrease in $\frac{P_{H_2O}}{C_T}$ in the dry feed with increasing Pd loading from 0.3wt.% to 6.5wt.% for both 330°C and 350°C, emphasizes the more significant effect of higher C_T values for the 6.5Pd/Al₂O₃ catalyst. Although higher CH₄ conversion for 6.5Pd/Al₂O₃ catalyst results in higher H₂O production (P_{H₂O}), the higher C_T value of 6.5Pd/Al₂O₃ catalyst has more impact. The ΔX_{dry-wet} (the difference between the CH₄ conversion in the dry feed after 24h TOS and the wet feed after removing the H₂O) values (Table 4.9) are also higher at lower Pd loadings, confirming the negative effect of higher $\frac{P_{H_2O}}{C_T}$ as shown by the higher values of this ratio at lower Pd loadings (Table 4.8). For both 330°C and 350°C the rate of CH₄ conversion recovery varies in this order: 6.5Pd/Al₂O₃ > 2.6Pd/Al₂O₃ > 0.3Pd/Al₂O₃ indicating faster

partial recovery at higher Pd loadings as a consequence of lower $\frac{P_{H_2O}}{C_T}$. This suggests less Pd-OH bond formation on the PdO crystals having higher Pd loadings.

Table 4.9. $\Delta X_{\text{dry-wet}}$ at t=24h for 0.3Pd/Al₂O₃, 2.6Pd/Al₂O₃, and 6.5Pd/Al₂O₃ catalysts

T °C	$\Delta X_{\text{dry-wet}}$		
	0.3Pd/Al ₂ O ₃	2.6Pd/Al ₂ O ₃	6.5Pd/Al ₂ O ₃
330	14.6	6.0	0.1
350	16.7	10.6	5.1

Comparing the $\frac{P_{H_2O}}{C_T}$ ratio as a function of temperature for each catalyst, shows an increase with both dry feed and 5vol.% extra H₂O, however, the increase is more significant for the dry feed, indicative of the larger effect of the produced H₂O during the CH₄ reaction in the dry feed than the wet feed. The $\frac{P_{H_2O}}{C_T}$ values are related to the extent of recovery of the catalyst activity when H₂O is removed from the feed gas. $\Delta X_{\text{dry-wet}}$ for all catalysts is shown in Table 4.9. $\Delta X_{\text{dry-wet}}$ at 330°C was 14.6, 6.0, and 0.1 for 0.3Pd/Al₂O₃, 2.6Pd/Al₂O₃, and 6.5Pd/Al₂O₃ catalysts, respectively. These values increased to 16.7, 10.6, and 5.1 at 350°C. The increase in $\Delta X_{\text{dry-wet}}$ values with temperature correlates with the higher $\frac{P_{H_2O}}{C_T}$ values for 5vol.% extra H₂O at higher temperature reported in Table 4.8. Hence with more H₂O present there is less recovery of the catalyst activity.

4.4 Discussion

The Pd is present as PdO following calcination of the catalysts in excess O₂ at 450°C for 15h. The XRD and XPS analyses confirm the formation of PdO only, since no Pd⁰ is observed by these analyses. The XPS data show a higher Pd/Al ratio on the surface at higher

Pd loadings, as expected [96]. In the study by Cullis et al. [71] the mean diameter of PdO catalysts with 2.7wt.%, 11wt.%, and 25wt.%Pd over γ -Al₂O₃ increased from 13 nm to 26 nm [71], indicating lower dispersion at higher Pd loading. Stasinska et al. [96] showed the Pd/Al ratio decreased from 0.555 to 0.217 as the Pd crystallite size increased from 4.6 nm to 13 nm on a 0.3Pd/Al₂O₃ catalyst [96]. They also reported a lower binding energy of Pd 3d in the case of lower Pd dispersion. This could be a result of the presence of more Pd⁰ formation. As long as the Pd crystallite size increased from 4.6 nm to 9.6 nm, Pd⁰ surface composition increased from 85.1 (at.%) to 98.0 (at.%) [96]. However, in our study the binding energy of Pd 3d did not show any significant change and no Pd⁰ was observed. The 0.3Pd/Al₂O₃, 2.6Pd/Al₂O₃, and 6.5Pd/Al₂O₃ catalysts do not show a significant difference in terms of the BET surface area, PdO crystallite size, or binding energies that is a result of a narrow range of Pd dispersion at different Pd loadings.

The structure sensitivity of Pd based catalysts in CH₄ oxidation is not clear. As shown by Castellazzi et al. [69], the TOF is not related to the PdO dispersion as obtained with different Pd loadings. Zhu et al. [73] also showed that the rate of reaction is not structure sensitive and is only dependent on the oxygen-oxygen interaction. Therefore, surface Pd with more adsorbed oxygen improves catalyst activity. Adsorbed hydroxyl groups on the support and PdO correlate with catalyst deactivation [97]. However, the role of Pd dispersion on the inhibiting effect of H₂O is not well understood. Stasinska et al. [96] showed the Pd/Al₂O₃ catalyst with Pd crystallite size smaller than 6.6 nm has the highest activity for CH₄ oxidation under lean-burn conditions. For Pd with a crystallite size of 4.6 nm the CH₄ conversion reached 100% at 500°C in the absence of extra H₂O, however, with 13 nm Pd crystallite size the complete oxidation of CH₄ occurred at 705°C in the absence of extra H₂O. Upon adding

20vol.% H₂O, 100% CH₄ conversion was reached at 650°C for 4.6 nm Pd and Pd 13 nm did not obtain 100% CH₄ conversion even at 750°C [96]. Hence larger crystallites were impacted more by the presence of H₂O. However, in the present study it was shown that catalysts with lower Pd dispersion have higher catalyst activity during TPO and TOS experiments due to lower $\frac{P_{H_2O}}{C_T}$ values and higher Pd loading. Some studies showed the dispersion of Pd decreased after the CH₄ oxidation reaction in the presence of H₂O [42,75,98–100]. Narui et al. [100] reported a drop in PdO dispersion from 14% to 11% for 0.5%Pd/Al₂O₃ catalyst after the combustion reaction at 350°C for 6h.

In this study, the effective diffusivity, D_{eff} , was calculated using the tortuosity factor and constriction factor values as $\tau=3$ and $\sigma=0.8$, respectively, and the D_{eff} values for all three catalysts with different Pd loadings were obtained in the order of $10^{-6} \frac{m^2}{s}$. In a study by Hayes et al. [101] for a washcoated monolith, the tortuosity factor was taken as $\tau=8.1$ resulting in a D_{eff} of $1.7 \times 10^{-7} \frac{m^2}{s}$. A value of $D_{eff}=5.6 \times 10^{-7} \frac{m^2}{s}$ was obtained for $\tau=2.44$, showing the sensitivity of the D_{eff} calculation to the tortuosity factor. In this study, the tortuosity factor was chosen based on the typical value reported in the literature ($\tau=3$) [92] and the obtained D_{eff} value for 6.5Pd/Al₂O₃ catalyst was $1.00 \times 10^{-6} \frac{m^2}{s}$ which is in the range of the reported diffusivity values for gas phase ($10^{-6} \frac{m^2}{s}$), however, the higher value for τ , e.g. 8, results in $D_{eff}=3.75 \times 10^{-7} \frac{m^2}{s}$. Using $D_{eff}=1.00 \times 10^{-6} \frac{m^2}{s}$, low values of the effectiveness factor, $\eta < 1$, for the 6.5Pd/Al₂O₃ catalyst were obtained, indicating internal mass transfer control.

The same value of the apparent activation energy and enthalpy of H₂O adsorption was applied to all 0.3Pd/Al₂O₃, 2.6Pd/Al₂O₃, and 6.5Pd/Al₂O₃ catalysts at different reaction temperatures and H₂O concentrations, accounting for the number of active sites on each catalyst. Although the initial activity and the loss in CH₄ conversion varied between the catalysts with different Pd loadings, the kinetic model that assumes the inhibiting effect of H₂O is independent of the Pd dispersion and is governed only by the H₂O adsorption equilibrium is shown to describe the catalyst activity data. This confirms the structure insensitivity of the catalysts for the conditions studied.

4.5 Conclusion

The initial CH₄ oxidation activity and stability of 0.3Pd/Al₂O₃, 2.6Pd/Al₂O₃, and 6.5Pd/Al₂O₃ catalysts were investigated by TPO, dry-TOS, and wet-TOS experiments. Higher Pd loadings led to a higher Pd/Al ratio on the catalyst surface and lower Pd dispersion. The highest initial activity and the lowest inhibiting effect of H₂O in the TOS experiments for the 6.5Pd/Al₂O₃ catalyst is a result of higher Pd loading. For both dry-TOS and wet-TOS experiments, the amount of H₂O adsorbed per active site was the lowest for the 6.5Pd/Al₂O₃ catalyst. This explains the faster recovery of the 6.5Pd/Al₂O₃ catalyst compared to the 0.3Pd/Al₂O₃ and 2.6Pd/Al₂O₃ catalysts upon removing the extra 5vol.%H₂O. H₂O adsorption is the main cause of activity loss in CH₄ oxidation and the rate of recovery depends on the amount of H₂O adsorbed on the active sites. The CH₄ oxidation reaction rate constant and the equilibrium constant for H₂O adsorption, as well as the correlated apparent activation energy (E_a) and enthalpy of H₂O adsorption (ΔH_{H_2O}) were obtained from the experimental data. Applying the reactor design equation to the values of CH₄ conversion

(X_{CH_4}) at $t=5h$ with and without H_2O in the feed, for all three catalysts, E_a and ΔH_{H_2O} were estimated as $60.6 \pm 11.5 \text{ kJ.mol}^{-1}$ and $-81.5 \pm 9.1 \text{ kJ.mol}^{-1}$, respectively, indicating that CH_4 oxidation reaction is not PdO structure sensitive in the narrow range of studied Pd dispersions (33%-57%). The low values of the effectiveness factors obtained in the range of 300-380°C confirm the slow internal diffusion as a consequence of fast CH_4 oxidation reaction.

Chapter 5: Reduced Inhibition of CH₄ Oxidation by H₂O with CeO₂ Addition to the PdO/Al₂O₃ Catalyst

5.1 Introduction

In this chapter, the effect of CeO₂ on the inhibition effects of H₂O during CH₄ oxidation over PdO catalysts at low temperatures has been investigated by monitoring the dynamic response of the CH₄ conversion following H₂O addition to the CH₄/O₂/He feed gas. By comparing the observed conversion over a co-Ce/Pd/ γ -Al₂O₃ and a Pd/ γ -Al₂O₃ catalyst, combined with catalyst characterization data, the beneficial effects of CeO₂ in reducing the inhibition effects of H₂O, are demonstrated. Furthermore, the relative importance of H₂O adsorption versus PdO sintering or other catalyst deactivation mechanism during CH₄ oxidation, is clarified.

5.2 Results

5.2.1 Catalyst Properties

The AAS analysis showed that the average Pd loading of all catalysts was 6.5 $\pm$ 0.3wt.%. The measured Ce loadings are reported in Table 5.1, together with other physical properties of the calcined catalysts. Table 5.1 shows that the BET surface area of the 6.5Pd/Al₂O₃ catalyst (218 m²/g) is close to that of the Al₂O₃ support (224 m²/g) and that the BET surface area decreases from 208 m²/g to 194 m²/g as the Ce loading increases from 0.9 to 9.5%. The total CO uptake of the 6.5Pd/Al₂O₃ catalyst is 204 μ mol/g_{cat}. However, for the co-0.9Ce/6.5Pd/Al₂O₃ catalyst the CO uptake is significantly lower (89 μ mol/g_{cat}). The reduced uptake of the 0.9Ce/6.5Pd/Al₂O₃ catalyst may be due to the presence of CeO₂ which may

limit the PdO→Pd conversion during the reduction step done prior to the CO uptake measurement [74] but then increases with increasing Ce content to 242 $\mu\text{mol/g}_{\text{cat}}$ for the co-9.5Ce/6.5Pd/Al₂O₃ catalyst, confirming increased PdO dispersion (smaller PdO particles) as Ce loading increased. Note that the CO uptake of the 9.4Ce/Al₂O₃ (no Pd) is 0.39 $\mu\text{mol/g}_{\text{cat}}$.

Table 5.1. Properties of calcined PdO, CeO₂, and co-xCe/yPd catalysts supported on Al₂O₃

	BET	Pore	Pore	CO	Pd	PdO	CeO ₂
Catalyst	SA ^a	Volume ^a	Size ^a	Uptake ^b	Dispersion ^b	C. Size ^c	C. Size ^c
	m ² .g ⁻¹	cm ³ .g ⁻¹	nm	$\mu\text{mol.g}_{\text{cat}}^{-1}$	%	nm	nm
6.5Pd/Al ₂ O ₃	218	0.43	7.9	204	33.5	6	-
co-0.9Ce/6.5Pd/Al ₂ O ₃	208	0.42	8.1	89	14.6	6	-
co-2.9Ce/6.5Pd/Al ₂ O ₃	206	0.41	7.9	153	25.1	5	-
co-4.8Ce/6.5Pd/Al ₂ O ₃	196	0.39	8.0	244	37.9	4	-
co-9.5Ce/6.5Pd/Al ₂ O ₃	194	0.36	7.4	242	38.1	4	5
9.4Ce/Al ₂ O ₃	191	0.41	8.5	0.4	N/A	N/A	5

^a Determined by N₂ adsorption at 77K

^b Obtained by CO chemisorption

^c PdO (101) and CeO₂ (111) crystallite size obtained by XRD

Figure 5.1b shows the XRD analysis of the 6.5Pd/Al₂O₃ catalyst with peaks for PdO observed at $2\theta = 39.49^\circ$ and 64.50° corresponding to PdO (101) and PdO (112), respectively. The PdO (101) peak was observed for all Pd-Ce catalysts with different loadings of Ce, however, the peak shifted slightly to lower 2θ as the Ce loading increased from 0.9% to 9.5%. This is a result of an overlap between the PdO (101) peak located at 39.49° and the CeO₂ (200) peak at 38.61° . The main peaks for CeO₂ appeared at $2\theta=33.27^\circ$, 38.61° , 55.75° and 66.49° corresponding to CeO₂ (111), (200), (220), and (311), respectively. At higher

loadings of Ce (4.8 and 9.5%), the peak at $2\theta=64.50^\circ$ appears as an overlap between PdO (112) and CeO₂ (311). The PdO crystallite size obtained from XRD analysis is consistent with the CO chemisorption results as a function of Ce loading, since they also show smaller PdO particles for the catalysts with higher loadings of Ce.

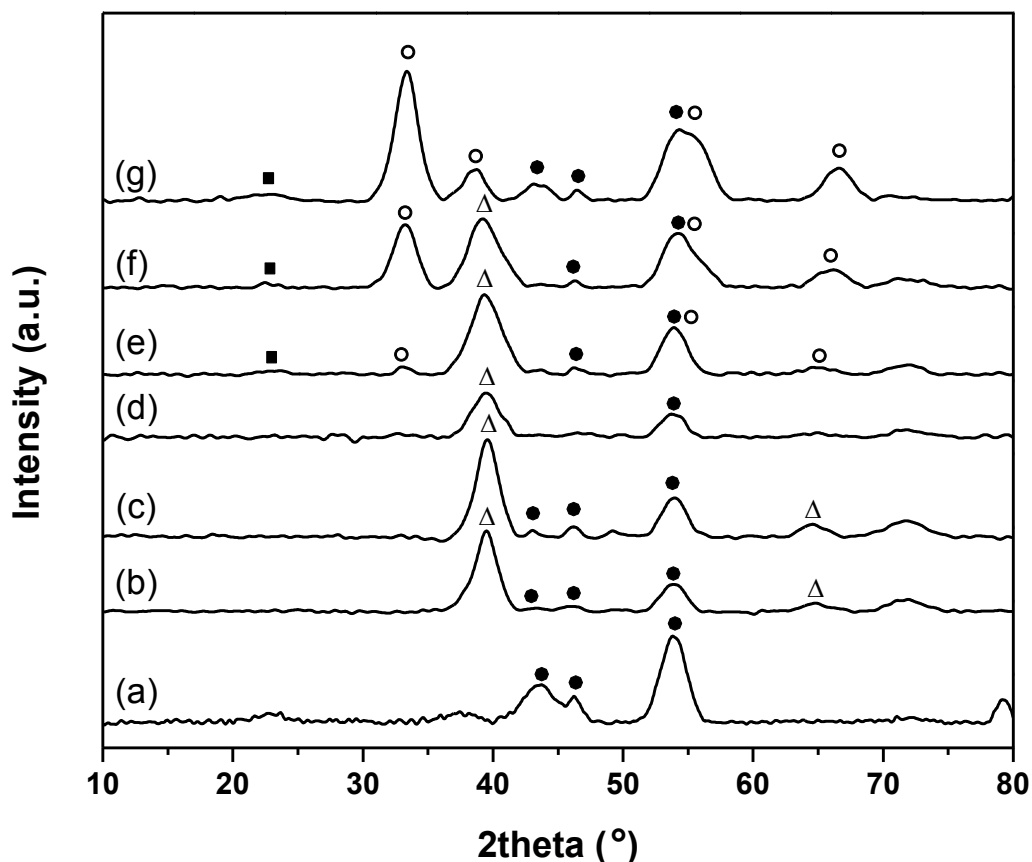


Figure 5.1. XRD patterns for (a) γ -Al₂O₃ (b) 6.5Pd/Al₂O₃, (c) co-0.9Ce/6.5Pd/Al₂O₃, (d) co-2.9Ce/6.5Pd/Al₂O₃, (e) co-4.8Ce/6.5Pd/Al₂O₃, (f) co-9.5Ce/6.5Pd/Al₂O₃, (g) 9.4Ce/Al₂O₃. Δ PdO, $\bullet$ Al₂O₃, $\circ$ CeO₂, $\blacksquare$ Ce₂O₃

Figure 5.2 reports the effect of different Ce loadings on the Pd and Ce surface composition, as measured by XPS. As the catalyst bulk composition increases in Ce (reported as the Ce to Al atom ratio i.e. (Ce/Al)_b), the Pd surface concentration Pd_s increases, indicative of

increased Pd dispersion since the Pd bulk composition is relatively constant for these catalysts (the $(\text{Pd}/\text{Al})_b$ atom ratio varies from 0.033 to 0.037 for the data of Figure 5.2 (not shown in Figure 5.2)). The Ce surface concentration (reported as the surface atom ratio Ce_s) increases almost linearly up to a $(\text{Ce}/\text{Al})_b$ ratio of 0.02, indicative of monodispersed Ce species [102]. Further increase in Ce content results in a smaller increase in the Ce_s ratio, suggesting agglomeration and reduced dispersion of the CeO_x . The reported Pd_s and Ce_s surface compositions are normalized excluding the C content measured by XPS.

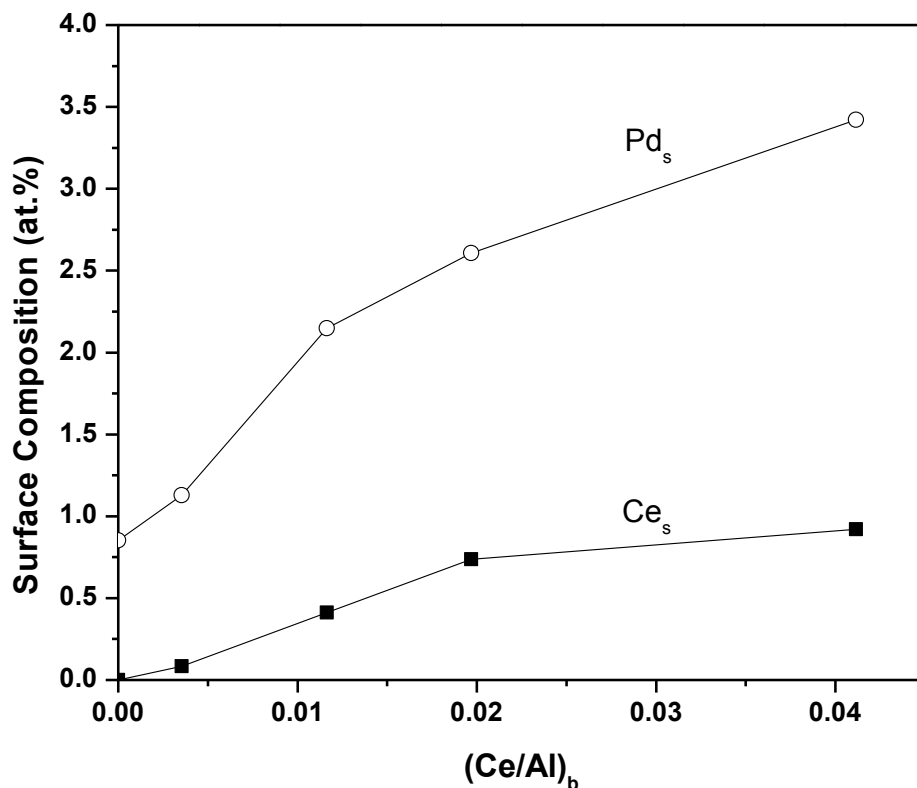


Figure 5.2. Measured Pd atomic percent ($\circ$) and Ce atomic percent ($\blacksquare$) on the catalyst surface as a function of calculated $(\text{Ce}/\text{Al})_b$

Figure 5.3 presents the XPS Pd 3d spectral analysis for the $6.5\text{Pd}/\text{Al}_2\text{O}_3$ and the co-Ce/Pd/ Al_2O_3 catalysts and Table 5.2 summarizes the binding energy (B.E.) of the Pd $3d_{5/2}$

and $3d_{3/2}$ electrons. The B.E.s for all the co-Ce/Pd/Al₂O₃ catalysts are the same (B.E.=337.0±0.1 eV and 342.3±0.1 eV), with the B.E. of the Pd/Al₂O₃ marginally lower (336.8 eV and 342.1 eV, respectively), suggesting some charge transfer to the PdO from the CeO₂.

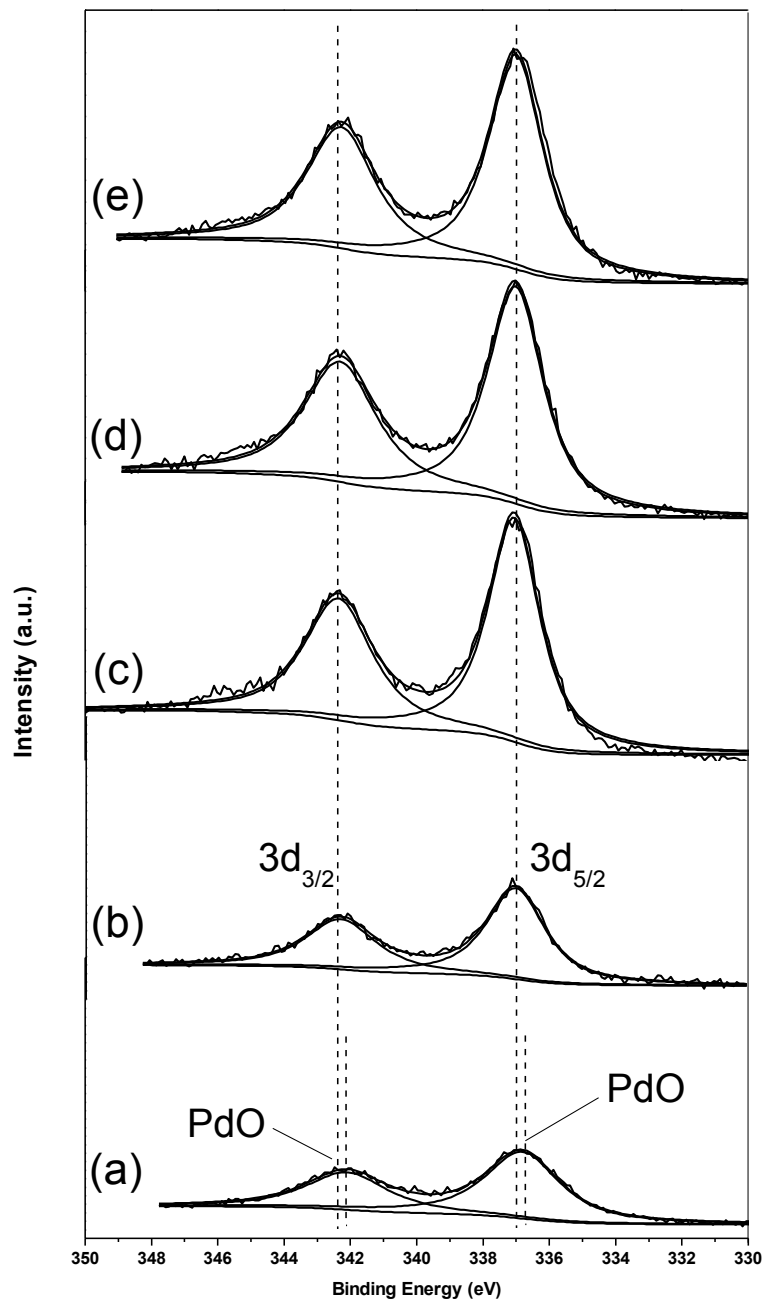


Figure 5.3. XPS Pd 3d spectra measured for (a) 6.5Pd/Al₂O₃, (b) co-0.9Ce/6.5Pd/Al₂O₃, (c) co-2.9Ce/6.5Pd/Al₂O₃, (d) co-4.8Ce/6.5Pd/Al₂O₃, (e) co-9.5Ce/6.5Pd/Al₂O₃

Table 5.2. Pd 3d spectra for Pd/Al₂O₃ and co-xCe/yPd/Al₂O₃ with different loadings of Ce

Catalyst	Pd 3d _{5/2}	Pd 3d _{3/2}	$\frac{\text{Ce}^{3+}}{\text{Ce}^{3+} + \text{Ce}^{4+}}$
	B.E.	B.E.	%
	eV	eV	
6.5Pd/Al ₂ O ₃	336.8	342.1	-
co-0.9Ce/6.5Pd/Al ₂ O ₃	337.0	342.3	-
co-2.9Ce/6.5Pd/Al ₂ O ₃	337.1	342.4	28.8
co-4.8Ce/6.5Pd/Al ₂ O ₃	337.0	342.3	23.3
co-9.5Ce/6.5Pd/Al ₂ O ₃	337.0	342.3	22.2
9.4Ce/Al ₂ O ₃	-	-	17.4

The Ce 3d spectra for the co-4.8Ce/6.5Pd/Al₂O₃, co-9.5Ce/6.5Pd/Al₂O₃ and 9.4Ce/Al₂O₃ catalysts are presented in Figure 5.4. Because of the complexity of the spectra, the XPS analysis of Ce is restricted to the 3d level from 872 to 925 eV and includes a mixture of Ce₂O₃ and CeO₂ oxidation states [103]. Two main peaks for Ce³⁺ (Ce₂O₃) located at 885.8 eV (v') and 903.6 eV (u') are attributed to 3d_{5/2} and 3d_{3/2} electrons, respectively. Six main peaks for Ce⁴⁺ (CeO₂) are located at 882.7 eV (v), 888.6 eV (v''), 898.3 eV (v''') for 3d_{5/2}, and 900.8 eV (u), 907.3 eV (u''), and 916.7 eV (u''') allocated to 3d_{3/2} [104–109]. The presence of the peak at 916.7 eV (u''') in all samples indicates that CeAlO₃ was not formed during calcination [109]. The fraction of Ce³⁺ was determined for each sample from the fitted peak areas. Table 5.2 presents the $\frac{\text{Ce}^{3+}}{\text{Ce}^{3+} + \text{Ce}^{4+}}$ ratio for the co-2.9Ce/6.5Pd/Al₂O₃, co-4.8Ce/6.5Pd/Al₂O₃, co-9.5Ce/6.5Pd/Al₂O₃, and 9.4Ce/Al₂O₃ catalysts. The $\frac{\text{Ce}^{3+}}{\text{Ce}^{3+} + \text{Ce}^{4+}}$ ratio increased with decreased Ce content from 17.4% for the 9.4Ce/Al₂O₃ to 28.8% for co-2.9Ce/6.5Pd/Al₂O₃ catalyst.

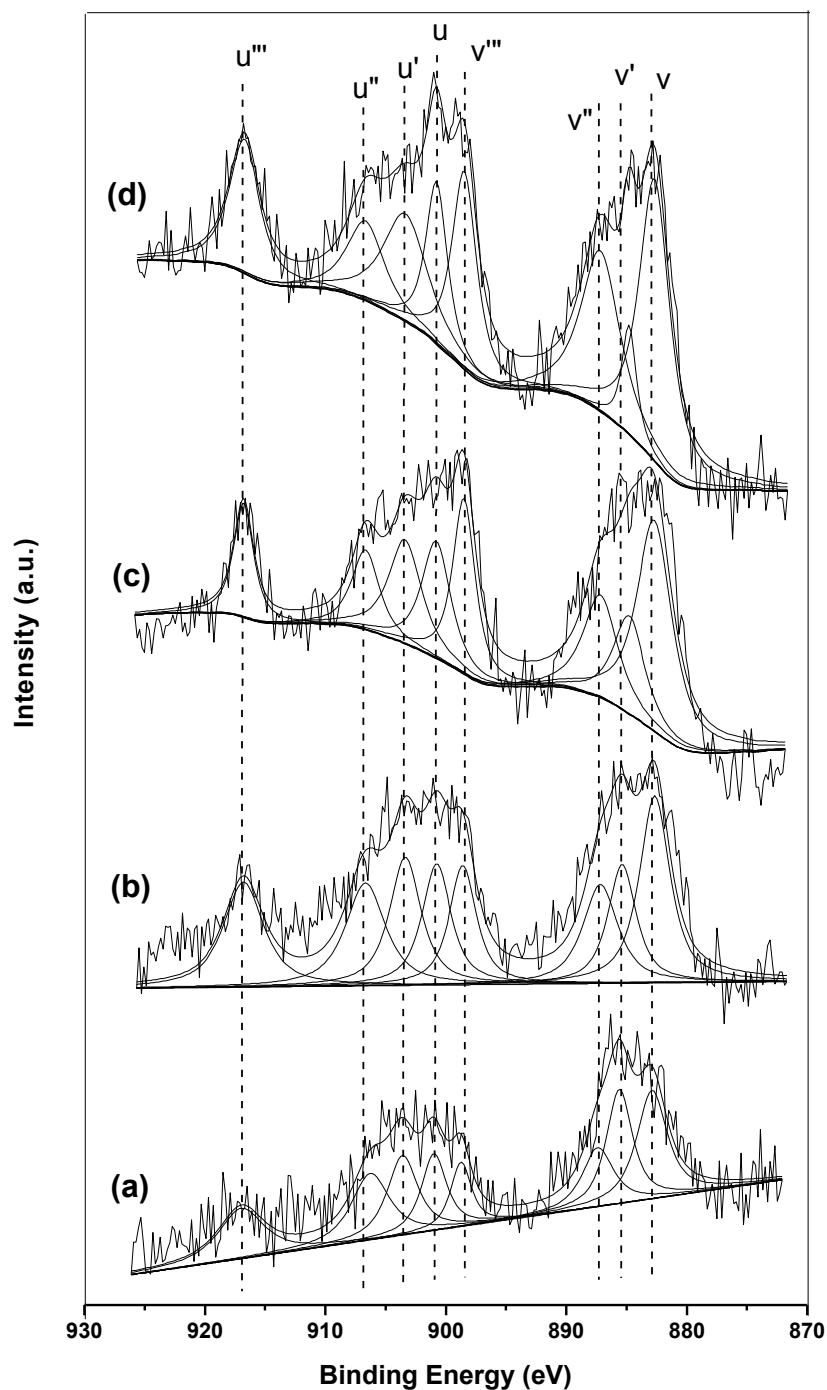


Figure 5.4. XPS Ce 3d spectra measured for (a) co-2.9Ce/6.5Pd/Al₂O₃, (b) co-4.8Ce/6.5Pd/Al₂O₃, (c) co-9.5Ce/6.5Pd/Al₂O₃, (d) 9.4Ce/Al₂O₃

This increase is attributed to the transition of Ce⁴⁺ to Ce³⁺ following addition of Pd to the Ce/Al₂O₃ and is indicative of the interaction between Pd and the Ce surface species of the

calcined catalysts, with O transfer from the CeO_2 to the PdO/Pd-^* , consistent with the Pd XPS analysis.

5.2.2 Catalyst Activities

Figure 5.5 reports the TPO results for the $6.5\text{Pd/Al}_2\text{O}_3$ catalyst and the Ce promoted $6.5\text{Pd/Al}_2\text{O}_3$ catalysts. The $6.5\text{Pd/Al}_2\text{O}_3$ catalyst had the highest activity for CH_4 oxidation with T_{50} of 251°C . Increased Ce content resulted in reduced activity and the $9.4\text{Ce/Al}_2\text{O}_3$ catalyst (not shown) was the least active with a T_{50} of 595°C . Table 5.3 presents the light-off temperatures corresponding to 10%, 50%, and 90% CH_4 conversion and these data show similar trends in terms of catalyst activity. Among the Ce-promoted catalysts, the co- $2.9\text{Ce/6.5Pd/Al}_2\text{O}_3$ catalyst has the highest activity.

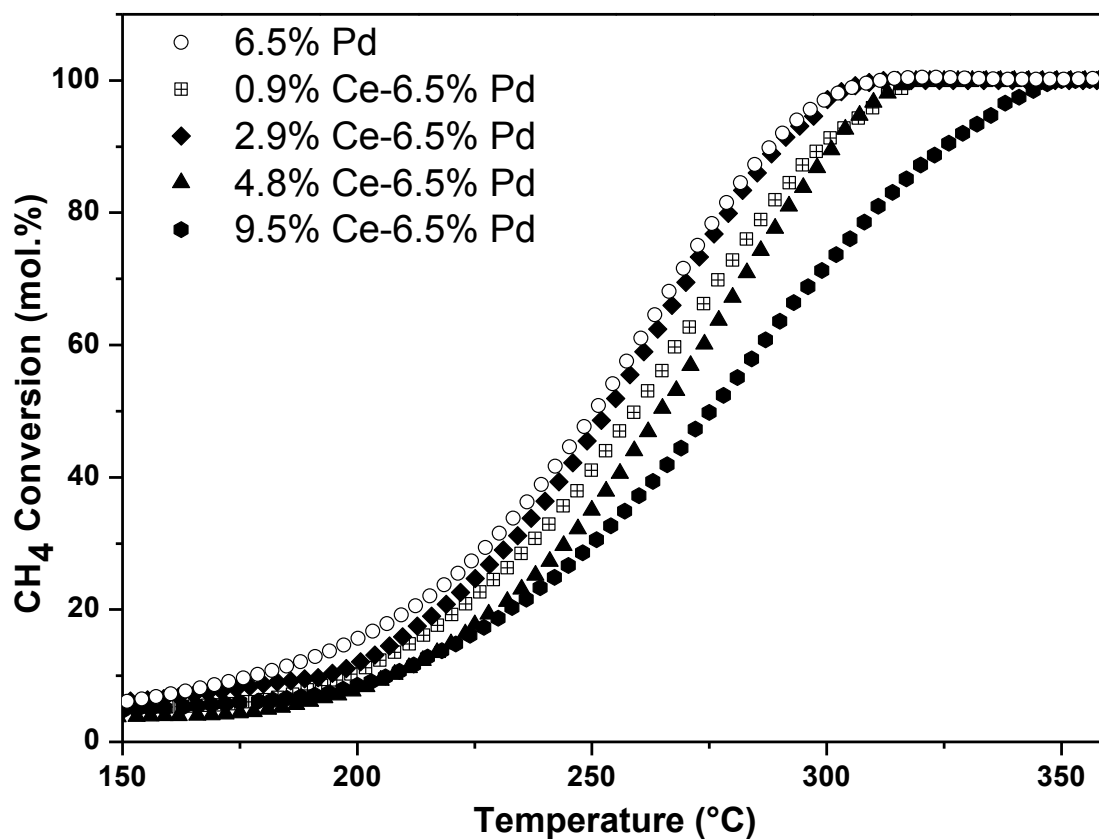


Figure 5.5. Temperature Programmed Oxidation profile. Effect of different loadings of Ce on the initial activity of 6.5Pd/Al₂O₃ as a function of temperature. GHSV=180,000 cm³(STP).g_{cat}⁻¹.h⁻¹, 1000 ppm CH₄, 20(v/v)% O₂, and the balance He and Ar

Table 5.3. Light-off temperatures for 6.5Pd/Al₂O₃ and co-xCe/yPd/Al₂O₃ catalysts

Catalyst	T ₁₀	T ₅₀	T ₉₀
	°C	°C	°C
6.5Pd/Al ₂ O ₃	142±6	251±4	285±6
co-0.9Ce/6.5Pd/Al ₂ O ₃	197±6	259±4	298±6
co-2.9Ce/6.5Pd/Al ₂ O ₃	193±6	253±4	290±6
co-4.8Ce/6.5Pd/Al ₂ O ₃	208±6	265±4	301±6
co-9.5Ce/6.5Pd/Al ₂ O ₃	208±6	275±4	325±6
9.4Ce/Al ₂ O ₃	485±6	595±4	-

Consequently, the $6.5\text{Pd}/\text{Al}_2\text{O}_3$ and $\text{co-}2.9\text{Ce}/6.5\text{Pd}/\text{Al}_2\text{O}_3$ catalysts were selected for assessment of CH_4 oxidation stability in the presence of H_2O . Figure 5.6 shows the TOS results for a 24h period using “dry” feed gas and “wet” feed gas with 5vol.% H_2O , at temperatures 300-380°C. For both the $6.5\text{Pd}/\text{Al}_2\text{O}_3$ and $\text{co-}2.9\text{Ce}/6.5\text{Pd}/\text{Al}_2\text{O}_3$ catalysts CH_4 conversion for the dry-TOS decreased as the catalysts were exposed to the reactants. At 350°C CH_4 conversion decreased after 24h from 100% to 84% and 46% for the $6.5\text{Pd}/\text{Al}_2\text{O}_3$ and $\text{co-}2.9\text{Ce}/6.5\text{Pd}/\text{Al}_2\text{O}_3$ catalysts, respectively, indicative of a slow catalyst deactivation with TOS (Figure 5.6c and 5.6e). With H_2O added to the feed gas, both $6.5\text{Pd}/\text{Al}_2\text{O}_3$ and $\text{co-}2.9\text{Ce}/6.5\text{Pd}/\text{Al}_2\text{O}_3$ catalysts showed a much faster exponential deactivation in the first 5h TOS, followed by a slower, linear deactivation from TOS=5h to TOS=24h. CH_4 conversion over the $6.5\text{Pd}/\text{Al}_2\text{O}_3$ catalyst decreased from 100% to 48% in the first 5h and then decreased to 42.8% after 24h. A significant inhibition is also observed for the $\text{co-}2.9\text{Ce}/6.5\text{Pd}/\text{Al}_2\text{O}_3$ catalyst, from 100% to 23% after 5h and then to 17.4% in 24h.

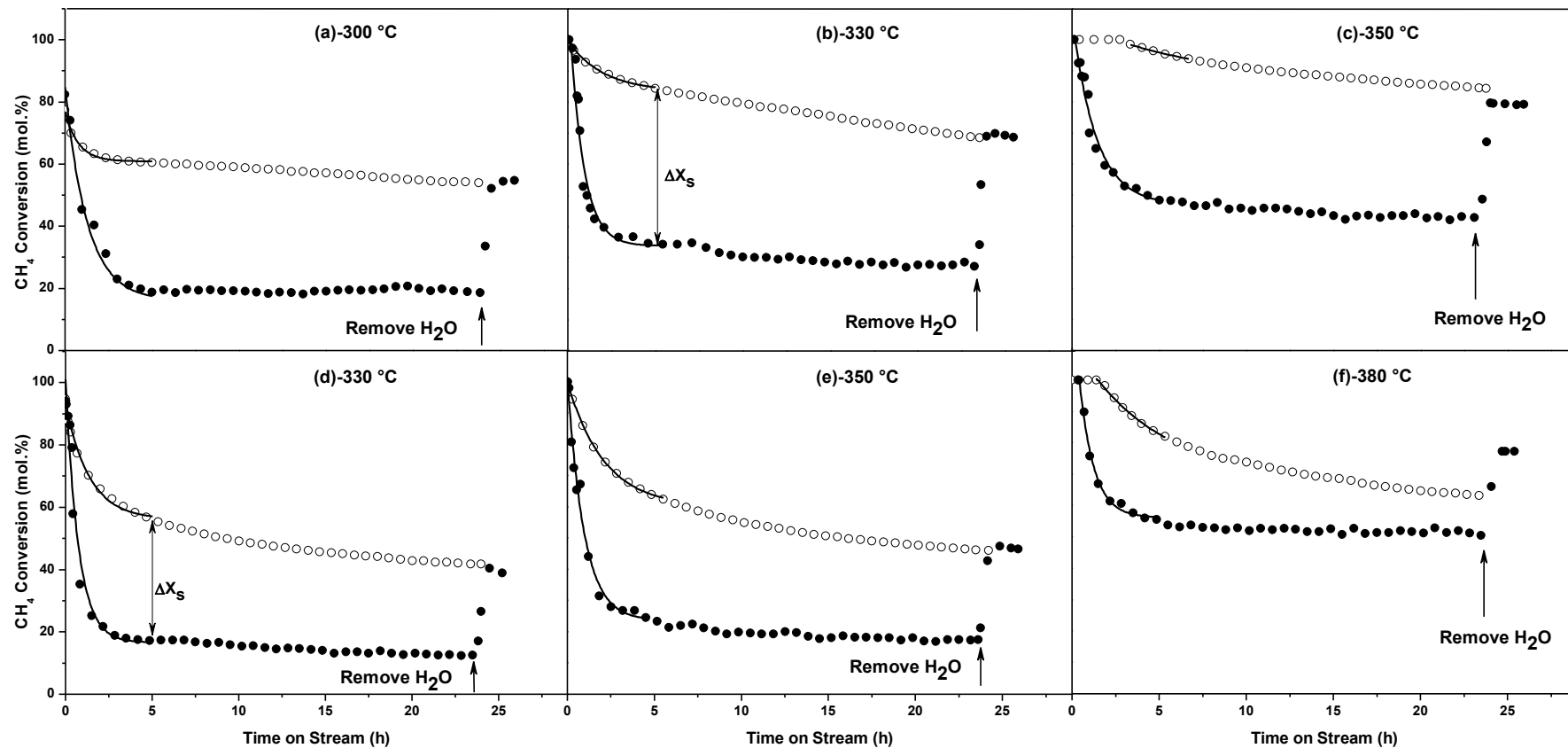


Figure 5.6. TOS results for 6.5Pd/Al₂O₃ and co-2.9Ce/6.5Pd/Al₂O₃ catalysts at different temperatures for dry (open symbol) and wet (closed symbol) conditions. GHSV=180,000 cm³(STP).g_{cat}⁻¹.h⁻¹. 5000 ppm CH₄, 20(v/v)% O₂, and the balance He. Top: 6.5Pd/Al₂O₃ at (a) T=300°C, (b) T=330°C, (c) T=350°C, Bottom: co-2.9Ce/6.5Pd/Al₂O₃ at (d) T=330°C, (e) T=350°C, (f) T=380°C

Similar to Chapter 4, the rate constant and equilibrium constant for H₂O adsorption, as well as the apparent activation energy (E_a) and enthalpy of H₂O adsorption (ΔH_{H_2O}) of the co-2.9Ce/6.5Pd/Al₂O₃ catalyst were obtained by applying the kinetic model and the reactor design Equation 4.20 to X_s , the stable CH₄ conversion at t=5h. Figure 5.7 shows the estimated X_{CH_4} values with the $R^2=0.98$ using the parameters reported in Table 5.4.

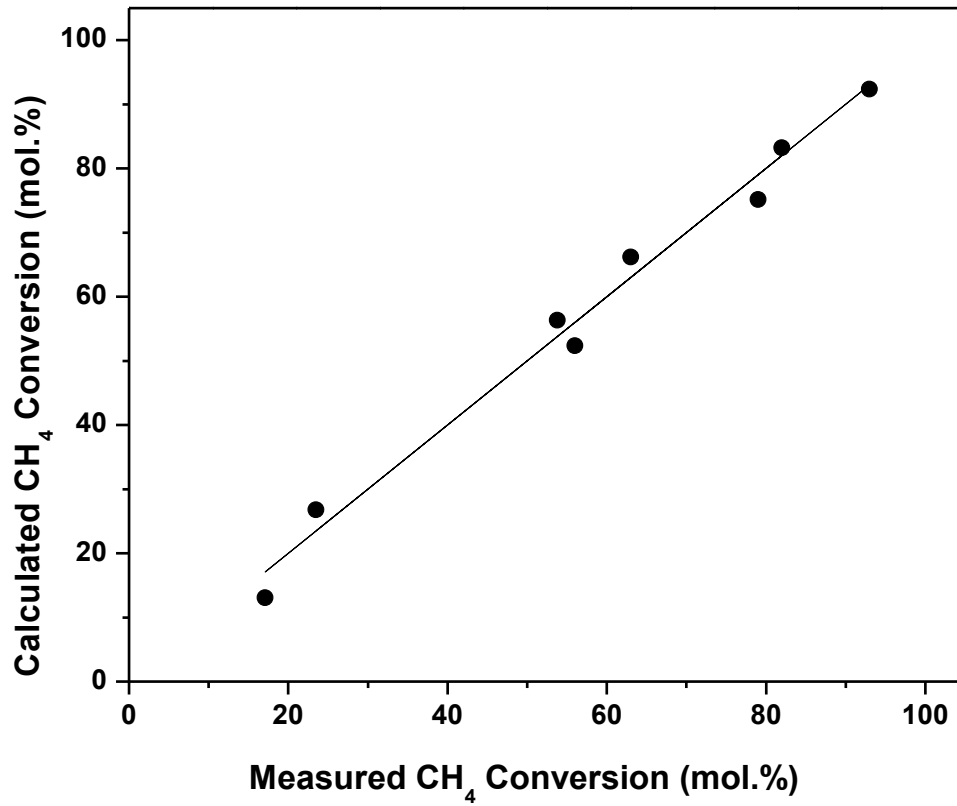


Figure 5.7. Calculated X_{CH_4} values from the kinetic model versus measured X_{CH_4} values from the experiments for co-2.9Ce/6.5Pd/Al₂O₃ catalyst

Table 5.4. Constant values for co-2.9Ce/6.5Pd/Al₂O₃ catalyst at T=330°C used in Equation 4.20

W_{cat} (g)	8.33×10^{-2}
Pd (wt.%)	6.5
$F_{\text{CH}_4}^0$ (mol.s ⁻¹)	373.6
$y_{\text{CH}_4}^0$	0.005
P (Pa)	101325
GHSV (mol.g _{cat} ⁻¹ .s ⁻¹)	2.23×10^{-3}
C_T (mol _{site} .g _{cat} ⁻¹)	1.53×10^{-4}
D_{eff}^0 at 330°C (m ² .s ⁻¹)	9.88×10^{-7}
ρ_{cat} (g.cc ⁻¹)	1.54
d_p (cm)	2.22×10^{-2}
$\alpha_{\text{H}_2\text{O}}$	0 and 10

Comparing the estimated kinetic parameters for 6.5Pd/Al₂O₃ (Table 4.6) and co-2.9Ce/6.5Pd/Al₂O₃ (Table 5.5) shows smaller η values for the 6.5Pd/Al₂O₃ catalyst than the co-2.9Ce/6.5Pd/Al₂O₃ catalyst. This is due to a higher reaction rate constant (k_s) on the 6.5Pd/Al₂O₃ catalyst than the co-2.9Ce/6.5Pd/Al₂O₃ catalyst. The data also show that $K_{\text{H}_2\text{O}}$ is greater on the 6.5Pd/Al₂O₃ catalyst than the CeO₂ promoted catalyst, confirming the beneficial effect of CeO₂ in regards to reducing the suppression of the CH₄ oxidation reaction by H₂O.

Table 5.5. Estimated values of η , rate constant, equilibrium constant for H₂O adsorption, and reaction rate at different temperatures for co-2.9Ce/6.5Pd/Al₂O₃ catalyst

T °C	η	k_s mol.g _{cat} .mol _{site} ⁻² .Pa ⁻¹ .s ⁻¹	$K_{\text{H}_2\text{O}}$ Pa ⁻¹	$-r_{\text{CH}_4}^m$ mol.(g _{cat} .s) ⁻¹
330	0.86	1.1	1.27×10^{-3}	1.42×10^{-6}
350	0.82	1.6	6.61×10^{-4}	3.19×10^{-6}
380	0.74	2.6	2.68×10^{-4}	5.71×10^{-6}
400	0.68	3.5	1.54×10^{-4}	4.65×10^{-6}

The values of E_a and ΔH_{H_2O} for the 6.5Pd/Al₂O₃ and co-2.9Ce/6.5Pd/Al₂O₃ catalysts are compared in Table 5.6. The higher negative value of ΔH_{H_2O} for co-2.9Ce/6.5Pd/Al₂O₃ than 6.5Pd/Al₂O₃ catalyst implies a stronger adsorption of the H₂O on the co-2.9Ce/6.5Pd/Al₂O₃ catalyst, although the amount adsorbed is lower on this catalyst as shown by the values of K_{H_2O} in Figure 5.8, calculated from the estimated parameters. The magnitude of the pre-exponential factor, $K_{H_2O}^0$, reported in Table 5.6 is related to the entropy change associated with the equilibrium process. Hence the differences in the pre-exponential factors are related to different entropy changes for the water adsorption modes on the Pd/Al₂O₃ versus the Ce/Pd/Al₂O₃ catalyst.

Table 5.6. Compared estimated values obtained from the design equation for 6.5Pd/Al₂O₃ and co-2.9Ce/6.5Pd/Al₂O₃ catalysts

Catalyst	E_a kJ.mol ⁻¹	k_s^0 mol.g _{cat} .mol _{site} ⁻² .Pa ⁻¹ .s ⁻¹	ΔH_{H_2O} kJ.mol ⁻¹	$K_{H_2O}^0$ Pa ⁻¹
6.5Pd/Al ₂ O ₃	60.6±11.5	13.5±1.7	-81.5±9.1	5.3×10 ⁻³ ±4.3×10 ⁻⁴
co-2.9Ce/6.5Pd/Al ₂ O ₃	56.1±8.5	1.1±0.1	-101.8±16.3	1.3×10 ⁻³ ±2.3×10 ⁻⁴

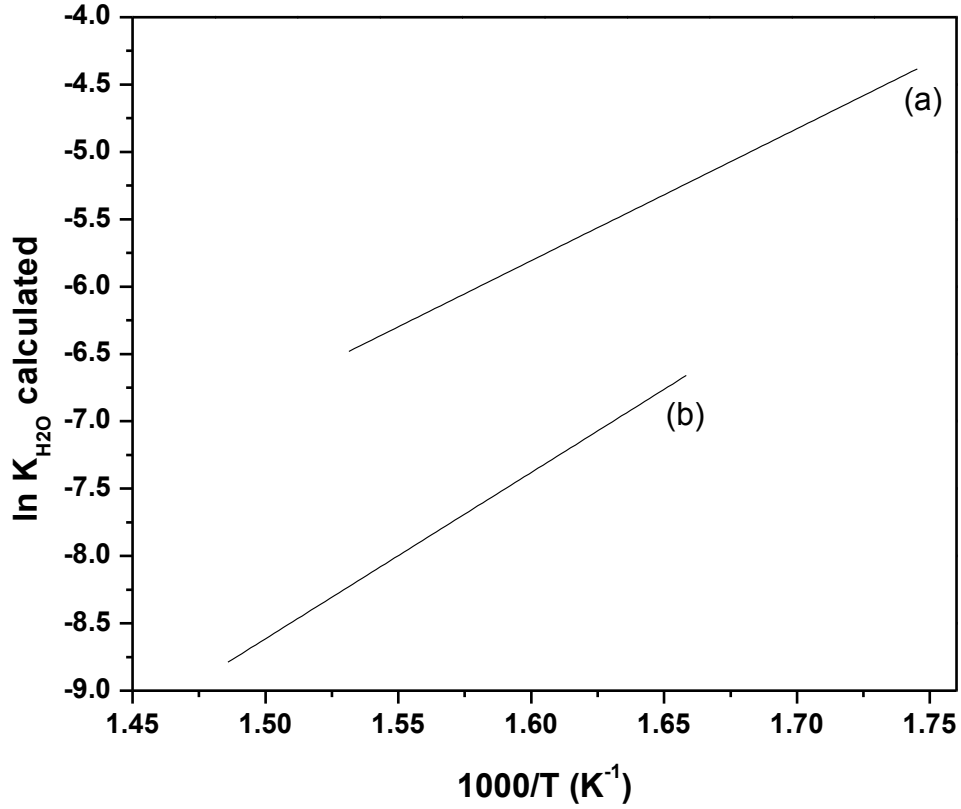


Figure 5.8. Calculated $\ln K_{H_2O}$ versus $\frac{1000}{T}$ for (a) 6.5Pd/Al₂O₃ catalyst, and (b) co-2.9Ce/6.5Pd/Al₂O₃ catalyst

In another approach to quantify the extent of catalyst activity loss, the conversion data of Figure 5.6 are conveniently correlated to an empirical deactivation equation of the form:

$$X_{CH_4} = X_s + A \exp(-k_d t) \quad 5.1$$

where X_{CH_4} is the CH₄ conversion, X_s represents the stable CH₄ conversion at infinite time (herein taken as TOS = 5h), k_d is the rate of catalyst deactivation (identified as $k_{d,d}$ for dry feed and $k_{d,w}$ for wet feed) and $(X_s + A)$ represents the initial CH₄ conversion. Tables 5.7 and 5.8 summarize the parameter values obtained by non-linear regression of Equation 5.1 using the TOS conversion data for the 6.5Pd/Al₂O₃ and co-2.9Ce/6.5Pd/Al₂O₃ catalysts, measured up to 5h TOS. The fit of the equation to each set of data was good ($R^2 \geq 0.92$ in all

cases) and is shown by the solid lines of Figure 5.6. The values reported in Tables 5.7 and 5.8 clearly show that for both catalysts, $k_{d,w}$ and $k_{d,d}$ decreased with increased temperature i.e. the inhibitory effects of H_2O were reduced at higher temperature, as has been reported previously [77,97].

Table 5.7. Rate of deactivation for 6.5Pd/Al₂O₃ catalyst as a function of temperature

T, °C	Dry feed				5vol.% extra H ₂ O			
	X _s	A	k _{d,d}	R ²	X _s	A	k _{d,w}	R ²
300	60.9±0.3	24.0±0.7	0.0217±0.0024	0.99	16.9±0.3	68.5±4.2	0.0270±0.0020	0.97
330	83.3±0.5	16.3±0.5	0.0081±0.0007	0.98	33.8±0.8	66.5±1.7	0.0210±0.0040	0.92
350	93.5±0.2	5.8±0.4	0.0019±0.0005	0.99	46.9±2.3	60.9±2.8	0.0120±0.0020	0.98

Table 5.8. Rate of deactivation for co-2.9Ce/6.5Pd/Al₂O₃ catalyst as a function of temperature

T, °C	Dry feed				5vol.% extra H ₂ O			
	X _s	A	k _{d,d}	R ²	X _s	A	k _{d,w}	R ²
330	56.1±1.1	39.9±0.2	0.0120±0.0010	0.99	16.6±0.1	84.5±0.3	0.0220±0.0040	0.96
350	59.9±0.4	40.1±0.4	0.0078±0.0002	0.99	23.6±0.5	77.8±0.9	0.0170±0.0020	0.98
380	80.2±0.2	20.5±0.3	0.0048±0.0003	0.99	54.7±0.8	43.8±0.2	0.0120±0.0050	0.99

The impact of Ce addition on the catalyst deactivation in the presence of H_2O can be quantified by considering ΔX_s (the difference between X_s measured for the dry and wet feed) and the ratio of k_d measured under wet and dry conditions ($\frac{k_{d,w}}{k_{d,d}}$). These values are reported in Table 5.9 and show that with Ce addition to the Pd catalyst, both ΔX_s and $\frac{k_{d,w}}{k_{d,d}}$ decreased, indicating that the inhibition of CH_4 conversion by H_2O is reduced by the addition of Ce to

the 6.5Pd/Al₂O₃ catalyst, both in terms of the rate of deactivation and the impact of the H₂O on the final conversion.

Table 5.9. ΔX_s and $\frac{k_{d,w}}{k_{d,d}}$ ratio for 6.5Pd/Al₂O₃ catalyst and co-2.9Ce/6.5Pd/Al₂O₃ catalyst

T	6.5Pd/Al ₂ O ₃ catalyst		co-2.9Ce/6.5Pd/Al ₂ O ₃	
°C	ΔX_s	$\frac{k_{d,w}}{k_{d,d}}$	ΔX_s	$\frac{k_{d,w}}{k_{d,d}}$
300	44.0	1.2	-	-
330	49.5	2.6	39.5	1.8
350	46.6	6.3	36.3	2.2
380	-	-	25.5	2.5

Upon removal of the H₂O added to the feed gas after 24h TOS, the CH₄ conversion increased to a value almost identical to that observed after 24h TOS without H₂O added to the feed gas (See Figure 5.6). Hence the inhibition of CH₄ conversion by H₂O is partially reversible, as has been reported in other studies [29,110]. These factors suggest that the activity loss is mostly a result of H₂O adsorption that is reduced at higher temperature and by the presence of CeO₂ on the catalyst surface. Note that upon H₂O removal for co-2.9Ce/6.5Pd/Al₂O₃ catalyst at 380°C the CH₄ conversion increased to a higher value than conversion at 24h for the dry-TOS (Figure 5.6f). The reason for this increase is not clear but one possible explanation is that at high temperature in the presence of H₂O, some CeO_x/PdO restructuring occurs, changing the PdO dispersion and this does not occur in the absence of added H₂O.

5.2.3 Properties of the Used Catalysts

The properties of the catalysts after the TOS experiments in the presence of 5vol.% extra H₂O are reported in Table 5.10 for both the 6.5Pd/Al₂O₃ and co-2.9Ce/6.5Pd/Al₂O₃ catalysts.

A reduction in BET surface area of both catalysts was observed after reaction (from 218 to 185 m²/g for the 6.5Pd/Al₂O₃ and from 206 to 152 m²/g for the co-2.9Ce/6.5Pd/Al₂O₃ catalyst). The decrease in BET surface area was accompanied by a small decrease in pore volume and a decrease in CO uptake, yet XRD analysis showed only a small reduction in PdO crystallite size. The difference in PdO crystallite size of the fresh and used catalysts is within the experimental error associated with the analysis. Together these results suggest some sintering of the Al₂O₃ occurs following 24h reaction, resulting in collapse of pores, which in turn occludes some of the PdO. Figures 5.9 and 5.10 show the XRD and XPS analysis of the fresh and used 6.5Pd/Al₂O₃ and co-2.9Ce/6.5Pd/Al₂O₃ catalysts. The PdO peaks from XRD appeared at the same 2θ and the two main peaks for Pd 3d from XPS were observed at the same binding energy after the TOS experiment for both catalysts. This confirms the stability of PdO at the reaction conditions even in the presence of H₂O and confirms that there is no evidence for the formation of Pd(OH)₂ or Pd⁰ following reaction. Note that the hydroxide species formed on the surface of the PdO may have decomposed during sample handling. However, if bulk Pd(OH)₂ was formed and all of the PdO was converted to Pd(OH)₂ then it would be expected to see Pd(OH)₂ from the XPS and the XRD since it is thermally stable up to 250 °C as a bulk chemical and up to 375 °C when supported on carbon [111].

Table 5.10. Properties of fresh and used catalysts after TOS experiment for 24h in wet condition at T=350°C

	BET	Pore	Pore	CO	Pd	PdO
Catalyst	SA ^a	Size ^a	Volume ^a	Uptake ^b	Dispersion ^b	Crystallite Size ^c
	m ² /g	nm	cm ³ /g	μmol/g _{cat}	%	nm
6.5Pd/Al ₂ O ₃ -fresh calcined	218	7.9	0.43	204	33.5	6
6.5Pd/Al ₂ O ₃ -wet used	185	8.6	0.40	170	27.8	5
co-2.9Ce/6.5Pd/Al ₂ O ₃ -fresh calcined	206	7.9	0.41	153	25.1	5
co-2.9Ce/6.5Pd/Al ₂ O ₃ -wet used	152	9.6	0.37	150	24.5	4

^a Determined by N₂ adsorption at 77K

^b Obtained by CO chemisorption

^c PdO (101) obtained by XRD

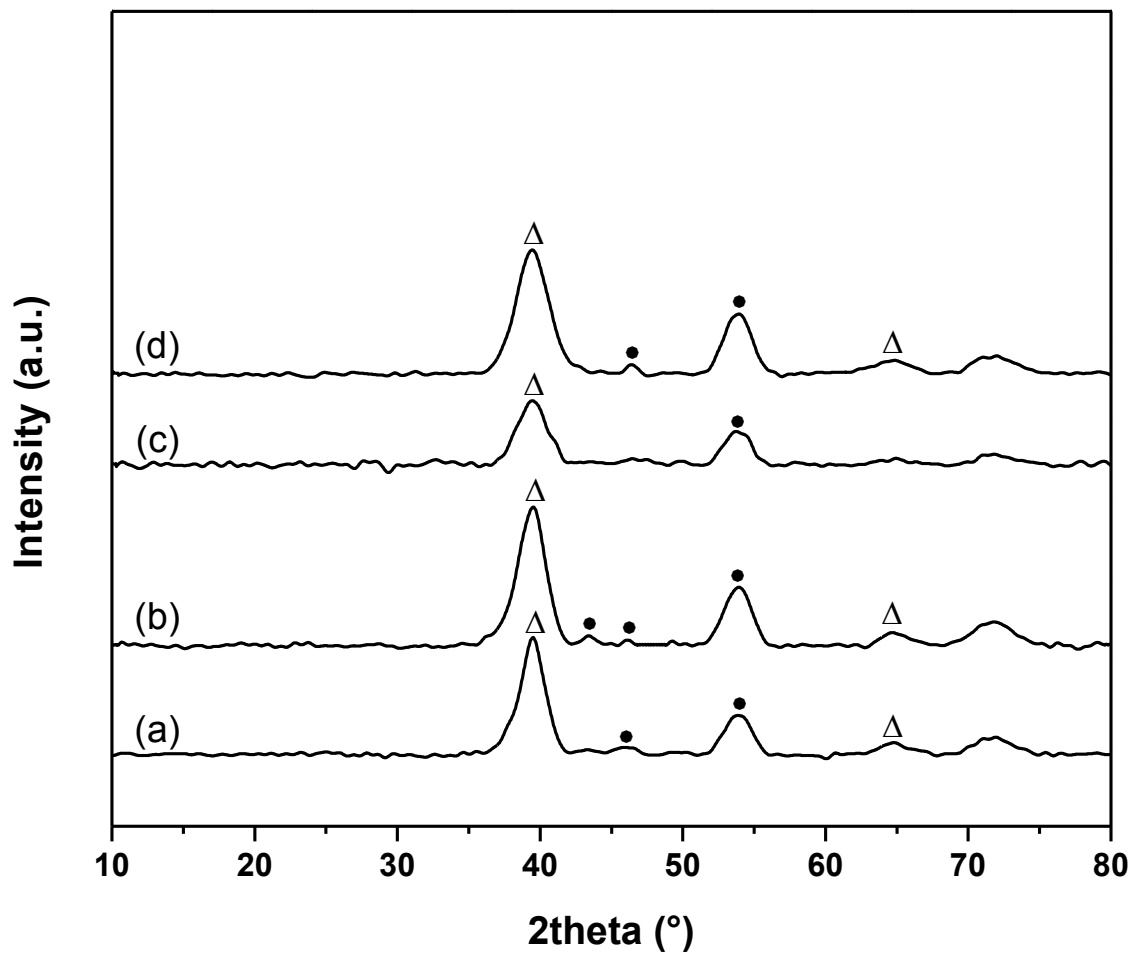


Figure 5.9. XRD for 6.5Pd/Al₂O₃ and co-2.9Ce/6.5Pd/Al₂O₃ for both fresh and used catalysts for 24h TOS. (a) Fresh 6.5Pd/Al₂O₃, (b) Used 6.5Pd/Al₂O₃, (c) Fresh co-2.9Ce/6.5Pd/Al₂O₃, (d) Used co-2.9Ce/6.5Pd/Al₂O₃. Δ PdO, ● Al₂O₃

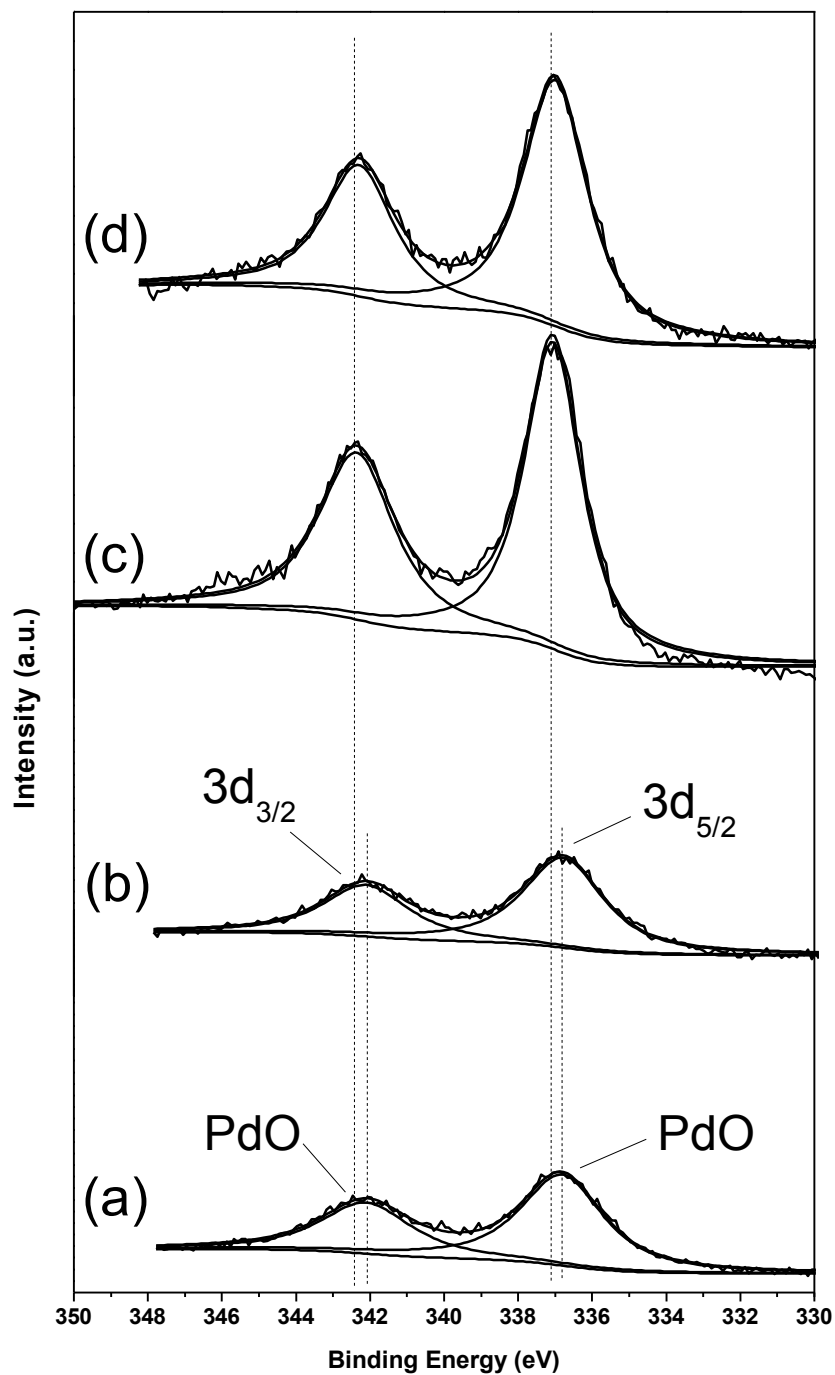


Figure 5.10. XPS binding energy for $6.5\text{Pd}/\text{Al}_2\text{O}_3$ and $\text{co-}2.9\text{Ce}/6.5\text{Pd}/\text{Al}_2\text{O}_3$ for both fresh and used catalysts for 24h TOS. (a) Fresh $6.5\text{Pd}/\text{Al}_2\text{O}_3$, (b) Used $6.5\text{Pd}/\text{Al}_2\text{O}_3$, (c) Fresh $\text{co-}2.9\text{Ce}/6.5\text{Pd}/\text{Al}_2\text{O}_3$, (d) Used $\text{co-}2.9\text{Ce}/6.5\text{Pd}/\text{Al}_2\text{O}_3$

5.3 Discussion

In order to oxidize the catalysts prior to reaction, the 6.5Pd/Al₂O₃ and co-xCe/6.5Pd/Al₂O₃ catalysts were calcined for 15h in air at 450°C in excess O₂ at reaction temperatures significantly below the PdO decomposition temperature [97,110]. Hence Pd and Ce are present as oxidized species at the operating conditions of the present study, as confirmed by XRD and XPS analysis. The XPS data show that the $\frac{\text{Ce}^{3+}}{\text{Ce}^{3+}+\text{Ce}^{4+}}$ surface ratio of the 9.4Ce/Al₂O₃ catalyst is lower than that of the co-9.5Ce/6.5Pd/Al₂O₃ and the Ce³⁺ content increased as the Ce:Pd ratio of the catalyst decreased. These results are consistent with CeO₂ strongly promoting the oxidation (or re-oxidation) of the Pd, resulting in some reduction of Ce⁴⁺ to Ce³⁺ [50,54]. The data also confirm that co-impregnation of the Pd and Ce species results in an interaction between the Ce and Pd species when supported on Al₂O₃. The CO uptake data of the Pd/Al₂O₃ catalyst decreased significantly from 204 μmol/g_{cat} to 89 μmol/g_{cat} with the addition of 0.9Ce to the Pd/Al₂O₃ catalyst (Table 5.1), suggesting a decrease in Pd dispersion. However, the XRD data show no change in the PdO crystallite size and the XPS data show only a marginal increase in the Pd surface atom ratio (from 0.8 to 1.1, see Figure 5.2), suggesting a small increase in Pd dispersion. The CO uptake measurements were made following a mild reduction of the calcined catalysts in H₂ for 1h at 100°C, with the intent to reduce only the outerlayer of the PdO particle [74]. However, in the case of the catalysts with Ce, it is likely that because of the high O exchange associated with the CeO₂, the reduction procedure results in significantly less PdO→Pd surface reduction prior to the CO uptake measurement, resulting in a significantly lower CO uptake on the Ce promoted catalyst compared to the Pd/Al₂O₃ catalyst. Note, however, that for all the Ce-

containing catalysts, the increase in CO uptake observed with increasing Ce content are in good agreement with the XPS Pd₅ measurements reported in Figure 5.2 and indicates that the PdO dispersion is increased with increased CeO₂ content of the catalysts. The addition of CeO₂ to the Pd/Al₂O₃ catalyst also reduces the catalyst surface area and CH₄ oxidation activity, similar to results reported in the literature [52].

Several studies have also reported on the effect of H₂O on CH₄ oxidation [23–25,33,79,88,96,110,112–116]. Kinetic studies show that the rate of CH₄ oxidation over Pd catalysts on a wide range of supports is negative 1st-order in H₂O partial pressure [97]. Some studies propose that the activity inhibition observed at low temperature (< 500°C) is due to the formation of Pd(OH)₂ [25,79,117]. Although Pd(OH)₂ decomposes at 250°C, in the presence of large amounts of H₂O the formation of Pd(OH)₂ can occur at T > 250°C [117]. In addition, the presence of PdO rather than Pd⁰ favors the formation of inactive Pd(OH)₂ since its formation is more likely from PdO than Pd⁰. However, in the present study, Pd(OH)₂ formation was not observed by either XPS or XRD analysis of the used catalysts after 24h reaction in the presence of 5vol.% H₂O (Figures 5.9 and 5.10). PdO sintering may be another explanation for the observed inhibition that is exacerbated in the presence of H₂O [99]. However, both Ostwald ripening and crystallite migration during a 24h TOS experiment at 350°C is unlikely because the reaction temperature is well below half the melting point of the metal oxides (melting point of PdO ~ 750°C) [8]. The data of Table 5.10 confirm this, since they show only minor changes in the PdO crystallite size as measured by XRD and a small reduction in the CO uptake. The drop in CO uptake is likely due to the loss in catalyst surface area, which appears to be a consequence of Al₂O₃ sintering that may also result in PdO encapsulation. The relatively small decrease in CO uptake and PdO crystallite

size are inconsistent with the rapid and significant inhibition in CH₄ conversion observed experimentally following H₂O addition to the feed gas. Furthermore, the fact that the catalyst activity is recovered once the H₂O is removed indicates that the activity loss by H₂O addition is not due to a permanent restructuring of the catalyst.

The kinetic analysis showed that the inhibition of CH₄ oxidation by H₂O is well described by the reversible adsorption of H₂O on active sites [23]. The loss of activity caused by H₂O adsorption is higher on the Pd/Al₂O₃ catalyst than the co-2.9Ce/6.5Pd/Al₂O₃ catalyst and the kinetic analysis shows that this is because of less H₂O adsorption on the latter catalyst, despite the strength of the adsorption being higher on the CeO₂ promoted catalyst. The high OSC of CeO₂ facilitates oxygen transfer between the Pd-* vacancies and the support that reduces the possibility of Pd-OH formation. Hence, the H₂O adsorption equilibrium constant for the co-2.9Ce/6.5Pd/Al₂O₃ catalyst is less than that for the 6.5Pd/Al₂O₃ catalyst. However, the vacant sites (Pd-*) of the co-2.9Ce/6.5Pd/Al₂O₃ catalyst have a stronger H₂O adsorption (i.e. a higher $|\Delta H_{H_2O}|$) than the 6.5Pd/Al₂O₃ catalyst.

Both catalysts showed some loss in activity following 24h reaction in dry and wet feed gas since the conversion after H₂O was removed from the wet experiment feed gas was similar to that measured after 24h in the dry feed gas (see Figure 5.6). Hence we conclude that the loss of activity in the absence of added H₂O could be a consequence of sintering or adsorption of H₂O produced during the reaction. However, during the wet TOS experiments in the presence of 5vol.% H₂O, sintering was negligible compared with H₂O adsorption effects.

The adsorption of H₂O may also occur on the support and one likely consequence is the interruption of the oxygen exchange between the support and Pd-vacancies on the catalyst, as

reported by Ciuparu et al. [36]. Hence, at higher temperature, the inhibitory effect of H₂O on the CH₄ oxidation is reduced, as shown by the data of Figure 5.6. Furthermore, with the addition of CeO₂, with a higher oxygen exchange rate compared to the Al₂O₃ support [50], one would anticipate less of an impact of added H₂O because of the high oxygen exchange capacity of the CeO₂, consistent with the data reported in Table 5.9.

5.4 Conclusions

Addition of Ce to the 6.5Pd/Al₂O₃ catalyst decreased the CH₄ conversion activity of the catalyst, as determined by TPO. Comparing the apparent activation energy (E_a) and enthalpy of H₂O adsorption (ΔH_{H_2O}) for 6.5Pd/Al₂O₃ and co-2.9Ce/6.5Pd/Al₂O₃ catalysts showed similar values of E_a for the catalysts while $|\Delta H_{H_2O}|$ is higher for the co-2.9Ce/6.5Pd/Al₂O₃ catalyst, although K_{H_2O} indicates less H₂O adsorption on the CeO₂ promoted catalyst. Hence the presence of Ce is shown to reduce the inhibition effect of H₂O on CH₄ oxidation. Catalyst characterization data show minimal changes in catalyst properties after reaction, and removal of H₂O from the reactant feed gas results in partial recovery of the catalyst activity. The data are consistent with H₂O adsorption on the catalyst/support that may also inhibit O exchange with Pd-*/PdO species, the effect of which is reversible. Addition of CeO₂ would be expected to enhance the exchange rate and reduce the extent of inhibition by the adsorbed H₂O.

Chapter 6: Effect of Preparation Method on the Activity and Stability of $\text{CeO}_x/\text{PdO}/\text{Al}_2\text{O}_3$ Catalysts in the Presence of H_2O

6.1 Introduction

In this chapter the effect of different preparation methods on the activity and stability of $\text{CeO}_x/\text{PdO}/\text{Al}_2\text{O}_3$ catalysts is reported. The catalysts used in Chapter 5 were prepared by a co-impregnation method in which the Al_2O_3 support was impregnated with a premixed solution of Pd and Ce salts. In the present chapter, the Ce and Pd salts were added either by co-impregnation or by sequential impregnation. In co-impregnation, three catalysts with a fixed Pd loading of 3.4wt.% and different Ce:Pd ratios varying in the range of 0-13.8 were prepared. For sequential impregnation, the maximum Ce:Pd ratio considered was 16.7, with a fixed Pd loading of 3.4wt.%. In Chapter 5 the catalysts had 6.5wt.% Pd and the maximum Ce:Pd ratio was selected as 1.46. In this chapter, we focus on a lower Pd loading and higher Ce loadings to investigate the effect of both preparation method and Ce loading. Since the sequentially impregnated catalysts were more promising than the co-impregnated catalysts in both initial activity and stability in the presence of H_2O , five sequentially impregnated catalysts were prepared, while only three catalysts were made by the co-impregnation method. The co-impregnated catalysts are identified as $\text{co-}x\text{Ce}/y\text{Pd}/\text{Al}_2\text{O}_3$ and the sequentially impregnated catalysts as $\text{seq-}x\text{Ce}/y\text{Pd}/\text{Al}_2\text{O}_3$. Five $x\text{Ce}/\text{Al}_2\text{O}_3$ supports with the same Ce loading as $\text{seq-}x\text{Ce}/y\text{Pd}/\text{Al}_2\text{O}_3$ catalysts were also prepared in order to determine the effect of adding Pd on the physical and chemical properties of the $\text{CeO}_x/\text{Al}_2\text{O}_3$. The OSC of

CeO₂ and ZrO₂ were compared by preparing seq-ZrO_x/PdO/Al₂O₃ catalysts presented in Appendix I.

6.2 Results

6.2.1 Catalyst Properties

Figure 6.1 presents the effect of varying the Ce loading and preparation method on the BET surface area, pore size and pore volume of the prepared catalysts. Detailed values are provided in Table G.1. The decrease in BET surface area, pore size and pore volume with increased Ce loading is observed for both the co-impregnated and sequentially impregnated catalysts and for the xCe/Al₂O₃ supports. There is no significant difference in the BET surface area, pore size or pore volume among the catalysts prepared by either co-impregnation or sequential impregnation. Figure 6.2 presents the Pd atom % on the surface, Pd_s, measured by XPS, as a function of (Ce/Al)_b for both co-impregnated and sequentially impregnated catalysts, all with 3.4wt.%Pd. The Pd_s surface concentration of both catalysts increases with increased Ce/Al in the bulk. For (Ce/Al)_b ≤ 0.073, the Pd_s ratio is almost equal for both co-impregnated and sequentially impregnated catalysts. However, for (Ce/Al)_b > 0.073, the Pd_s is higher for the sequentially impregnated catalyst than the co-impregnated catalysts.

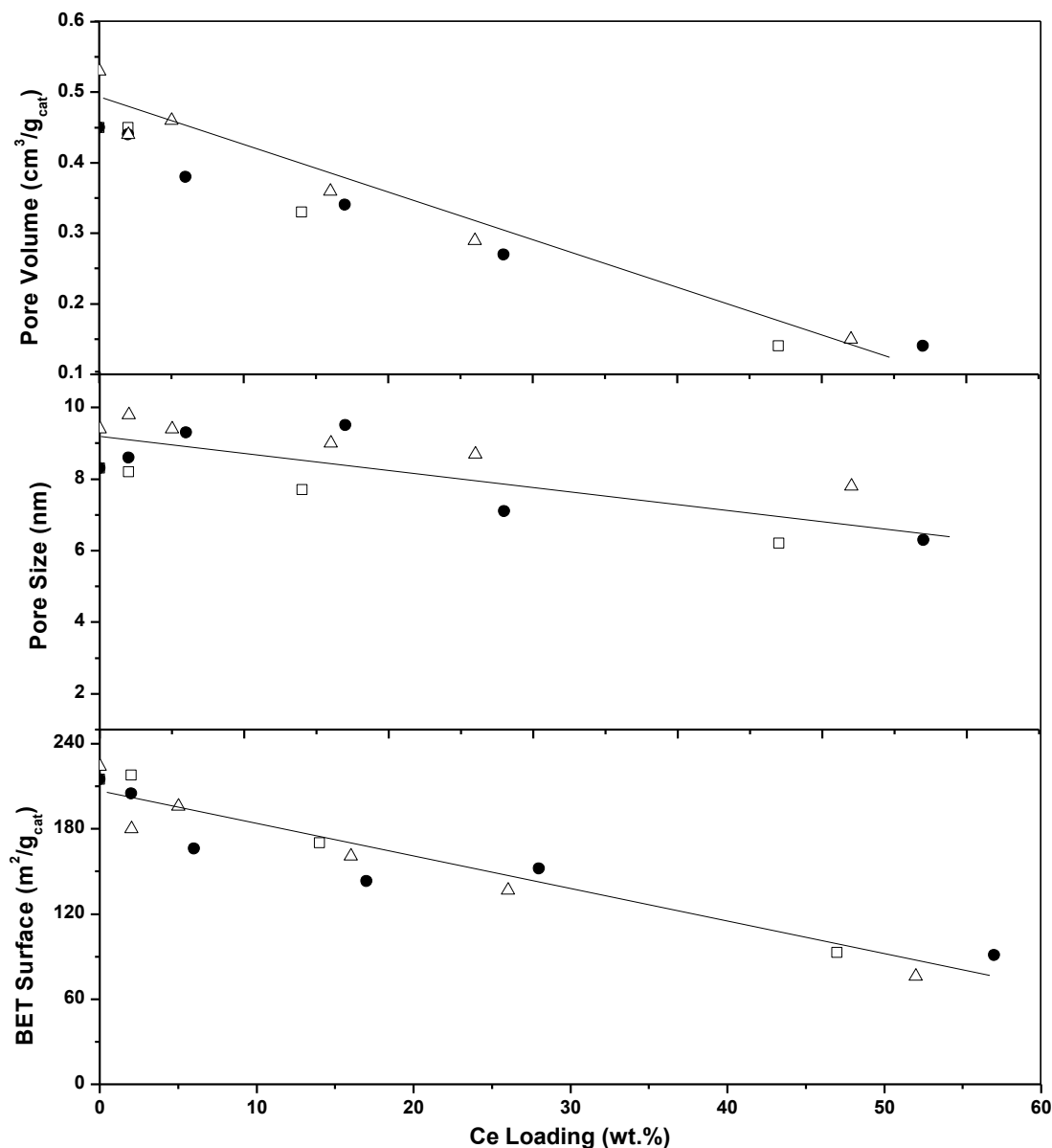


Figure 6.1. Effect of Ce loading on BET surface area, pore size, and pore volume for co-impregnated catalysts (□), sequentially impregnated catalysts (●), and xCe/Al₂O₃ supports (Δ)

Figure 6.3 shows the Ce_s for both co-impregnated and sequentially impregnated catalysts and the xCe/Al₂O₃ supports as a function of $(Ce/Al)_b$. Clearly Ce_s increases as the $(Ce/Al)_b$ increases. However, the co-impregnated catalysts have higher values than the sequentially impregnated catalysts with the same $(Ce/Al)_b$ ratio.

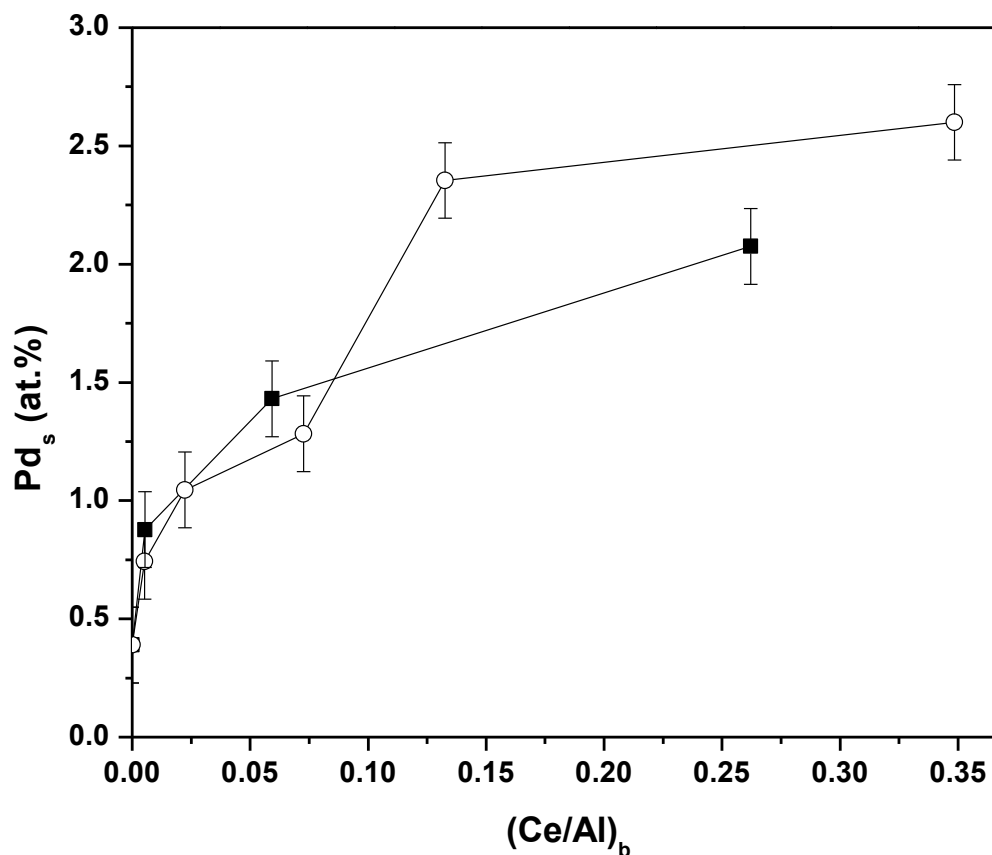


Figure 6.2. Pd atomic percent on the surface of co-impregnated (■) and sequentially impregnated (○) catalysts as a function of $(\text{Ce}/\text{Al})_b$

Comparing the sequentially impregnated catalysts and $\text{xCe}/\text{Al}_2\text{O}_3$ supports shows the same Ce on the surface at $(\text{Ce}/\text{Al})_b \leq 0.11$, however, at $(\text{Ce}/\text{Al})_b > 0.11$, the sequentially impregnated catalysts have lower Ce_s than the $\text{xCe}/\text{Al}_2\text{O}_3$ support alone. The lower Ce surface composition of the sequentially impregnated catalysts than the $\text{xCe}/\text{Al}_2\text{O}_3$ supports at $(\text{Ce}/\text{Al})_b > 0.11$ ratios is due to coverage of the Ce_s by the Pd impregnation in the sequentially impregnated catalysts.

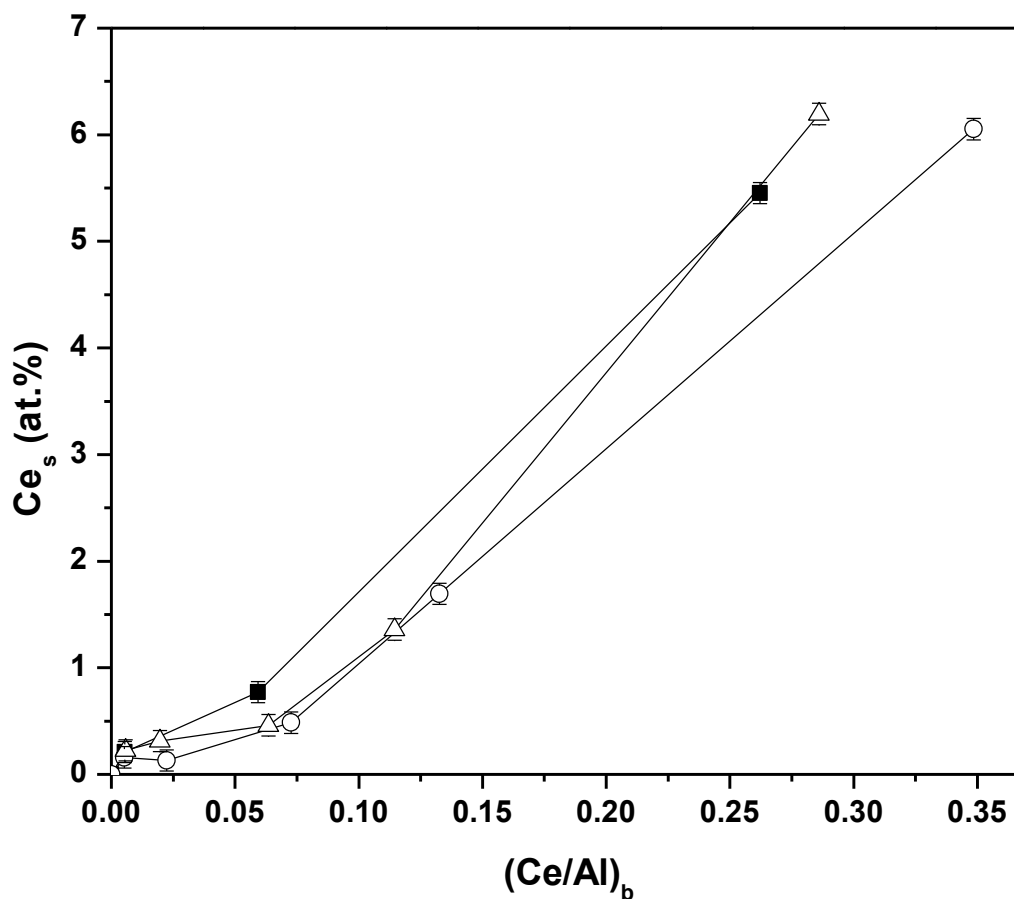


Figure 6.3. Ce atomic percent on the surface of co-impregnated catalysts (■), sequentially impregnated catalysts (○), and $x\text{Ce}/\text{Al}_2\text{O}_3$ supports (Δ) as a function of $(\text{Ce}/\text{Al})_b$

Figure 6.4 shows the Al atom % on the surface of both co-impregnated and sequentially impregnated catalysts and the $x\text{Ce}/\text{Al}_2\text{O}_3$ supports as a function of $(\text{Ce}/\text{Al})_b$. The values for the co-impregnated catalysts are slightly smaller than those for the sequentially impregnated catalysts. As before, the surface composition values reported for Pd_s , Ce_s , and Al_s are normalized, based on the XPS measurement, excluding C.

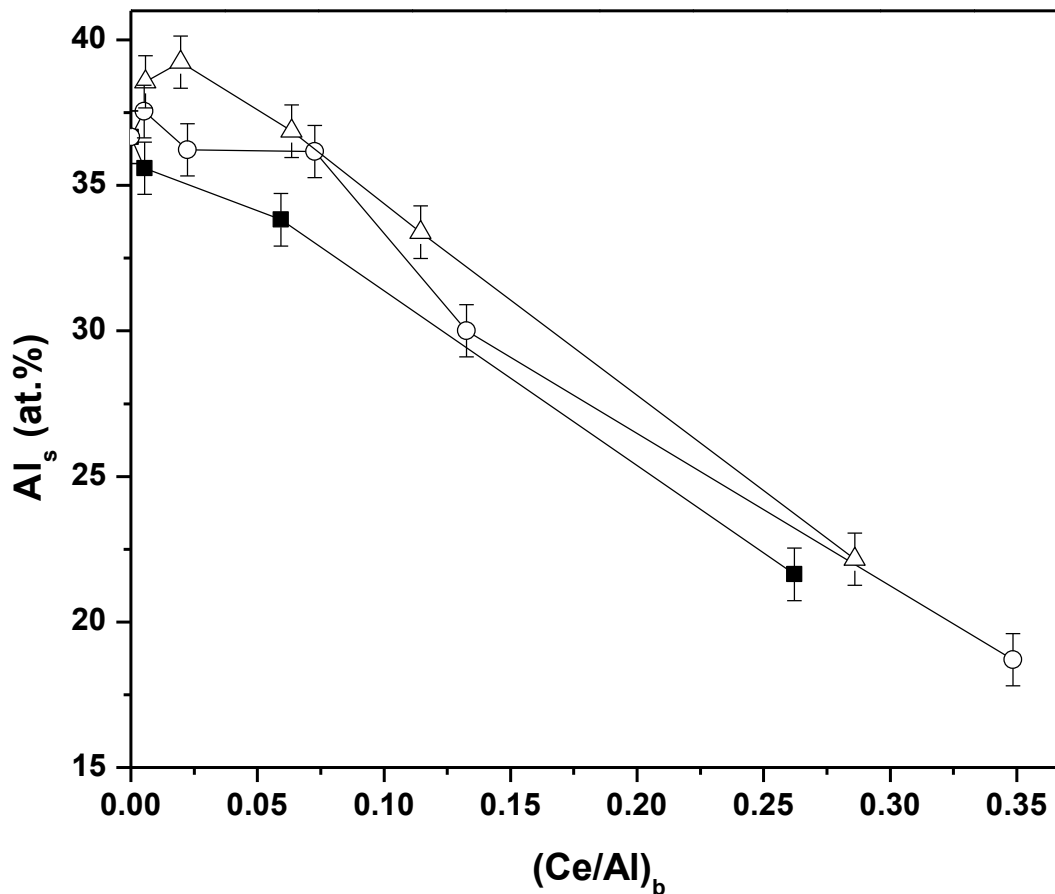


Figure 6.4. Al atomic percent on the surface of co-impregnated catalysts (■), sequentially impregnated catalysts (○), and $x\text{Ce}/\text{Al}_2\text{O}_3$ supports (Δ) as a function of $(\text{Ce}/\text{Al})_b$

Pd, Ce, and Al surface compositions were also determined for a thinner layer of catalyst surface (an approximate depth of 2 nm) using the ToF-SIMS technique. Figure 6.5 shows the distribution of Pd, Ce, and Al on the surface of the seq-17Ce/3.4Pd/ Al_2O_3 catalyst, as an example of the analysis. The scale bar in Figure 6.5 represents the change in color which is due to the relative intensity of the signals.

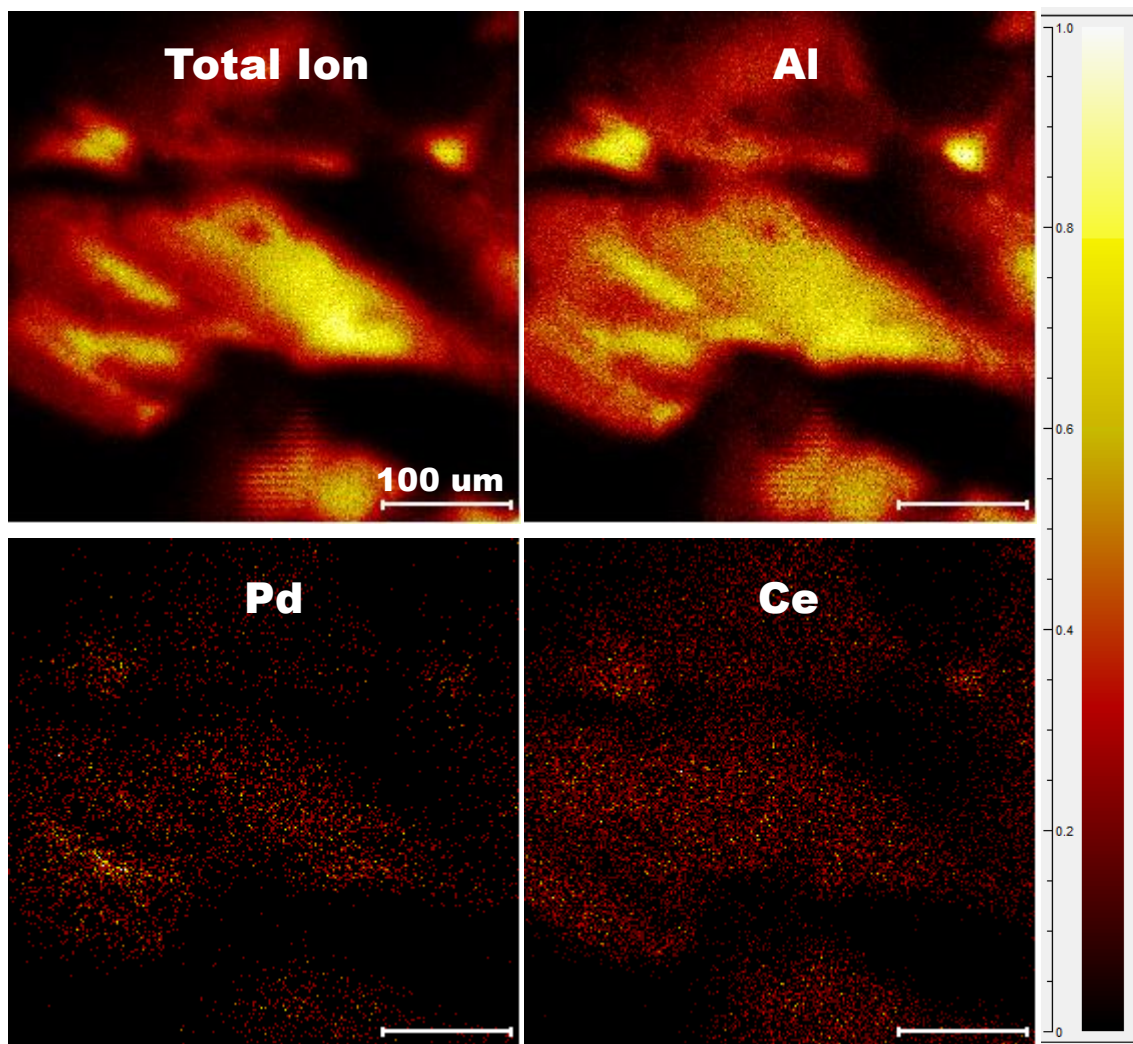


Figure 6.5. ToF-SIMS analysis for seq-17Ce/3.4Pd/Al₂O₃ catalyst

The TOF-SIMS data reported in Table 6.1 show a higher Pd/Al ratio for seq-17Ce/3.4Pd/Al₂O₃ and co-14Ce/3.4Pd/Al₂O₃ catalysts than 3.4Pd/Al₂O₃, confirming the increased Pd surface concentration that results from Ce addition, as observed from the XPS analysis (Figure 6.2). Higher Pd/Al and Ce/Al ratios for the co-14Ce/3.4Pd/Al₂O₃ catalyst than the seq-17Ce/3.4Pd/Al₂O₃ catalyst is in agreement with the higher Pd_s and Ce_s values shown in Figures 6.2 and 6.3 (at (Ce/Al)_b=0.073). These results show higher surface compositions of Pd and Ce in the case of the co-impregnated catalysts.

Table 6.1. Effect of adding Ce on the surface composition ratio obtained by ToF-SIMS

Surface ratio (at.%)	Pd/Al	Ce/Al
3.4PdAl ₂ O ₃	0.14	-
seq-17Ce/3.4Pd/Al ₂ O ₃	0.38	1.43
co-14Ce/3.4Pd/Al ₂ O ₃	0.75	2.30

Figure 6.6(a) shows the Pd XPS spectra of the 3.4Pd/Al₂O₃ catalyst. The Pd3d_{5/2} and Pd3d_{3/2} B.E.s are 336.9 eV and 342.2 eV consistent with those reported by Datye et al. [118] and similar values of 336.9±0.1 eV and 342.2±0.1 eV were determined for the co-2Ce/3.4Pd/Al₂O₃ and co-14Ce/3.4Pd/Al₂O₃ catalysts (Figure 6.6(b) and (c)). Adding 47wt.%Ce to the catalyst caused the Pd B.E. to increase to 337.3 eV and 342.6 eV for the 3d_{5/2} and 3d_{3/2} electrons, respectively, indicating charge transfer from the CeO₂ to the PdO by adding 47wt.%Ce to the 3.4Pd/Al₂O₃ catalyst. The PdO peaks from the XPS analysis for the sequentially impregnated catalysts with 2wt.%, 17wt.%, and 57wt.%Ce are shown in Figure 6.7 with Pd3d_{5/2} and Pd3d_{3/2} B.E.s of 336.9±0.2 eV and 342.2±0.2 eV. Note that adding 17wt.%Ce results in a decrease in Pd B.E. (336.6 eV and 341.9 eV), suggesting a weaker oxidation of PdO for the seq-17Ce/3.4Pd/Al₂O₃ catalyst compared to other catalysts prepared sequentially. The Pd3d_{5/2} and Pd3d_{3/2} peaks for Pd⁰ are at B.E.s 335.4 eV and 340.5 eV, respectively, 1.2 eV and 1.4 eV lower than the PdO B.E.s and not present in the samples shown in Figures 6.6 and 6.7. Note that the 0.4 eV shift in B.E. observed by adding CeO₂ to the catalyst is within the B.E. measurement error expected for porous catalysts, so these changes in oxidation state are not definitive since a minimum 1.0 eV shift is probably needed to confirm PdO→Pd⁰ transformation on these porous catalysts.

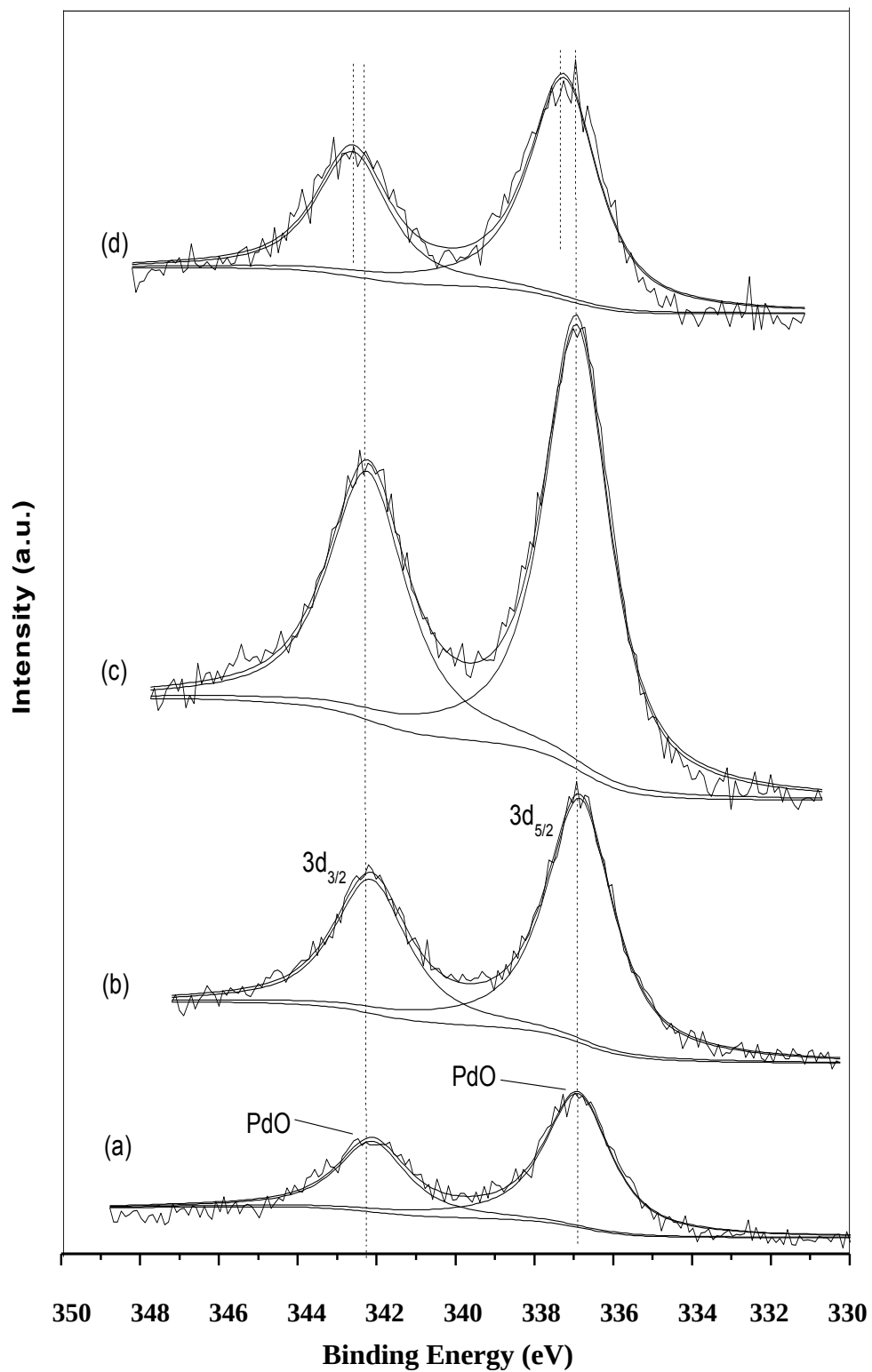


Figure 6.6. XPS Pd 3d spectra measured for (a) 3.4Pd/Al₂O₃ and co-impregnated (b) co-2Ce/3.4Pd/Al₂O₃, (c) co-14Ce/3.4Pd/Al₂O₃, and (d) co-47Ce/3.4Pd/Al₂O₃ catalysts

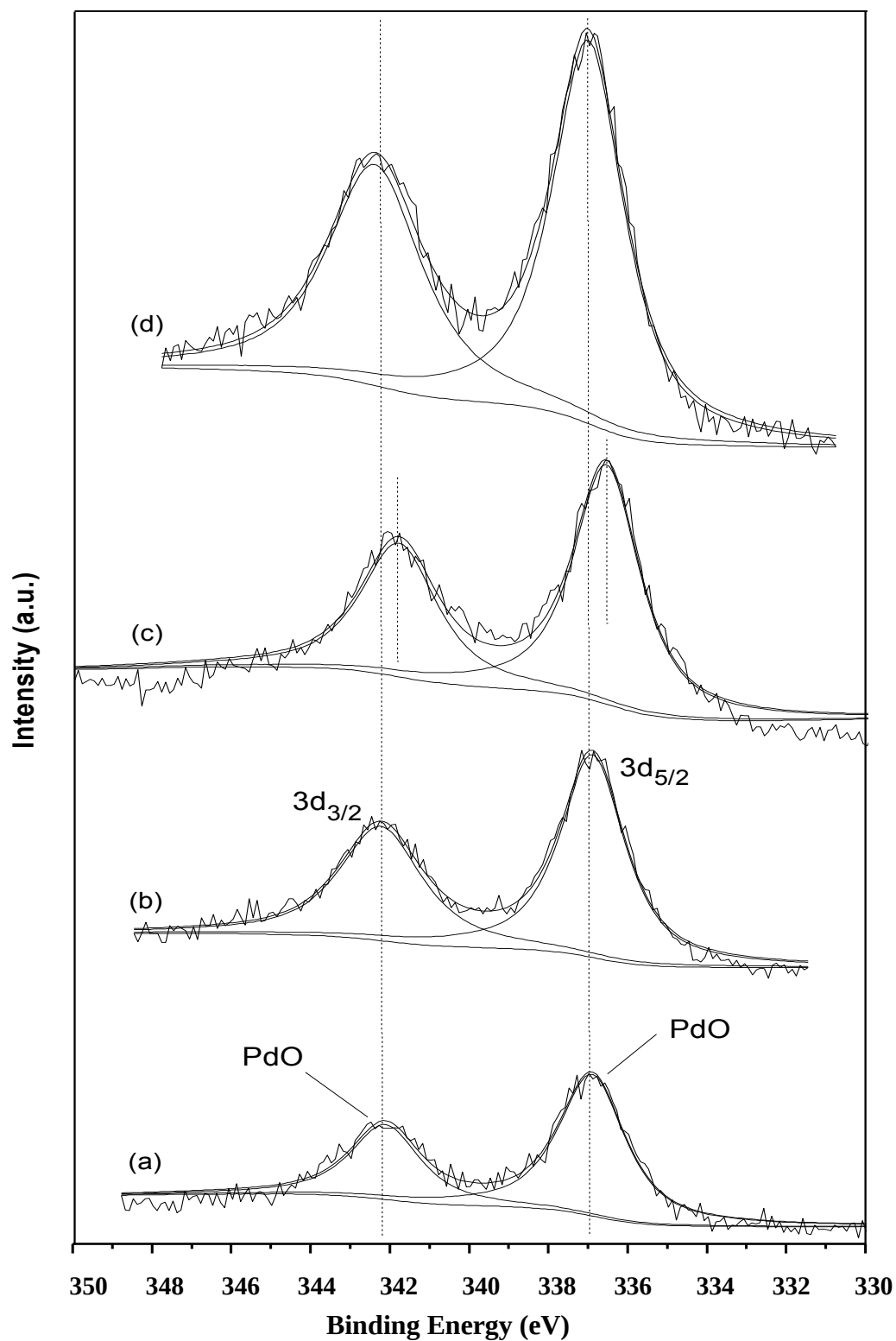


Figure 6.7. XPS Pd 3d spectra measured for (a) 3.4Pd/Al₂O₃ and sequentially impregnated (b) seq-2Ce/3.4Pd/Al₂O₃, (c) seq-17Ce/3.4Pd/Al₂O₃, and (d) seq-57Ce/3.4Pd/Al₂O₃ catalysts

The Ce 3d spectra for the sequentially impregnated catalysts are presented in Figure 6.8. Because of the low intensity of Ce 3d peaks of the seq-2Ce/3.4Pd/Al₂O₃ catalyst, only the Ce 3d spectra of seq-17Ce/3.4Pd/Al₂O₃, seq-28Ce/3.4Pd/Al₂O₃, and seq-57Ce/3.4Pd/Al₂O₃ catalysts are shown in Figure 6.8 and the B.E.s of Ce 3d for all seq-2Ce/3.4Pd/Al₂O₃, seq-17Ce/3.4Pd/Al₂O₃, seq-28Ce/3.4Pd/Al₂O₃, and seq-57Ce/3.4Pd/Al₂O₃ catalysts are reported in Table 6.2. The two main peaks attributed to Ce³⁺ (Ce₂O₃) are located at 885.0 eV (v') and 903.6 eV (u'), respectively for all catalysts. The three main peaks assigned to 3d_{3/2} for Ce⁴⁺ (CeO₂) appeared at 901.0±0.2 eV (u), 906.9 eV (u''), and 917.0 eV (u''') for all catalysts. There are also three peaks for Ce⁴⁺ (CeO₂) 3d_{5/2} identified as v, v'', and v'''. For all sequentially impregnated catalysts, the v and v''' peaks appear at 882.9±0.3 eV and 898.7±0.4 eV, respectively. However, the peak attributed to Ce⁴⁺ (CeO₂) 3d_{5/2} appeared at 887.4 eV (v'') for the seq-2Ce/3.4Pd/Al₂O₃ catalyst but it shifts to 888.6 eV once the Ce loading reaches 17wt.% and remains unchanged for higher Ce loadings (28wt.% and 57wt.%). The Ce 3d spectra for co-impregnated catalysts and xCe/Al₂O₃ supports are presented in Figures G.1 and G.2 and Tables G.3 and G.4. The B.E.s are similar as the sequentially impregnated catalysts and the peak attributed to Ce⁴⁺ (CeO₂) 3d_{5/2} shifted from 887.4 eV (v'') to 888.4 eV and 888.7 eV, respectively, for co-impregnated catalysts and xCe/Al₂O₃ supports.

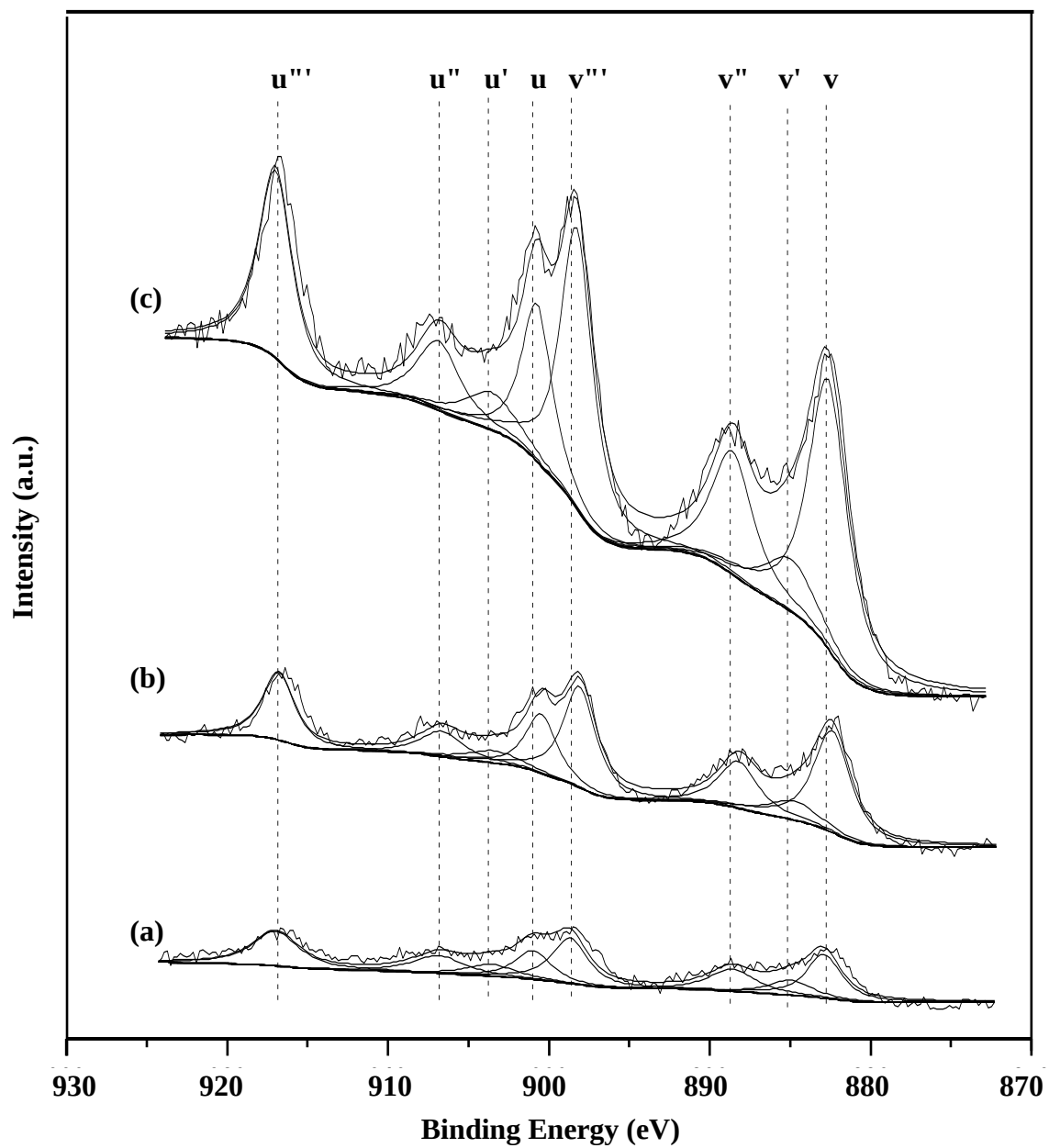


Figure 6.8. Ce 3d for sequentially impregnated (a) seq-17Ce/3.4Pd/Al₂O₃, (b) seq-28Ce/3.4Pd/Al₂O₃, (c) seq-57Ce/3.4Pd/Al₂O₃ catalysts

Table 6.2. Ce 3d peaks and $\frac{\text{Ce}^{3+}}{\text{Ce}^{3+}+\text{Ce}^{4+}}$ ratio for sequentially impregnated catalysts with different loadings of Ce

Catalyst	Ce 3d _{5/2}				Ce 3d _{3/2}				$\frac{\text{Ce}^{3+}}{\text{Ce}^{3+} + \text{Ce}^{4+}}$
	Ce ⁴⁺	Ce ³⁺	Ce ⁴⁺	Ce ⁴⁺	Ce ⁴⁺	Ce ³⁺	Ce ⁴⁺	Ce ⁴⁺	
	eV	eV	eV	eV	eV	eV	eV	eV	
seq-2Ce/3.4Pd/Al ₂ O ₃	882.9	885.0	887.4	898.7	901.0	903.6	906.9	917.0	31.9
seq-6Ce/3.4Pd/Al ₂ O ₃	882.9	885.0	887.6	898.7	901.0	903.6	906.9	917.0	29.3
seq-17Ce/3.4Pd/Al ₂ O ₃	882.9	885.0	888.6	898.7	901.0	903.6	906.9	917.0	13.8
seq-28Ce/3.4Pd/Al ₂ O ₃	882.6	885.0	888.5	898.3	900.7	903.6	906.9	917.0	10.4
seq-57Ce/3.4Pd/Al ₂ O ₃	882.7	885.0	888.6	898.3	900.8	903.6	906.9	917.0	10.9

Figure 6.9 presents the $\frac{\text{Ce}^{3+}}{\text{Ce}^{3+}+\text{Ce}^{4+}}$ ratios for all the catalysts. For the co-impregnated catalysts, sequentially impregnated catalysts, and the $\text{xCe}/\text{Al}_2\text{O}_3$ supports, the ratio decreases with increased Ce loading. For instance, the $\frac{\text{Ce}^{3+}}{\text{Ce}^{3+}+\text{Ce}^{4+}}$ ratio for the sequentially impregnated catalysts decrease from 31.9% to 10.9% as the loading of Ce increases from 2wt.% to 57wt.%. Similar to Chapter 5, the decrease is attributed to less transition of Ce^{4+} to Ce^{3+} with higher Ce loading.

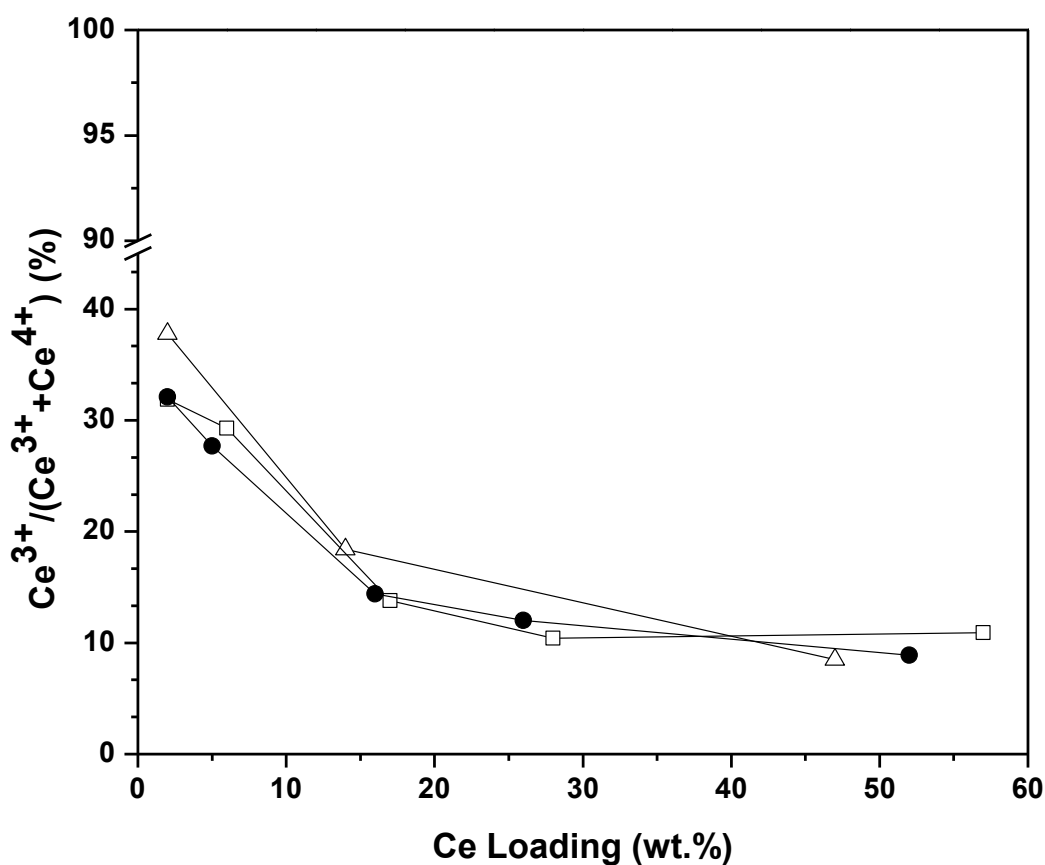


Figure 6.9. $\frac{\text{Ce}^{3+}}{\text{Ce}^{3+}+\text{Ce}^{4+}}$ ratio obtained by XPS analysis for co-impregnated catalysts (Δ), sequentially impregnated catalysts (□), and $\text{xCe}/\text{Al}_2\text{O}_3$ supports (●) as a function of varying loadings of Ce

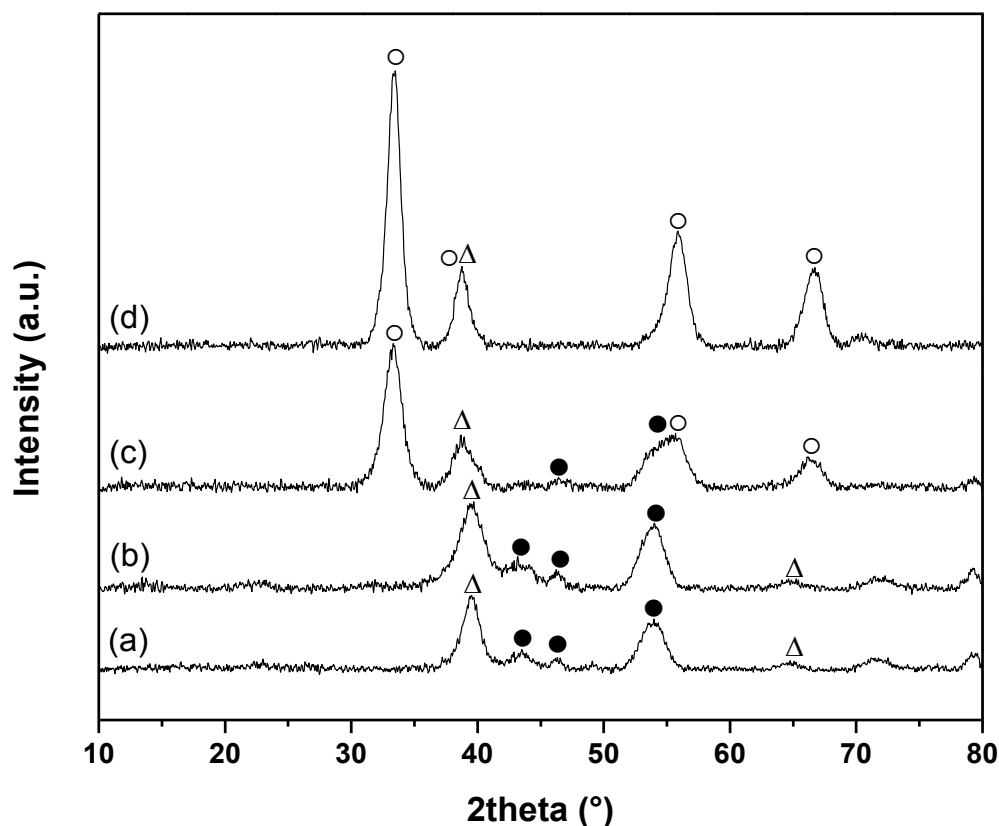


Figure 6.10. XRD patterns for co-impregnated catalysts (a) 3.4Pd/Al₂O₃, (b) co-2Ce/3.4Pd/Al₂O₃, (c) co-14Ce/3.4Pd/Al₂O₃, and (d) co-47Ce/3.4Pd/Al₂O₃ catalysts. Δ PdO, $\bullet$ Al₂O₃, $\circ$ CeO₂

Figure 6.10(a) shows the XRD analysis of the 3.4Pd/Al₂O₃ catalyst with peaks for PdO observed at $2\theta=39.50^\circ$ and 64.50° corresponding to PdO (101) and PdO (112), respectively. The PdO (101) peak was observed for all co-impregnated catalysts with different loadings of Ce, however, the peak shifted slightly to lower 2θ as the Ce loading increased from 2wt.% to 47wt.%. This is a result of an overlap between the PdO (101) peak located at 39.50° and the CeO₂ (200) peak at 38.61° . The main peaks for CeO₂ appear at $2\theta=33.27^\circ$, 38.61° , 55.75° and 66.49° corresponding to CeO₂ (111), (200), (220), and (311), respectively. At higher loadings of Ce (14wt.% and 47wt.%), the peak at $2\theta=55.75^\circ$ has an overlap between Al₂O₃

and CeO_2 (220) and the peak at $2\theta=64.50^\circ$ is a result of overlap between the PdO (112) and CeO_2 (311) peaks.

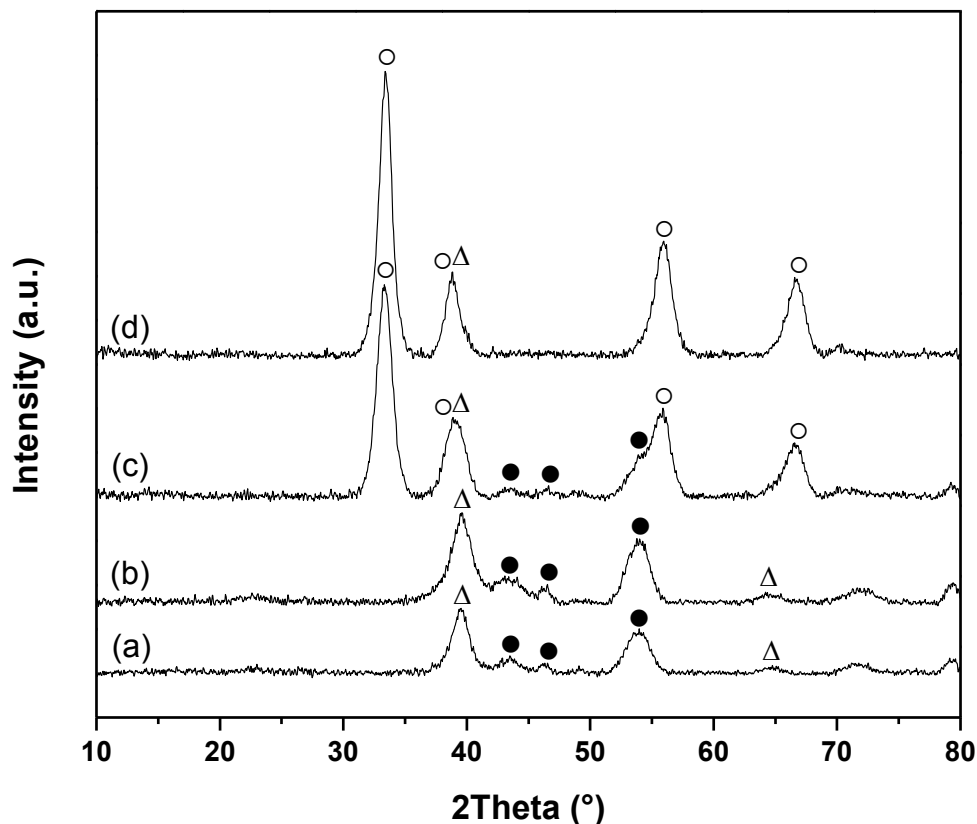


Figure 6.11. XRD patterns for sequentially impregnated (a) $3.4\text{Pd}/\text{Al}_2\text{O}_3$, (b) $\text{seq-2Ce}/3.4\text{Pd}/\text{Al}_2\text{O}_3$, (c) $\text{seq-17Ce}/3.4\text{Pd}/\text{Al}_2\text{O}_3$, and (d) $\text{seq-57Ce}/3.4\text{Pd}/\text{Al}_2\text{O}_3$ catalysts. Δ PdO , $\bullet$ Al_2O_3 , $\circ$ CeO_2

Figure 6.11 shows the XRD analysis for sequentially impregnated catalysts. The position of the peaks for PdO and CeO_2 are the same as those for the co-impregnated catalysts. The PdO (101) and CeO_2 (111) crystallite sizes are reported in Table 6.3. For $3.4\text{Pd}/\text{Al}_2\text{O}_3$ catalyst the PdO (101) crystallite size was calculated as 7 nm. This number is slightly smaller for co-impregnated and sequentially impregnated catalysts. The CeO_2 (111) crystallite size increases with increased Ce loading for both co-impregnated and sequentially impregnated catalysts and $\text{xCe}/\text{Al}_2\text{O}_3$ supports.

Table 6.3. CeO₂ and PdO crystallite size of calcined co-impregnated and sequentially impregnated catalysts and xCe/Al₂O₃ supports

Catalyst	XRD Crystallite Size	
	CeO ₂	PdO
	(111)	(101)
	nm	nm
3.4Pd/Al ₂ O ₃	-	7
co-2Ce/3.4Pd/Al ₂ O ₃	-	5
co-14Ce/3.4Pd/Al ₂ O ₃	7	-
co-47Ce/3.4Pd/Al ₂ O ₃	8	-
seq-2Ce/3.4Pd/Al ₂ O ₃	-	5
seq-6Ce/3.4Pd/Al ₂ O ₃	7	6
seq-17Ce/3.4Pd/Al ₂ O ₃	7	-
seq-28Ce/3.4Pd/Al ₂ O ₃	9	-
seq-57Ce/3.4Pd/Al ₂ O ₃	9	-
2Ce/Al ₂ O ₃	-	-
5Ce/Al ₂ O ₃	5	-
16Ce/Al ₂ O ₃	8	-
26Ce/Al ₂ O ₃	9	-
52Ce/Al ₂ O ₃	9	-

The characterization data show very similar physical and chemical properties of the sequentially impregnated and co-impregnated catalysts. However, with increased (Ce/Al)_b ratio, the surface area and the $\frac{Ce^{3+}}{Ce^{3+}+Ce^{4+}}$ ratio decreased for both preparation methods. The catalyst surface composition analysis showed that the surface Pd concentration (Pd_s) for (Ce/Al)_b > 0.073 was higher for the sequentially impregnated catalyst than co-impregnated catalysts, while the Ce_s values were smaller. The lower Ce_s values suggest stronger interaction between Ce and Al₂O₃ in the sequentially impregnated catalysts that may improve the oxygen exchange capacity of the sequentially impregnated catalysts during the CH₄ oxidation reaction.

6.2.2 Catalyst Activities

Figures 6.12 and 6.13 compare the TPO results for the 3.4Pd/Al₂O₃ and the co-impregnated and sequentially impregnated catalysts. The 3.4Pd/Al₂O₃ catalyst had a T₅₀ of 273°C.

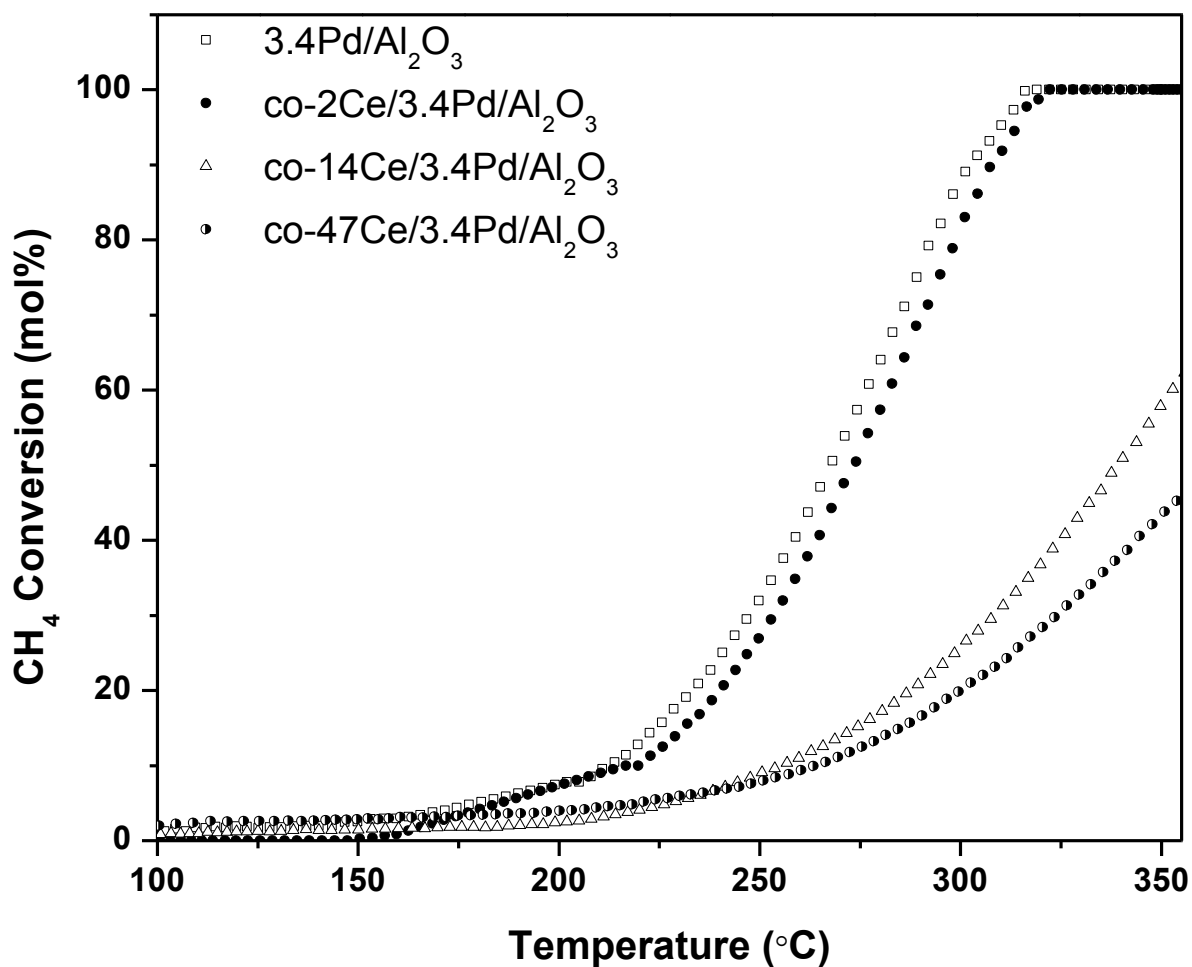


Figure 6.12. Temperature Programmed Oxidation profile for co-impregnated catalysts. Effect of different loadings of Ce on the initial activity of 3.4Pd/Al₂O₃ as a function of temperature.

GHSV=180,000 cm³(STP).g_{cat}⁻¹.h⁻¹, 1000 ppm CH₄, 20(v/v)% O₂, and the balance He and Ar

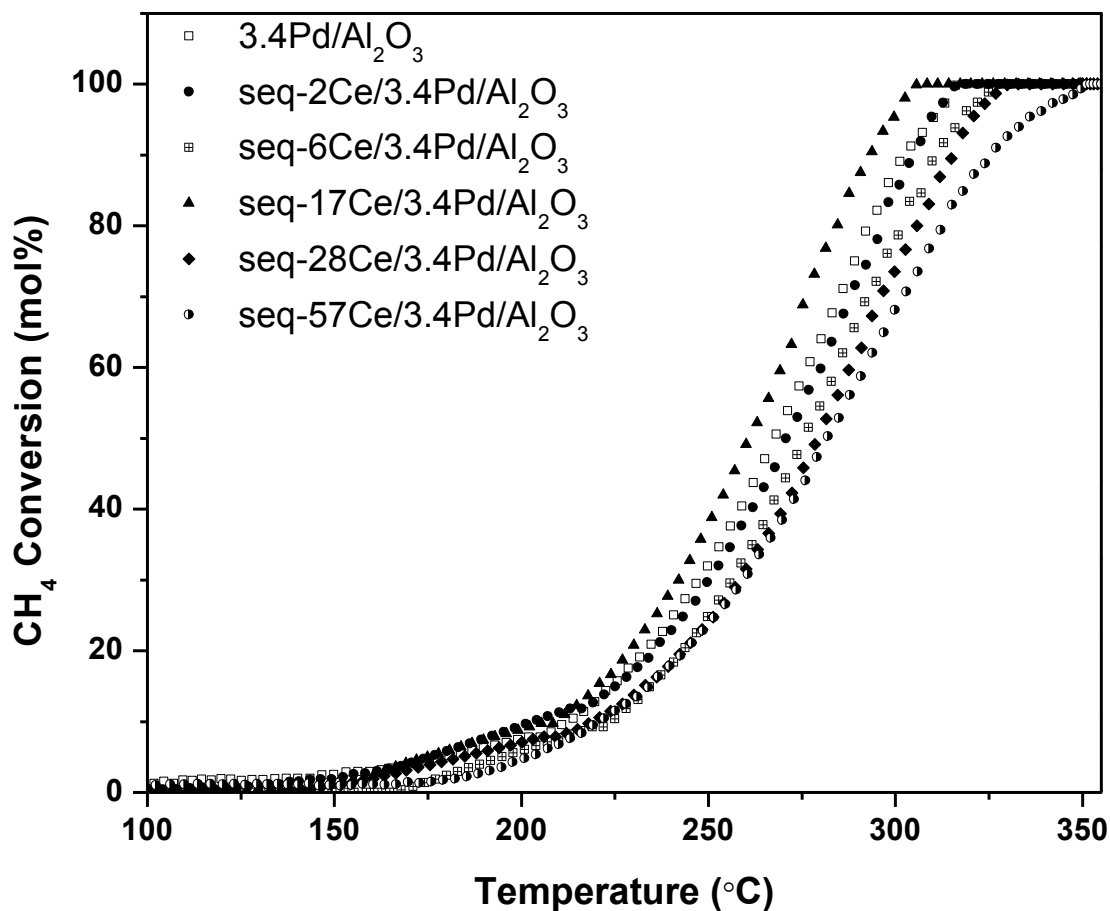


Figure 6.13. Temperature Programmed Oxidation profile for sequentially impregnated catalysts. Effect of different loadings of Ce on the initial activity of 3.4Pd/Al₂O₃ as a function of temperature.

GHSV=180,000 cm³(STP).g_{cat}⁻¹.h⁻¹, 1000 ppm CH₄, 20(v/v)% O₂, and the balance He and Ar

Increased Ce content resulted in reduced activity and the co-47Ce/3.4Pd/Al₂O₃ and seq-57Ce/3.4Pd/Al₂O₃ catalysts were the least active catalysts with T₅₀ of 351°C and 288°C, respectively. However, the seq-17Ce/3.4Pd/Al₂O₃ catalyst showed the highest activity among 3.4Pd/Al₂O₃ and the other co-impregnated and sequentially impregnated catalysts. The initial activity of the catalysts decreases in the following order as the basis of T₅₀:

seq-17Ce/3.4Pd/Al₂O₃ > seq-2Ce/3.4Pd/Al₂O₃ > 3.4Pd/Al₂O₃ > seq-6Ce/3.4Pd/Al₂O₃ > co-2Ce/3.4Pd/Al₂O₃

Comparing the initial activity of the catalysts shown in Figures 6.12 and 6.13 confirms that the co-impregnated catalysts are less active and also more sensitive to Ce loading compared with the sequentially impregnated catalysts. For the co-47Ce/3.4Pd/Al₂O₃ catalyst with the highest Ce loading, the T₅₀ was 78°C higher than the 3.4Pd/Al₂O₃ catalyst, however, the T₅₀ for the seq-57Ce/3.4Pd/Al₂O₃ was only 15°C higher than the 3.4Pd/Al₂O₃ catalyst. More details of the light-off temperatures corresponding to 10%, 50%, and 90% CH₄ conversion are presented in Table G.2 and these data show similar trends in terms of catalyst activity.

The assessment of the effect of different preparation methods on the stability of the catalysts during CH₄ oxidation was done under dry-TOS and wet-TOS experimental conditions for a 24h period at temperatures 310-370°C. At 350°C under dry-TOS conditions, CH₄ conversion decreased as the catalysts were exposed to the reactants. A slower loss in CH₄ conversion is observed for the co-2Ce/3.4Pd/Al₂O₃ catalyst compared with the other co-impregnated catalysts with higher Ce loadings (Figure G.9). The sequentially impregnated catalysts also show a loss in the CH₄ conversion as a function of TOS (Figure G.10), however, this loss is reduced compared to the co-impregnated catalysts with the same Ce loadings. The rate of catalyst deactivation for the dry-TOS experiment was assessed using the empirical deactivation model discussed previously (Equation 5.1), with the model parameters summarized in Figure 6.14. $k_{d,d}$ values are reported at 350°C and 320°C. At a constant temperature (350°C), $k_{d,d}$ is significantly higher for the co-impregnated catalysts than the sequentially impregnated catalysts. In the case of the 3.4Pd/Al₂O₃ and the seq-17Ce/3.4Pd/Al₂O₃ catalysts, the $k_{d,d}$ values are compared at lower temperature (320°C), showing less deactivation in the case of the seq-17Ce/3.4Pd/Al₂O₃ catalyst.

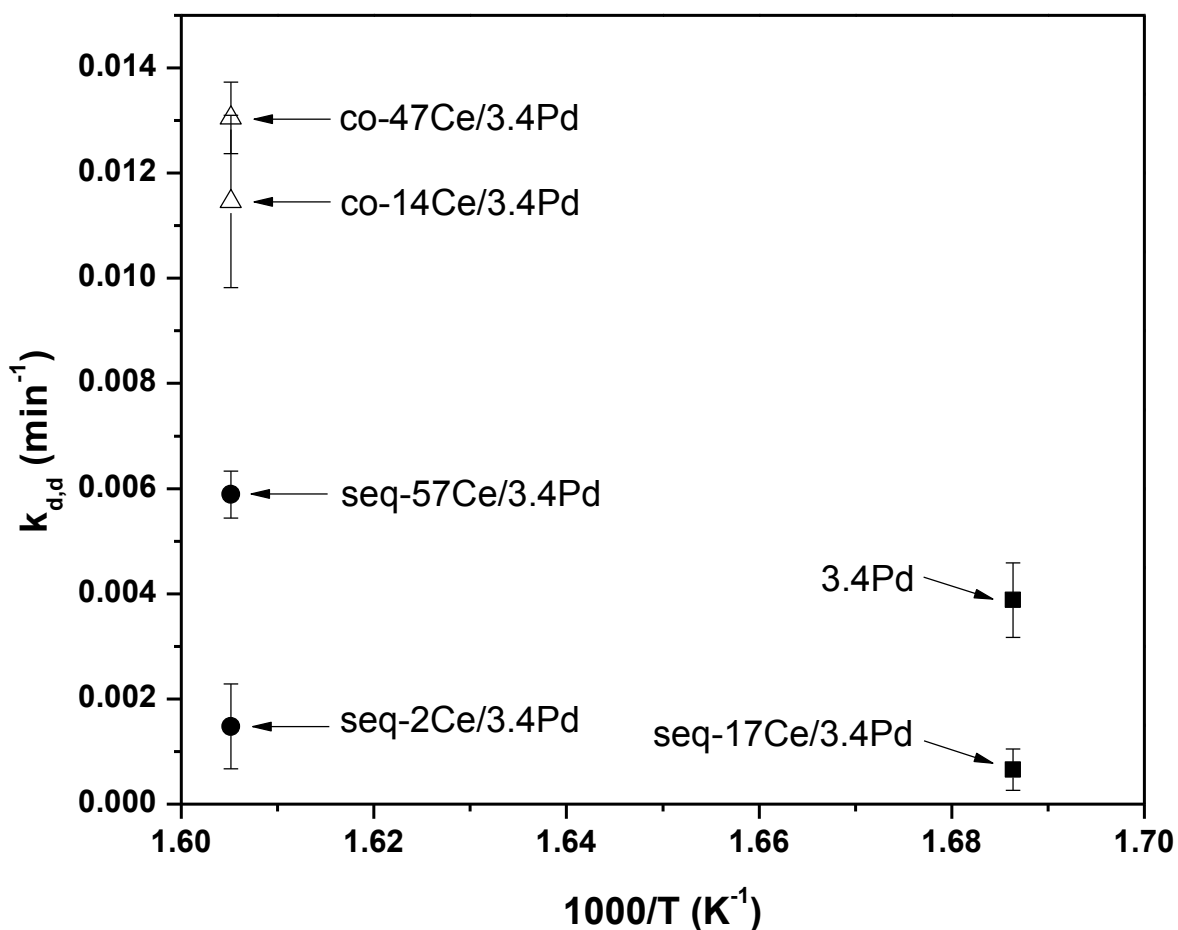


Figure 6.14. Rate of catalyst deactivation ($k_{d,d}$) as a function of Ce loading for co-impregnated catalysts (Δ), and sequentially impregnated catalysts ($\bullet$) at $T=350^{\circ}\text{C}$ and ($\blacksquare$) at $T=320^{\circ}\text{C}$. Obtained from dry-TOS results. GHSV= $180,000\text{ cm}^3(\text{STP})\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$, 1000 ppm CH_4 , 20(v/v)% O_2 , and the balance He and Ar

The same comparison for the wet-TOS results at 350°C is shown in Figure 6.15 for the co-impregnated and sequentially impregnated catalysts in the presence of 2vol.% H_2O . The rate of catalyst deactivation is much lower for the sequentially impregnated catalysts than the co-impregnated catalysts with identical Ce loading. Higher Ce loading results in a higher loss of catalyst activity.

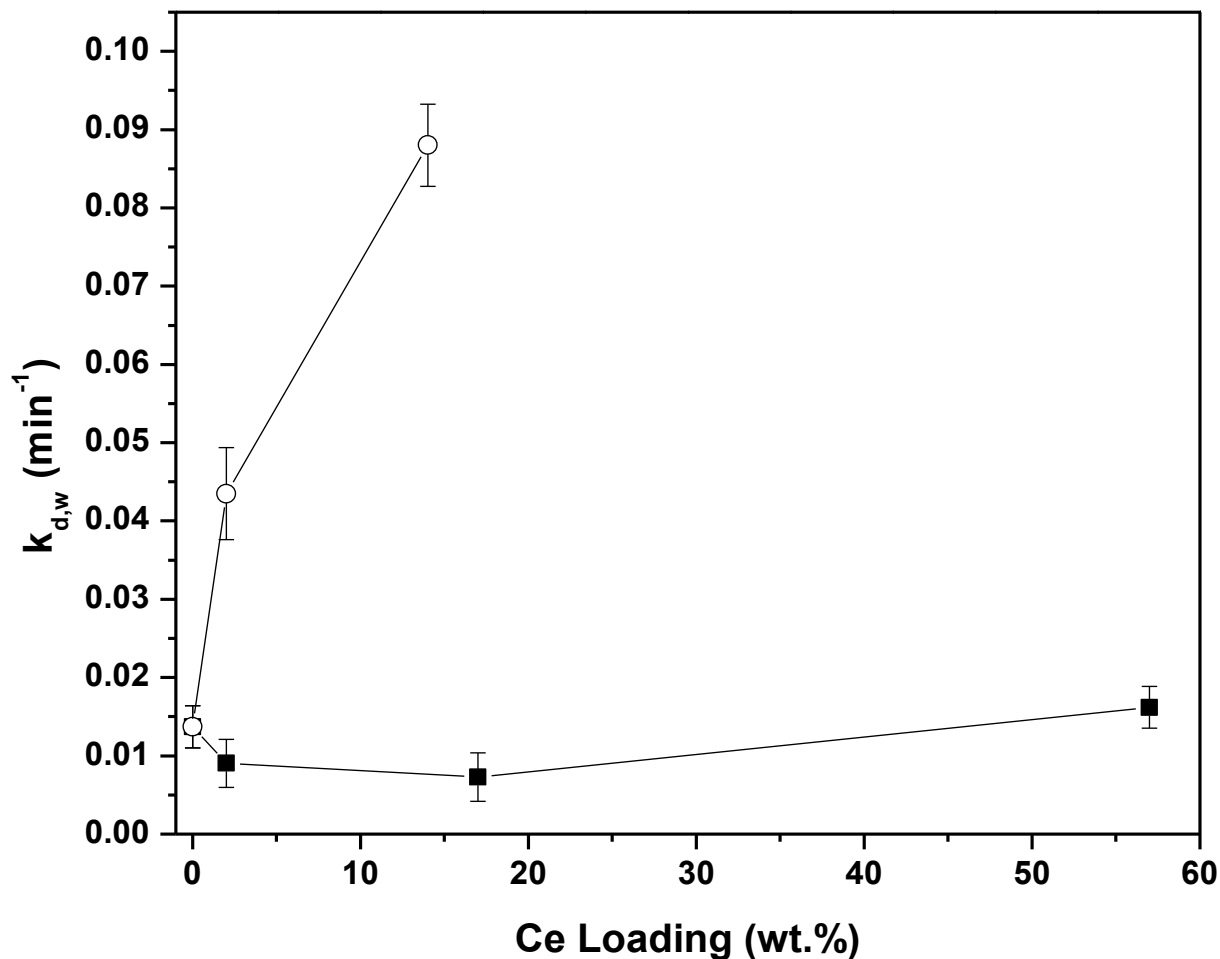


Figure 6.15. Rate of catalyst deactivation ($k_{d,w}$) as a function of Ce loading for co-impregnated catalysts (○), and sequentially impregnated catalysts (■). Obtained from wet-TOS results at $T=350^{\circ}\text{C}$ and 2vol.% H_2O . GHSV=180,000 $\text{cm}^3(\text{STP})\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$, 1000 ppm CH_4 , 20(v/v)% O_2 , and the balance He and Ar

The seq-17Ce/3.4Pd/ Al_2O_3 catalyst was selected as the most active and stable catalyst among the co-impregnated and sequentially impregnated catalysts and was compared to 3.4Pd/ Al_2O_3 catalyst in terms of stability at different temperatures and in the presence of different H_2O concentrations under wet-TOS reaction conditions. Figure 6.16 presents the wet-TOS results for both the 3.4Pd/ Al_2O_3 and the seq-17Ce/3.4Pd/ Al_2O_3 catalysts, with 2vol.% H_2O and varying temperature between 310°C - 370°C . The TOS results show higher CH_4 conversion at

higher temperature for both catalysts, indicating less H₂O adsorption at higher temperatures as discussed in Chapters 4 and 5.

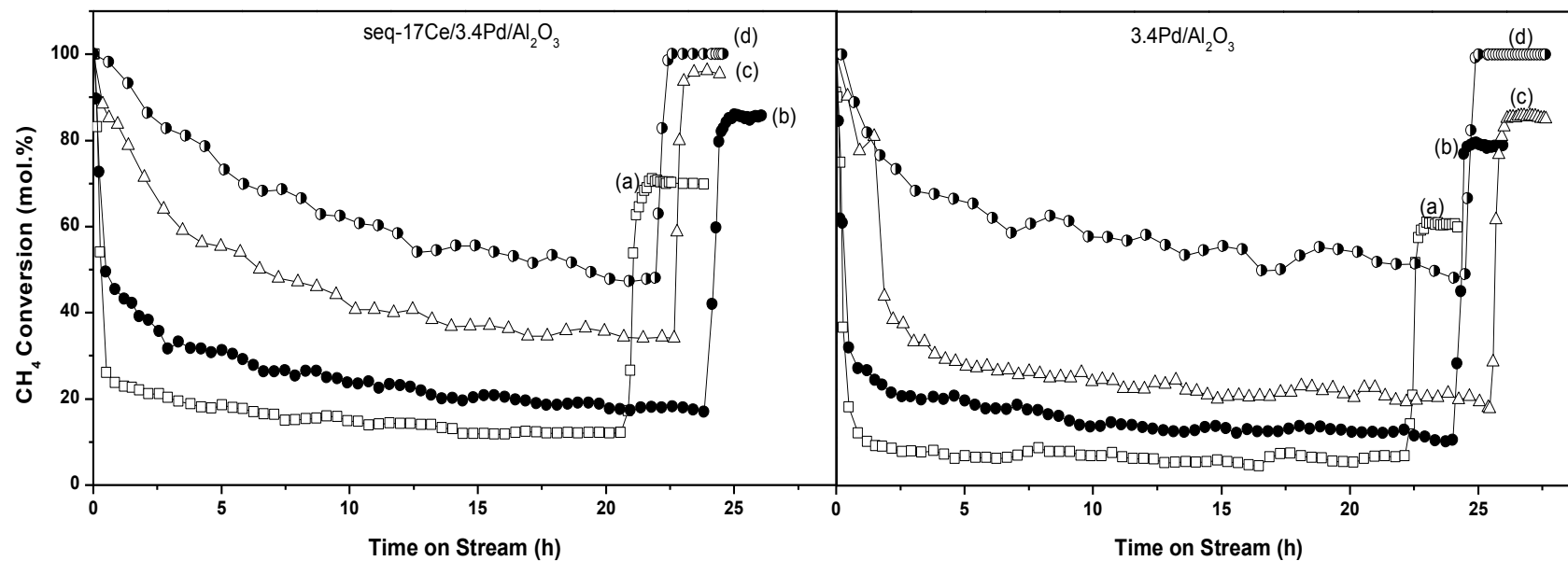


Figure 6.16. Wet-TOS results for seq-17Ce/3.4Pd/Al₂O₃ and 3.4Pd/Al₂O₃ catalysts with 2vol.% H₂O. GHSV=180,000 cm³(STP).g_{cat}⁻¹.h⁻¹, 1000 ppm CH₄, 20(v/v)% O₂, and the balance He and Ar. (a) T=310°C, (b) T=330°C, (c) T=350°C, and (d) T=370°C

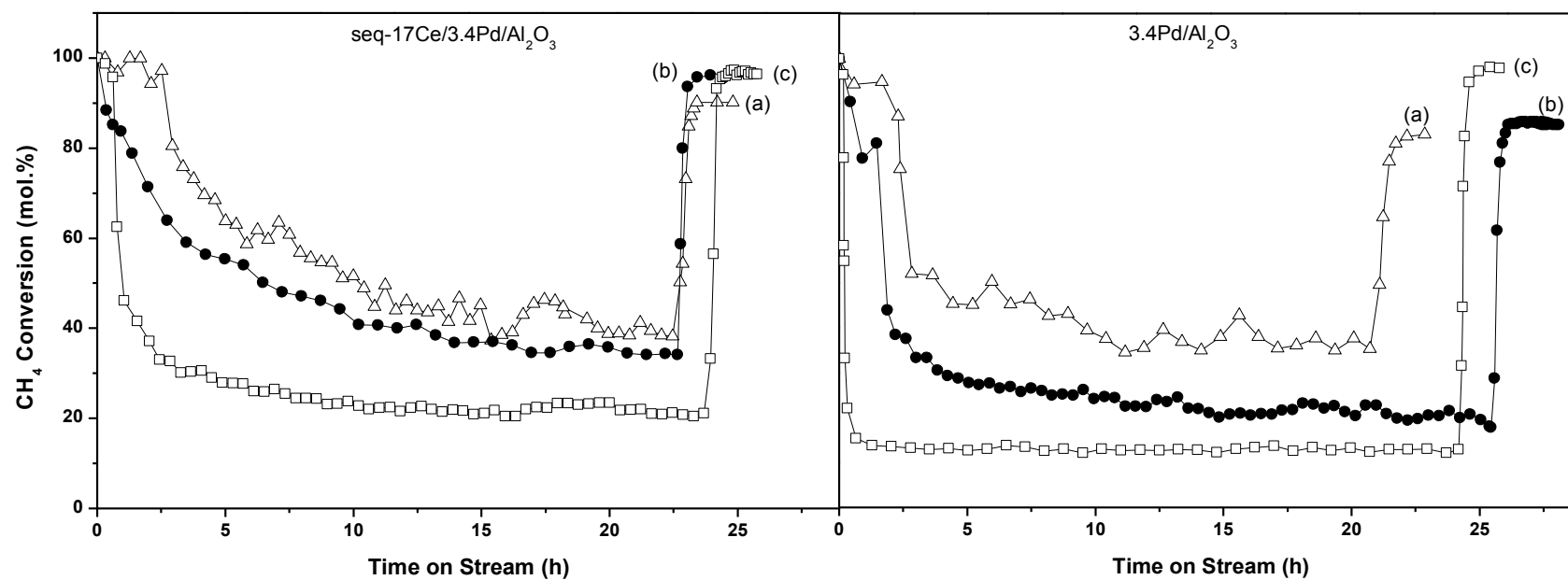


Figure 6.17. Wet-TOS results for seq-17Ce/3.4Pd/Al₂O₃ and 3.4Pd/Al₂O₃ catalysts at T=350°C and (a) 1vol.% H₂O, (b) 2vol.% H₂O, and (c) 5vol.% H₂O. GHSV=180,000 cm³(STP).g_{cat}⁻¹.h⁻¹, 1000 ppm CH₄, 20(v/v)% O₂, and the balance He and Ar

Comparing the TOS results from the two catalysts, as reported in Figure 6.16, shows higher CH₄ conversion in the case of seq-17Ce/3.4Pd/Al₂O₃ catalyst at all temperatures. Upon removal of the 2vol.% extra H₂O to the feed gas after 24h, the CH₄ conversion increased to a higher value, however, the increase in CH₄ conversion was higher at higher reaction temperatures. Wet-TOS results for both the 3.4Pd/Al₂O₃ and the seq-17Ce/3.4Pd/Al₂O₃ catalysts with different H₂O concentration in the feed gas and constant temperature at 350°C are shown in Figure 6.17. Comparing the TOS results between the two catalysts at the same H₂O concentration indicates higher CH₄ conversion for the seq-17Ce/3.4Pd/Al₂O₃ catalyst.

6.3 Discussion

The decrease in BET surface area and pore volume with addition of Ce to the 3.4Pd/Al₂O₃ catalyst is a result of the partial filling and blocking of the Al₂O₃ pores by CeO₂. The XRD data showed that the CeO₂ crystallites are ≤ 9 nm in size, increasing from about 5 nm as the Ce loading increased. The CeO₂ and PdO crystallites are smaller than the catalyst pore size (Table G.1), except at the highest Ce loading. Therefore, in the latter case some of the CeO₂ may not interact with the Pd located within the pores of the support. The decrease in BET surface area with increased Ce loading indicating coverage of Al₂O₃ pores by CeO₂ is also reported in other studies [51,53,59]. Colussi et al. [59] showed the BET surface area of 10%Pd/Al₂O₃ and 10%Pd/15%CeO₂/Al₂O₃ catalysts was 124 m²/g and 110 m²/g, respectively, significantly lower than the Al₂O₃ surface area reported as 148 m²/g [59].

To prepare the catalysts with the highest Ce:Pd ratio, the premixed Pd-Ce solution and the Ce solution for the co-47Ce/3.4Pd/Al₂O₃ and seq-57Ce/3.4Pd/Al₂O₃ catalysts, respectively, were added to the Al₂O₃ support in three steps with a calcination at 450°C for 15h between each

step. Hence, the low BET surface area for both co-47Ce/3.4Pd/Al₂O₃ and seq-57Ce/3.4Pd/Al₂O₃ catalysts could be a result of partial pore filling because of both the high amount of Ce and also the multiple calcination steps. The effect of different loadings of CeO₂ on Al₂O₃ reported in [119] shows that after calcination under air for 6h at 1273K, the BET surface area decreased from 147 m²/g for the pure Al₂O₃ to 142 m²/g and 123 m²/g for 5%CeO₂/Al₂O₃ and 15%CeO₂/Al₂O₃ samples, respectively, indicative of the high specific weight and low porosity of ceria.

Figures G.3-G.5 show the N₂ adsorption-desorption isotherms for the co-impregnated catalysts, sequentially impregnated catalysts, and the xCe/Al₂O₃ support of the present study. The hysteresis observed for all samples indicates the presence of mesopores [120], however, the hysteresis decreases with increasing Ce loading indicating a loss of mesopores at high Ce loadings. Decreasing the pore size as a function of increasing the Ce amount could also be explained by the pore filling. Decreasing the pore volume is the consequence of doping metals on the internal surface of the Al₂O₃ support [121].

The Pd 3d B.E.s show that palladium is present in the form of PdO only and with no other phases, e.g. Pd⁰, present. The comparison of the Pd 3d spectra of 0.6%Pd/CeO₂ and 6.8%Pd/Al₂O₃ catalysts by Shyu et al. [122] confirmed the role of ceria in increasing the oxidation state of Pd. After calcination at 800°C a peak at 337.0±0.1 eV corresponding to PdO was observed for both 0.6%Pd/CeO₂ and 6.8%Pd/Al₂O₃ catalysts. In the case of reduction at 500°C, a peak at 335.0±0.1 eV appeared for both catalysts indicating the formation of Pd⁰. By reducing the catalysts at higher temperature (920°C) and then exposing to ambient air, a peak at 337.0 eV corresponding the formation of PdO in the case of

0.6%Pd/CeO₂ catalyst was observed. However, in the case of 6.8%Pd/Al₂O₃ catalyst under the same treatment condition the palladium remained as Pd⁰ [122]. In another study by Xiao et al. [60] it was also claimed that the XPS analysis of the reduced 2wt.%Pd/CeO₂ did not show the presence of any Pd⁰. The Pd3d_{5/2} B.E. at 336.68±0.3 eV for the 2wt.%Pd/CeO₂ catalyst, indicates Pd present as PdO not Pd⁰ due to the strong Pd-Ce interaction that causes low reducibility of the catalysts under reducing conditions [60].

The ability of ceria to release and store oxygen and also to enhance the thermal stability of Al₂O₃, is well known [44,45]. However, the oxygen storage capacity of CeO₂ is affected by its loading, the presence of precious metals, and also the pretreatment temperature [44]. Yao et al. [44] showed the presence of Pd can increase the oxygen storage capacity of CeO₂. A comparison between oxygen chemisorption of CeO₂/Al₂O₃ with different loadings of CeO₂ shows less oxygen uptake at higher CeO₂ loadings. This behavior was explained by lower CeO₂ dispersion at higher CeO₂ loadings. The O₂ chemisorption was measured for the reduced samples at 500°C for 2h. At low CeO₂ loadings (< 2.5μmol CeO₂/m²[BET]) the oxygen uptake increases as CeO₂ loading increases. However, the O₂ uptake per unit weight of CeO₂ decreases by increasing the CeO₂ loading that indicates lower Ce dispersion at higher CeO₂ loadings. Table 6.4 shows the decrease in O₂ chemisorption as the CeO₂ loading increases from 0.48wt.% to 35.35wt.% [44].

In the present study, Ce_s increased with increased Ce loading. However, increasing Ce_s does not necessarily confirm higher Ce dispersion. As shown in Chapter 5, the increase in Ce_s increases linearly, indicative of a monodispersed Ce_s. For Ce loading higher than 4.8wt.%, agglomeration of CeO_x results in a small increase in Ce_s (Figure 5.2). However, the opposite

behavior is observed for the co-impregnated and sequentially impregnated catalysts and $x\text{Ce}/\text{Al}_2\text{O}_3$ supports shown in Figure 6.3, where the rate of the increase in Ce_s increases at $(\text{Ce}/\text{Al})_b > 0.073$. The faster increase can be explained by comparing the CeO_2 crystal size in Table 6.3 and the catalyst pore size reported in Table G.1. The pore size of the catalysts prepared by co-impregnation and sequential impregnation methods as well as the $x\text{Ce}/\text{Al}_2\text{O}_3$ supports are smaller than the CeO_2 crystal size for $(\text{Ce}/\text{Al})_b > 0.073$, resulting in more CeO_2 on the outside of the pores of support than inside. This results in an increase in Ce_s as measured by XPS. The higher Ce_s at high $(\text{Ce}/\text{Al})_b$ is in agreement with Yao et al. [44] who reported larger CeO_2 crystals at higher CeO_2 loadings.

Table 6.4. O_2 chemisorption on $\text{CeO}_2/\text{Al}_2\text{O}_3$ samples with different loadings of CeO_2 (Reproduced with permission from [44])

CeO_2 Concentration %	O_2 Chemisorption ^a ($\mu\text{mol O}_2/\mu\text{mol CeO}_2$)
0.48	0.27
0.83	0.18
2.04	0.09
3.72	0.06
6.14	0.05
11.69	0.05
21.63	0.06
35.38	0.06

^a Reduced $\text{CeO}_2/\text{Al}_2\text{O}_3$ samples at 500°C for 2h

As shown in Figure 6.9, in the present study the $\frac{\text{Ce}^{3+}}{\text{Ce}^{3+}+\text{Ce}^{4+}}$ ratio decreased at higher Ce loading, which together with the XRD data of Table 6.3, showing increased CeO_2 crystallite size with increased Ce loading, is consistent with the trend reported by Hailstone et al. [46] that the fraction of Ce^{3+} decreases as the Ce dispersion decreases or particle size increases.

The significant decrease in $\frac{\text{Ce}^{3+}}{\text{Ce}^{3+}+\text{Ce}^{4+}}$ surface ratio is also in agreement with the observation

by Monteiro et al. [123] that showed u''' peak corresponding to Ce^{4+} is larger in Pd/20CeO₂/Al₂O₃ catalyst than Pd/3CeO₂/Al₂O₃ catalyst. The CeO₂ (111) crystallite size increases from 7 nm for seq-6Ce/3.4Pd/Al₂O₃ catalyst to 9 nm for seq-57Ce/3.4Pd/Al₂O₃ catalyst. As shown by Hailstone [46], increasing the crystallite size from 1.1 nm to 11.8 nm facilitates the OSC as a result of lower $\frac{Ce^{3+}}{Ce^{3+}+Ce^{4+}}$ surface ratio. In another study the measured crystallite size of CeO₂ by XRD analysis for the CeO₂/Al₂O₃ samples with ceria loadings in the 9-27wt.% range shows a constant crystallite size in the range of 55-67Å [44].

By comparing the catalyst activity of the co-impregnated and sequentially impregnated catalysts, it was shown that the sequentially impregnated catalysts are more active than the co-impregnated catalysts with equivalent loadings of Pd and Ce (Figures 6.12 and 6.13). The characterization results show the BET surface area, Pd_s, Ce_s, and $\frac{Ce^{3+}}{Ce^{3+}+Ce^{4+}}$ ratios vary as a function of Ce loading. However, they are not significantly different between the co-impregnated and sequentially impregnated catalysts. The decrease in BET surface area and consequently the blockage of pore volume of the catalysts has a negative effect in terms of the activity of the Pd based catalysts. On the other hand, the increase in Pd dispersion that is a consequence of the added Ce may or may not improve the activity since the higher Pd-support interaction at higher Pd dispersion suppresses the activity.

However, the effect of CeO₂, having higher oxygen storage capacity than Al₂O₃, can provide the oxygen transfer to the palladium active sites during the CH₄ oxidation reaction and improve the catalyst activity. In addition, the increase in Ce^{4+} obtained by increasing the Ce loading enhances the OSC and should result in more active catalyst. Comparing the catalyst activity of the PdO/Al₂O₃ and co-impregnated CeO_x/PdO/Al₂O₃ catalysts shows lower

activity of the co-impregnated $\text{CeO}_x/\text{PdO}/\text{Al}_2\text{O}_3$ catalysts than the $3.4\text{Pd}/\text{Al}_2\text{O}_3$ catalyst (Figures 6.12). However, in the case of the sequentially impregnated catalysts, $17\text{Ce}/3.4\text{Pd}/\text{Al}_2\text{O}_3$ is more active than $3.4\text{Pd}/\text{Al}_2\text{O}_3$ catalyst. The difference in the catalyst activity shows the impact of the preparation method, emphasizing that high OSC of Ce is significant for the CH_4 oxidation reaction. However, in terms of chemical and physical properties of the catalysts using different preparation methods, a minor difference was observed between the sequentially impregnated and co-impregnated catalysts.

As shown by Fujimoto et al. [74] small PdO_x crystals or those PdO_x in close contact with the support, have stronger Pd-O bond than larger crystals, which leads to lower oxygen vacancies of the catalyst surface. Ciuparu et al. [124] emphasized the oxygen exchange between the support and PdO for the CH_4 combustion at low temperatures. They showed that in the case of the supports with a high oxygen mobility (e.g. CeO_2), the oxygen vacancies are partially refilled with the oxygen from the support, however, the surface oxygen vacancies in the case of Al_2O_3 support are mainly replenished with oxygen from the gas phase. Therefore, in the case of co-impregnated $\text{CeO}_2/\text{PdO}/\text{Al}_2\text{O}_3$ catalysts, PdO is still in a contact with the Al_2O_3 support and the density of oxygen vacancies is expected to be lower than those prepared sequentially where PdO is in close contact with CeO_2 and much less so with the Al_2O_3 .

As shown in other studies the surface oxygen exchange is affected by the hydroxyl desorption [32–34]. The oxygen vacancies formed from H_2O desorption are refilled by the oxygen from both PdO and the support:



The recombination of the hydroxyl group is slow and their tendency to migrate on the catalyst surface is higher than desorption. Thus, slow H_2O desorption suppresses the oxygen exchange between the support and surface. Figure 6.18 shows the oxygen exchange processes between the gas phase, PdO , and the oxide support proposed by Ciuparu et al. [124]. The oxygen exchange for a reduced Pd catalyst over the oxide support consists of five different steps. The oxygen uptake by Pd^0 from the gas phase (1), the oxygen exchange from the new formed PdO_x and the vacancy on the catalyst surface (2), the oxygen exchange between the new formed PdO_x and the gas phase (3), oxygen exchange between gas phase and the oxygen vacancy on the catalyst surface (4), and finally the equilibrium oxygen exchange between the surface vacancy and the oxygen in the bulk of the catalyst.

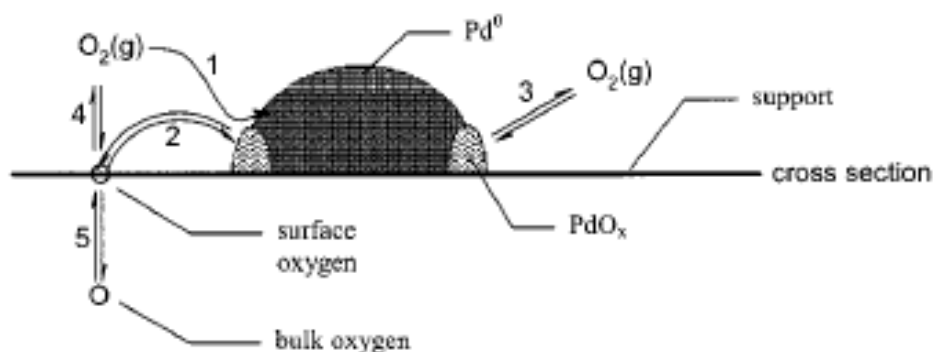


Figure 6.18. Oxygen exchange mechanism of the PdO_x (PdO phase formed during the temperature programmed isotopic exchange) [124] (Copyright © 2002 American Chemical Society)

The isotopic exchange study of oxygen at low temperature (100-500°C) showed an increase in $^{16}\text{O}^{18}\text{O}$ concentration for both oxidized and reduced Pd catalysts over either Al_2O_3 or ZrO_2 support, with increasing temperature. On the other hand, no significant difference in $^{16}\text{O}^{18}\text{O}$ concentration between the oxidized Pd over Al_2O_3 or ZrO_2 was observed. However, the reduced Pd/ ZrO_2 catalyst had higher $^{16}\text{O}^{18}\text{O}$ concentration than the reduced Pd/ Al_2O_3 , indicating the positive effect of ZrO_2 support with high oxygen exchange capacity for the reduced Pd catalyst. This difference was a result of formation of double isotopic exchange oxygen, $^{16}\text{O}_2$, that confirms the higher oxygen exchange activity of ZrO_2 support for the reduced Pd catalysts [124]. It was also suggested that in the case of reduced Pd supported catalysts, more oxygen from the ZrO_2 support is involved in order to reoxidize the Pd^0 and form PdO than that used for reduced Pd catalyst over Al_2O_3 . The temperature programmed isotopic exchange analysis also confirmed the oxidation of Pd^0 is mostly dependent on steps 1, 2, 3, and 5. Since in our study it is known that palladium is in the oxide phase, the oxygen uptake from the gas phase in order to form PdO is unlikely. Therefore, the most important mechanisms for the oxygen exchange are limited to the three steps shown in Figure 6.19, indicating the importance of oxygen exchange from the bulk oxide support to the PdO active sites. This mechanism can also emphasize the effect of high oxygen capacity of the support to facilitate the oxygen exchange (steps 1 and 3) and suppress the negative effect of H_2O .

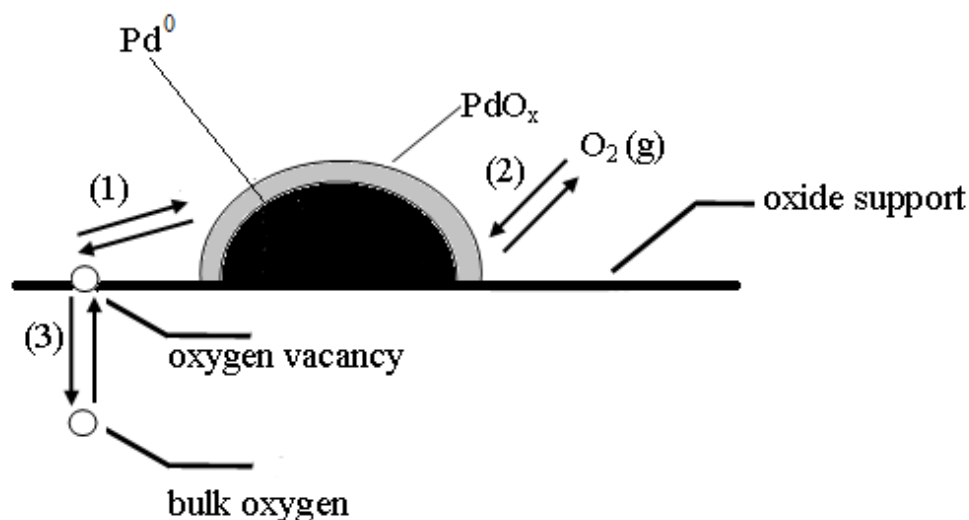


Figure 6.19. Possible oxygen exchange mechanism based on the activity results for 3.4Pd/Al₂O₃ and seq-17Ce/3.4Pd/Al₂O₃ catalysts. Oxygen exchange between the PdO and oxygen vacancy (1), between the PdO and gas phase (2), and between the oxygen vacancy and bulk oxide support (3)

(Adopted with permission from [124])

In the present study, the higher initial activity of the seq-17Ce/3.4Pd/Al₂O₃ catalyst than the 3.4Pd/Al₂O₃ catalyst can be ascribed to the faster oxygen exchange (steps 1 and 3 of Figure 6.19) in the presence of CeO₂. In addition, the lower H₂O inhibition observed for the seq-17Ce/3.4Pd/Al₂O₃ catalyst than the 3.4Pd/Al₂O₃ catalyst at temperatures in the range of 310-370°C and different H₂O concentration of 0-5vol.% can be explained by a faster H₂O desorption as a result of higher oxygen exchange from CeO₂/Al₂O₃ support to Pd-* sites in the case of seq-17Ce/3.4Pd/Al₂O₃ catalyst.

6.4 Conclusion

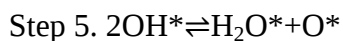
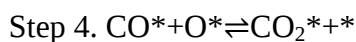
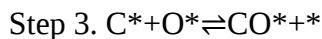
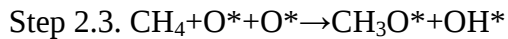
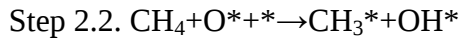
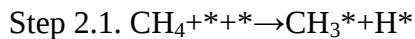
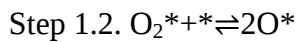
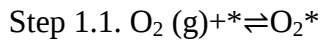
The effect of different preparation methods along with different Ce:Pd ratios on the catalytic properties and catalytic activity of a series of Ce/Pd/Al₂O₃ catalysts was examined. Catalysts

with the Ce:Pd ratio varying in the range of 0-17 using co-impregnation and sequential impregnation methods were prepared. The BET surface area decreased with increased Ce loading, indicating the partial filling and/or blocking of the Al₂O₃ pores by CeO₂ crystals. The Pd_s surface composition increased with increased Ce loading, indicating higher Pd dispersion at higher Ce loading. The Pd3d B.E. did not change significantly with Ce loading, emphasizing the stable PdO phase and no Pd⁰ formation in the presence of CeO₂. On the other hand, $\frac{Ce^{3+}}{Ce^{3+}+Ce^{4+}}$ ratio decreased at higher Ce loading that suggests higher OSC at higher Ce loading. The physical and chemical properties of the catalysts with the same Ce loading prepared by co-impregnation or sequential impregnation methods are similar, confirming that the properties of the CeO₂/PdO/Al₂O₃ catalysts are mostly affected by the presence of Ce not by the preparation methods. The characterization techniques used to observe the properties of the catalysts were not sufficient to differentiate the interaction between the Pd, Ce, and Al₂O₃ that likely resulted from the different preparation methods. However, the preparation method had an impact on the catalytic activity during CH₄ oxidation. Comparing PdO/Al₂O₃, co-CeO_x/PdO/Al₂O₃, and seq-CeO_x/PdO/Al₂O₃ catalysts for CH₄ oxidation showed that the sequentially impregnated catalyst with Ce:Pd ratio of 5 was the most active and stable catalyst among those examined here. The role of CeO₂ in increasing the oxygen exchange capacity during the CH₄ oxidation reaction is dependent on the catalyst preparation and Ce:Pd ratio. The proposed oxygen exchange mechanism explains the importance of oxygen exchange from the bulk oxide support to the PdO active sites. This mechanism emphasizes the presence of CeO₂ with high OSC that facilitates the oxygen transfer from the bulk oxide to the PdO active sites.

Chapter 7: Kinetics of the Inhibition by H₂O

7.1 Introduction

In this chapter the inhibition of the CH₄ oxidation kinetics by H₂O on Pd based catalysts is analyzed under non-steady state reaction conditions. As explained in Chapter 4, the packed bed reactor is modeled assuming one dimensional plug flow. The external mass transfer is neglected and the internal mass transfer effect is considered in the reactor model. For the kinetic model, it is assumed that the CH₄-O₂ reaction follows a Langmuir-Hinshelwood mechanism as presented in the literature [82,85,86]. The dissociation of CH₄ takes place on active sites and C-H bond activation on the active sites is the rate determining step. The oxygen transfer from the oxide support to the Pd-* can provide the active sites for C-H bond activation [82]. The mechanistic steps can be written as follows [82]:



Step 6. $\text{H}_2\text{O}^* \rightleftharpoons \text{H}_2\text{O} + ^*$

Step 7. $\text{CO}_2^* \rightleftharpoons \text{CO}_2 + ^*$

Step 8. $\text{CO}^* \rightleftharpoons \text{CO} + ^*$

7.2 Kinetic Model of H_2O Inhibition in a Non-steady State System

The fixed-bed micro-reactor operating under non-steady state conditions, was modeled for the reaction conditions with an inlet feed stream of 5000 ppmv CH_4 with 0vol.% and 5vol.% H_2O entering the catalyst bed at a fixed temperature as shown in Equation 4.19.

By replacing P_{CH_4} with $P_{\text{CH}_4} = P_{\text{CH}_4}^0 (1 - X_{\text{CH}_4})$. Equation 4.19 is converted to:

$$\frac{dX_{\text{CH}_4}}{d(W/F_{\text{CH}_4}^0)} = \beta(1 - X_{\text{CH}_4})[1 - \gamma(1 - \exp(-\delta t))] \quad 7.1$$

where $\beta = \eta k_s C_T^2 P_{\text{CH}_4}^0$, $\gamma = \frac{K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}}{1 + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}}$, and $\delta = k_r(1 + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}})$. η , k_s , and $K_{\text{H}_2\text{O}}$ values for 6.5Pd/ Al_2O_3 and co-2.9Ce/6.5Pd/ Al_2O_3 catalysts were obtained in Chapters 4 and 5 at different temperatures and applied to Equation 7.1 to calculate β and γ .

As defined in Chapter 4, $P_{\text{H}_2\text{O}} = P_{\text{CH}_4}^0 (\alpha_{\text{H}_2\text{O}} + 2X_{\text{CH}_4})$ results in γ & $\delta = f(X_{\text{CH}_4})$. However, $\alpha_{\text{H}_2\text{O}} \gg 2X_{\text{CH}_4}$ with H_2O added to the feed gas, so γ and δ could be assumed to be independent of X_{CH_4} .

Using these assumptions, integration of Equation 7.1 results in:

$$-\ln(1 - X_{\text{CH}_4}) = \frac{\beta W}{F_{\text{CH}_4}^0} [1 - \gamma(1 - \exp(-\delta t))] \quad 7.2$$

Defining $a = \frac{\beta W}{F_{CH_4}^0} (1 - \gamma)$ and $b = \frac{\beta W \gamma}{F_{CH_4}^0}$, Equation 7.2 is written as:

$$\ln(1 - X_{CH_4}) = -a - b \exp(-\delta t) \quad 7.3$$

$$\ln \left[\frac{-(a + \ln(1 - X_{CH_4}))}{b} \right] = -\delta t \quad 7.4$$

A linear regression of Equation 7.4 was applied to the experimental data of CH₄ conversion as a function of TOS from t=0h to t=5h for the 0.3Pd/Al₂O₃, 2.6Pd/Al₂O₃, 6.5Pd/Al₂O₃ and co-2.9Ce/6.5Pd/Al₂O₃ catalysts. The linear regression at different reaction temperatures (300°-380°C) and 5vol.%H₂O are shown in Figures 7.1 and 7.2. The obtained δ values from the linear regression were used to determine the H₂O desorption rate constant values (k_r) at different temperatures. The calculated values are reported in Table 7.1.

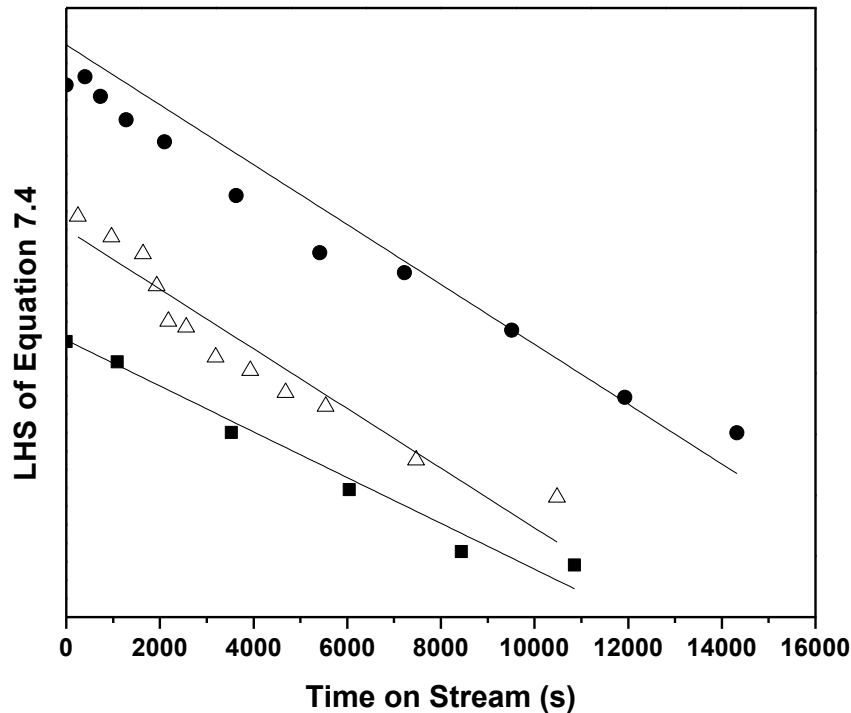


Figure 7.1. Fitting Equation 7.4 to the experimental results for the wet-TOS with 5vol.%H₂O at T=300°C (■), 330°C (Δ), and 350°C (●) for 6.5Pd/Al₂O₃ catalyst

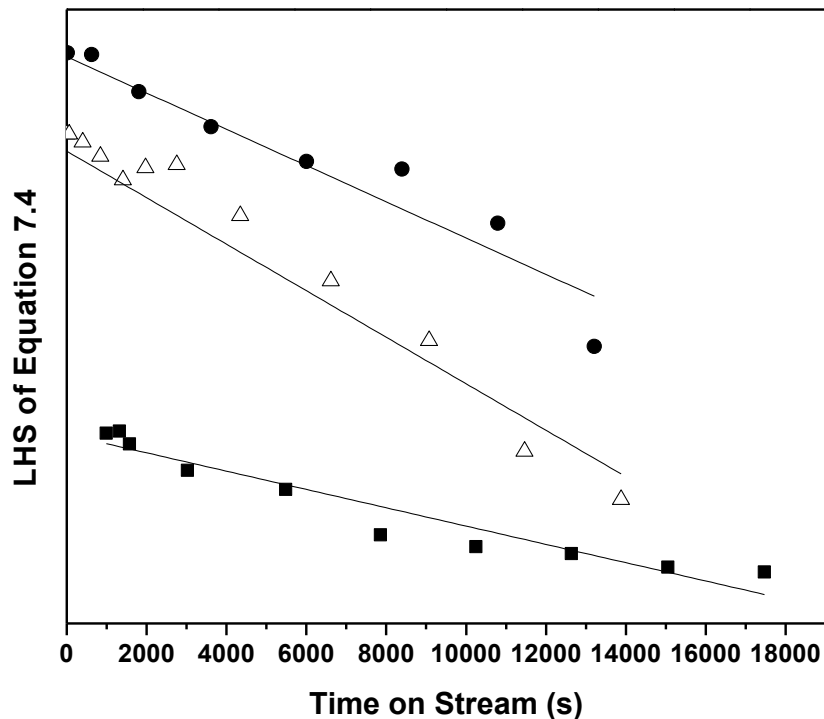


Figure 7.2. Fitting Equation 7.4 to the experimental results for the wet-TOS with 5vol.%H₂O at T=330°C (■), 350°C (Δ), and 380°C (●) for co-2.9Ce/6.5Pd/Al₂O₃ catalyst

Table 7.1. Rate constant for H₂O desorption obtained by the proposed kinetic model in Equation 7.4

6.5Pd/Al ₂ O ₃					co-2.9Ce/6.5Pd/Al ₂ O ₃				
T (°C)	k _r (s ⁻¹)		R ²		T (°C)	k _r (s ⁻¹)		R ²	
300	3.94×10 ⁻⁶	±	3.83×10 ⁻⁷	0.95	300	-	-	-	-
330	1.21×10 ⁻⁵	±	1.89×10 ⁻⁶	0.80	330	4.80×10 ⁻⁵	±	6.37×10 ⁻⁶	0.86
350	1.39×10 ⁻⁵	±	1.14×10 ⁻⁶	0.94	350	1.25×10 ⁻⁴	±	5.60×10 ⁻⁶	0.98
380	4.28×10 ⁻⁵	±	4.18×10 ⁻⁶	0.95	380	1.89×10 ⁻⁴	±	2.15×10 ⁻⁵	0.92

k_r values increase with increasing reaction temperature for both 6.5Pd/Al₂O₃ and co-2.9Ce/6.5Pd/Al₂O₃ catalysts, indicating a higher rate of H₂O desorption from active sites at higher temperatures. Comparing the k_r values for 6.5Pd/Al₂O₃ and co-2.9Ce/6.5Pd/Al₂O₃ catalysts show larger k_r for co-2.9Ce/6.5Pd/Al₂O₃ than 6.5Pd/Al₂O₃, indicating faster H₂O desorption for co-2.9Ce/6.5Pd/Al₂O₃ catalyst than 6.5Pd/Al₂O₃ catalyst. The activation energy of the H₂O desorption rate constant (E_{a_r}) for both 6.5Pd/Al₂O₃ and co-

2.9Ce/6.5Pd/Al₂O₃ catalysts were obtained from Figure 7.3 by plotting $\ln(k_r)$ values as a function of $\frac{1000}{T}$. E_{ar} values were obtained as 89.6 ± 7.9 kJ.mol⁻¹ and 87.2 ± 28.8 kJ.mol⁻¹ for 6.5Pd/Al₂O₃ and co-2.9Ce/6.5Pd/Al₂O₃ catalysts showing almost identical values of E_{ar} , while k_r values are higher in the case of co-2.9Ce/6.5Pd/Al₂O₃ catalyst.

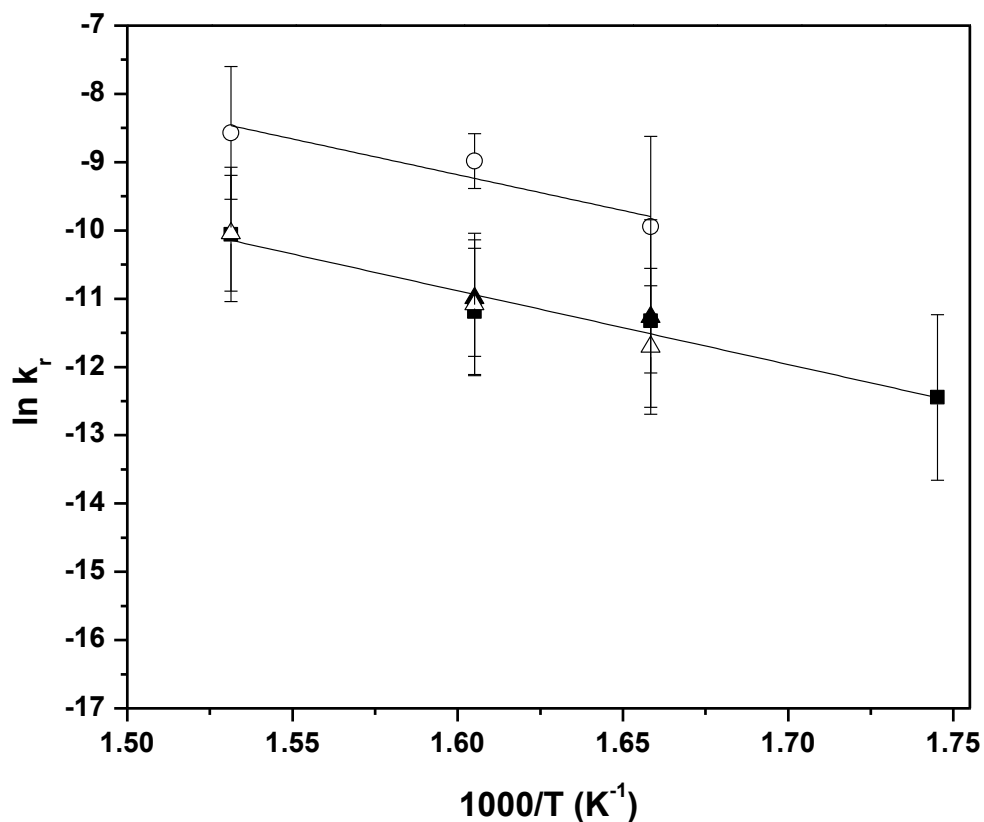


Figure 7.3. $\ln k_r$ values as a function of $\frac{1000}{T}$ for 0.3Pd/Al₂O₃ catalyst (▲), 2.6Pd/Al₂O₃ catalyst (Δ), 6.5Pd/Al₂O₃ catalyst (■), and co-2.9Ce/6.5Pd/Al₂O₃ catalyst (○)

7.3 Discussion

The effect of H₂O is significant at low temperatures (< 500°C) and at high concentrations of H₂O. Following the study by Kikuchi et al. [23], and as presented in Chapters 4 and 5, it is

assumed that H₂O adsorption-desorption on active sites is the cause of catalyst deactivation. Since the CH₄ dissociation on the Pd-*/PdO surface is affected by H₂O [30,77,86], it is more likely that the rate of H₂O adsorption is faster than the rate of desorption. In addition, based on the TOS results presented in the previous chapters, the CH₄ conversion at a constant temperature with H₂O added to the CH₄/O₂ feed varies with TOS, indicating that the H₂O adsorption-desorption needs a significant time period to reach equilibrium. The data presented in previous chapters suggest that a TOS of 5h is needed for the catalyst activity to reach steady state after the addition of H₂O to the feed gas. Therefore, in this chapter the effect of H₂O was accounted for through a non-equilibrium adsorption of H₂O applied to the CH₄ conversion data measured within the first 5h TOS, prior to steady state activity being achieved. The obtained k_r values using the linear regression of Equation 7.4 indicates higher k_r values for co-2.9Ce/6.5Pd/Al₂O₃ catalyst than 6.5Pd/Al₂O₃ catalyst which is in agreement with the results presented in Chapter 5, showing H₂O adsorption is reduced by the presence of CeO₂ on the catalyst surface compared to the catalysts without CeO₂.

7.4 Conclusion

The negative effect of H₂O on the CH₄-O₂ reaction under wet-TOS reaction conditions at constant temperature was modeled by extending the kinetic model with H₂O inhibition to the case of non-steady state operation. A Langmuir-Hinshelwood mechanism along with C-H bond activation as a rate determining step in the presence of H₂O adsorption-desorption was assumed to model the negative effect of H₂O. The active sites are mainly covered by H₂O molecules, assuming negligible coverage by CH₄, O₂, and CO₂. The non-equilibrium H₂O adsorption indicates a higher rate of adsorption than desorption, confirming less inhibiting

effect of H₂O by increasing the temperature. The number of active sites, n , was considered as 1, assuming the dissociation of a CH₄ molecule takes place on a unit Pd-*/PdO site pair. The non-steady state mole balance equation was fitted to the experimental data for 6.5Pd/Al₂O₃ and co-2.9Ce/6.5Pd/Al₂O₃ catalysts in the range of 300-380°C in order to explain the exponential activity loss for the first 5h of TOS. The H₂O desorption rate constants, k_r , obtained by this linear regression fitting showed the higher values for co-2.9Ce/6.5Pd/Al₂O₃ catalyst than 6.5Pd/Al₂O₃ catalyst and at higher temperatures concluding the positive effect of CeO₂ and temperature to increase the H₂O desorption from the catalyst surface.

Chapter 8: Conclusions and Recommendations

8.1 Conclusions

This study focuses on the inhibiting effects of H₂O during CH₄ oxidation over PdO/Al₂O₃ and CeO₂/PdO/Al₂O₃ catalysts. A kinetic analysis of the steady-state and dynamic response of the catalyst activity to H₂O addition to the feed gas is reported. This approach provides a kinetic interpretation of the role of CeO₂ in reducing the inhibiting effects of H₂O on the CH₄ oxidation reaction. A comparison of the kinetic parameters in the presence of H₂O for the PdO/Al₂O₃ and CeO₂/PdO/Al₂O₃ catalysts studied in this thesis also confirms the role of high oxygen storage capacity materials such as CeO₂ on the catalyst activity.

The inhibiting effects of H₂O on the CH₄ oxidation activity of PdO/Al₂O₃ catalysts at temperatures in the range of 300-380°C were examined. Increasing the loading of Pd from 0.3wt.% to 6.5wt.% resulted in increasing the Pd/Al ratio on the catalyst surface and decreasing Pd dispersion. A higher initial activity and smaller activity loss was observed for the 6.5Pd/Al₂O₃ catalyst compared to the 0.3Pd/Al₂O₃ and the 2.6Pd/Al₂O₃ catalysts as a result of having a higher number of active sites. H₂O adsorption is determined to be the main cause of activity loss in CH₄ oxidation and the rate of recovery when the H₂O is removed from the feed depends on the amount of H₂O adsorbed on active sites. The H₂O partial pressure per number of active sites ($\frac{P_{H_2O}}{C_T}$) was lowest for the 6.5Pd/Al₂O₃ catalyst compared with 0.3Pd/Al₂O₃ and 2.6Pd/Al₂O₃ catalysts, indicating a faster recovery of catalyst activity for the 6.5Pd/Al₂O₃ catalyst upon removal of the extra 5vol.%H₂O from the feed gas.

The rate constant and equilibrium constant for H₂O adsorption were obtained from kinetic analysis. Applying the design equation to the values of CH₄ conversion (X_{CH_4}) at t=5h with and without H₂O in the feed, for three catalysts with different Pd loadings, E_a and ΔH_{H_2O} were estimated as $60.6 \pm 11.5 \text{ kJ.mol}^{-1}$ and $-81.5 \pm 9.1 \text{ kJ.mol}^{-1}$, respectively. Since the same kinetic parameters were able to describe the measured activity data, one concludes that the CH₄ oxidation reaction is not structure sensitive. The low values of effectiveness factors obtained in the range of 300-380°C confirm the slow internal diffusion as a consequence of a fast CH₄ oxidation reaction.

The effect of Ce loading with a constant Pd loading of 6.5wt.% was examined using catalysts prepared by the co-impregnation method. The initial activity of the catalysts decreased with increased Ce loading, because of a loss in BET area and consequently PdO encapsulation at higher Ce loading. However, by comparing the ratio of the deactivation rate ($\frac{k_{d,w}}{k_{d,d}}$) between the 6.5Pd/Al₂O₃ and the co-2.9Ce/6.5Pd/Al₂O₃ catalysts, showed that CeO₂ addition reduced the inhibiting effect of H₂O adsorption on the active sites. The lower magnitude of K_{H_2O} for the co-2.9Ce/6.5Pd/Al₂O₃ catalyst comparing to the 6.5Pd/Al₂O₃ catalyst, confirmed less H₂O adsorption on the CeO₂ promoted catalyst. However, a higher $|\Delta H_{H_2O}|$ for the co-2.9Ce/6.5Pd/Al₂O₃ catalyst than the 6.5Pd/Al₂O₃ catalyst implies stronger H₂O adsorption on the active sites of the CeO₂ promoted catalyst. The small loss in BET surface area and CO uptake for the used 6.5Pd/Al₂O₃ and co-2.9Ce/6.5Pd/Al₂O₃ catalysts following the wet-TOS experiments, confirms some permanent change in physical and chemical properties of the catalysts. The permanent change of the used catalysts properties is attributed to sintering of the catalysts that leads to activity loss. In addition, the inhibiting effect of H₂O adsorption is

another possible mechanism for loss in catalyst activity. In the dry-TOS experiment, both sintering and H₂O adsorption are significant mechanisms of activity loss. However, the effect of H₂O adsorption on the active sites is more dominant than sintering in the wet-TOS experiments, as a fast drop in activity is observed once H₂O is added to the feed. Upon removal of H₂O after 24h wet-TOS, the CH₄ conversion is almost identical to that obtained in the dry-TOS, indicating the reversible effect of H₂O adsorption caused by extra H₂O addition. The reversible effect of H₂O is also confirmed by the decrease in the $k_{d,d}$ and $k_{d,w}$ values as a function of temperature, showing less H₂O adsorption at higher temperature and hence lower activity loss.

The effect of preparation methods was also examined in order to investigate the effect of CeO₂ on the activity of CeO_x/PdO/Al₂O₃. The Al₂O₃ support was impregnated using different loadings of Ce at a constant Pd loading of 3.4wt.%, using two different preparation methods, co-impregnation and sequential impregnation. Higher catalyst activity and lower rate of deactivation were found for the sequentially impregnated catalysts compared to the co-impregnated catalysts at the same Ce loading. However, the physical and chemical properties of the catalysts prepared by co-impregnation and sequential impregnation methods were not significantly different, confirming that the OSC of CeO₂ influences the catalytic properties during the CH₄ oxidation reaction. Higher activity and stability of the seq-17Ce/3.4Pd/Al₂O₃ catalyst than the 3.4Pd/Al₂O₃ catalyst was explained by the importance of oxygen exchange from the bulk oxide support to the active sites and the role of CeO₂ to facilitate this mechanism.

A Langmuir adsorption of H_2O along with C-H bond activation as a rate determining step were assumed to model the inhibiting effect of H_2O on the CH_4 oxidation rate. The non-steady state mole balance equation was applied to a set of experimental data obtained with a feed gas of 5000 ppm CH_4 , 5vol.% H_2O and temperature in the range of 300-380°C. The H_2O desorption rate constants, k_r , showed higher values at higher temperatures concluding the positive effect of temperature to increase the H_2O desorption from the catalyst surface. In addition, the higher values of k_r for co-2.9Ce/6.5Pd/ Al_2O_3 catalyst than 6.5Pd/ Al_2O_3 catalyst quantifies the beneficial effect of CeO_2 through the increase in the H_2O desorption rate constant.

8.2 Recommendations

8.2.1 Kinetic Model Applied to Co-impregnated and Sequentially Impregnated Catalysts

In this study a reactor model was applied to the TOS experimental data for 6.5Pd/ Al_2O_3 and co-2.9Ce/6.5Pd/ Al_2O_3 catalysts in order to calculate the activation energy and enthalpy of H_2O adsorption. Since the number of experimental data points reported in Chapter 6 considering both dry-TOS and wet-TOS for co-impregnated and sequentially impregnated catalysts were insufficient for kinetic analysis, calculating the activation energy and enthalpy of H_2O adsorption was not possible. It is recommended that the reactor model be extended to the co-impregnated and sequentially impregnated catalysts in order to quantify the effect of preparation method on the activity and stability of the catalysts. In addition, the presented reactor model can be applied to the experimental data in order to predict the kinetic

parameters for the co-impregnated and sequentially impregnated catalysts. It is anticipated that the estimated parameters for the co-impregnated catalysts presented in Chapter 6 are similar to the co-2.9Ce/6.5Pd/Al₂O₃ catalyst presented in Chapter 5 with the same Ce:Pd ratio.

8.2.2 Studying the Effect of CeO₂ on O₂ Concentration

The purpose of this study was to investigate the initial activity and stability of the catalysts in a lean-burn condition. Therefore, an excess amount of O₂ (20(v/v)%) was fed to the reactor, however, it was kept constant. Groppi et al. [58] showed that a large excess of O₂ in CH₄ oxidation, as used in the present study, does not significantly affect the activity of the catalysts at low temperature, even in the case of a CeO₂/PdO/Al₂O₃ catalyst. Furthermore, the reported zero-order dependence in oxygen of the rate of reaction means that the high O₂ content used in the present study does not impact the kinetics significantly. To confirm the zero order of the reaction rate with respect to O₂ (either the O₂ in the gas phase or in the bulk of the support), it is suggested that the effect of different preparation methods, the role of different Ce loadings on oxygen exchange capacity of the support, and the inhibiting effect of H₂O be investigated as a function of various O₂ concentrations. This can lead to a better understanding of the role of the oxygen transfer mechanism during the CH₄ oxidation reaction. These experiments should also be extended to examine the degree of CH₄ oxidation in the absence of gas phase O₂.

8.2.3 Studying the Effect of Support on H₂O Adsorption

Enthalpy of H₂O adsorption and the rate constant for H₂O desorption were compared for

PdO/Al₂O₃ and CeO_x/PdO/Al₂O₃ catalysts to emphasize the effect of CeO₂ promoted Al₂O₃ on the inhibiting effect of H₂O. However, the role of Al₂O₃ on H₂O adsorption is not clear. Hence, it is suggested that the ΔH_{H_2O} value for the Al₂O₃ support should also be obtained using FTIR and Raman spectroscopy. Comparing the ΔH_{H_2O} values of the Al₂O₃ support, PdO/Al₂O₃ catalyst, and CeO_x/PdO/Al₂O₃ catalyst can help to better understanding of the inhibiting effect of H₂O. The same approach could also be applied to different types of supports (CeO₂ or ZrO₂) to study the inhibiting effect of H₂O on different supports. It is also recommended to investigate the effect of hydrophobicity of the support on H₂O adsorption.

8.2.4 Studying the Catalytic Properties during CH₄ Oxidation Reaction

The effect of different Pd loadings and Ce:Pd ratios on the physical and chemical properties of the catalysts were confirmed using different characterization techniques such as BET, XPS, XRD, CO chemisorption, and ToF-SIMS. However, the effect of different preparation methods on the catalyst properties was not significant based on these analyses. Hence the preparation methods have an influence on the properties of the catalysts during the CH₄ oxidation reaction that are not observable by ex situ characterization techniques. It is recommended that the surface properties of the catalysts be determined by online reaction monitoring. The in situ techniques should include FTIR and Raman spectroscopy to monitor the O transfer between the oxide support, Pd-*, and gas phase. Interaction of PdO and Al₂O₃ in the presence and absence of CeO_x could also be monitored in order to determine the effect of CeO₂ promoted support to facilitate H₂O desorption.

8.2.5 Studying the Partially Reversible Effect of H₂O by TPO

The partially reversible effect of H₂O was confirmed upon removing the extra H₂O after 24h wet-TOS experiments. Since a slight activity loss was observed after 24h for both dry-TOS and wet-TOS, it is concluded that a permanent change in properties of the catalyst occurs during TOS experiments. This permanent change was also confirmed by characterization of the used catalysts. However, the small activity loss could also be the effect of H₂O produced during the CH₄ oxidation reaction. To understand this, the activity of the used catalysts can be measured by TPO following purging the catalyst bed with an inert gas (e.g. He) for 2h to remove all the reactants and produced H₂O. Comparing the CH₄ conversion obtained by fresh and used catalysts can explain if the activity loss is permanent or only caused by the presence of H₂O.

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Appendices

Appendix A: Catalyst Preparation

The required amounts of chemicals to prepare the catalysts with different loadings of Pd and Ce are reported in Table A.1. The initial calculations for the nominal 10wt.%Pd/Al₂O₃ are as follows:

1. Total amount of 10wt.%Pd/Al₂O₃=3 g

2. Amount of Pd in 10wt.%Pd/Al₂O₃ catalyst

$$= \frac{10 \text{ g Pd}}{100 \text{ g Pd/Al}_2\text{O}_3} \times 3 \text{ g Al}_2\text{O}_3 = 0.3 \text{ g Pd}$$

3. Total mass of N₂O₆Pd.xH₂O salt (Palladium (II) Nitrate Hydrate)

$$= \frac{230.43 \frac{\text{g}}{\text{mol}} \text{N}_2\text{O}_6\text{Pd.xH}_2\text{O}}{106.42 \frac{\text{g}}{\text{mol}} \text{Pd}} \times 0.3 \text{ g Pd} = 0.65 \text{ g}$$

4. Required amount of Al₂O₃

$$= 3 \text{ g 10wt. \%Pd/Al}_2\text{O}_3 - 0.3 \text{ g Pd} = 2.7 \text{ g Al}_2\text{O}_3$$

5. Required amount of 0.1N HNO₃ solution

$$= 2.7 \text{ g Al}_2\text{O}_3 \times 0.53 \frac{\text{cc}}{\text{g Al}_2\text{O}_3} = 1.43 \text{ cc}$$

The same calculations are applied for 10wt.%Ce/Al₂O₃ catalyst using Cerium (III) Nitrate Hexahydrate salt, Ce(NO₃)₃.6H₂O, that the molecular weight for Ce and Ce(NO₃)₃.6H₂O are 140.116 g/mol and 434.23 g/mol, respectively. Table A.1 also reports the required amounts of salts and Al₂O₃ support for co-impregnated and sequentially impregnated catalysts consisting of both Pd and Ce.

Table A.1. Required amounts of $\text{N}_2\text{O}_6\text{Pd} \cdot x\text{H}_2\text{O}$ salt, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ salt, and Al_2O_3 support

Catalyst	Pd Loading (wt.%)	Ce Loading (wt.%)	Total Mass of Catalyst (g)	Mass of $\text{N}_2\text{O}_6\text{Pd} \cdot x\text{H}_2\text{O}$ Salt (g)	Mass of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ Salt (g)	Mass of Al_2O_3 (g)
10Pd/ Al_2O_3	10	0	3	0.65	0.00	2.70
co-1Ce/10Pd/ Al_2O_3	10	1	3	0.65	0.09	2.67
co-3Ce/10Pd/ Al_2O_3	10	3	3	0.65	0.28	2.61
co-5Ce/10Pd/ Al_2O_3	10	5	3	0.65	0.46	2.55
co-10Ce/10Pd/ Al_2O_3	10	10	3	0.65	0.93	2.40
10Ce/ Al_2O_3	0	10	3	0	0.93	2.70
1Pd/ Al_2O_3	1	0	3	0.06	0.00	2.97
5Pd/ Al_2O_3	5	0	3	0.32	0.00	2.85
co-1.5Ce/5Pd/ Al_2O_3	5	1.5	3	0.32	0.14	2.80
co-15Ce/5Pd/ Al_2O_3	5	15	3	0.32	1.39	2.40
co-50Ce/5Pd/ Al_2O_3	5	50	3	0.32	4.65	1.35
seq-1.5Ce/5Pd/ Al_2O_3	5	1.5	3	0.32	0.14	2.80
seq-5Ce/5Pd/ Al_2O_3	5	5	3	0.32	0.46	2.70
seq-15Ce/5Pd/ Al_2O_3	5	15	3	0.32	1.39	2.40
seq-25Ce/5Pd/ Al_2O_3	5	25	3	0.32	2.32	2.10
seq-50Ce/5Pd/ Al_2O_3	5	50	3	0.32	4.65	1.35

Appendix B: Catalyst Characterization

B.1 BET

Surface area, pore size, and pore volume are important properties of a catalyst. The most common method for measuring the surface area and pore size of a mesoporous material is by gas adsorption (normally N₂). The amount of N₂ adsorbed as a function of pressure at 77K is measured volumetrically. The BET (Brunauer-Emmett-Teller) isotherm describes multilayer gas adsorption on the surface of a solid.

$$V = \frac{CV_m P}{(P_0 - P) \left[1 + (C - 1) \frac{P}{P_0} \right]} \quad \text{B.1}$$

The BET equation in linear form is expressed as:

$$\frac{P}{V(P_0 - P)} = \frac{1}{CV_m} + \frac{C - 1}{CV_m} \left(\frac{P}{P_0} \right) \quad \text{B.2}$$

$$x = \frac{P}{P_0}, \quad y = \frac{P}{V(P_0 - P)} = \frac{1}{V \left(\frac{1}{x} - 1 \right)} \quad \text{B.3}$$

$$\text{So, } y = \frac{1}{CV_m} + \frac{C - 1}{CV_m} x \quad \text{B.4}$$

P is the partial pressure of N₂, P₀ is the saturation pressure at the adsorption temperature, V is the volume of adsorbed gas at P, V_m is volume adsorbed at monolayer coverage, and C is a constant. By calculating V_m from the isotherm fit to the experimental adsorption data and knowing the area occupied by each N₂ molecule, the surface area is obtained.

By plotting y versus x for the P/P₀ < 0.3, a line with a specific slope and intercept in which C and V_m would be obtained. Hence the BET surface area is calculated as:

$$S_{\text{BET}} = \frac{V_m \sigma N_A}{V_0} \quad \text{B.5}$$

σ is the occupied area by adsorption of a single molecule of N_2 ($16.2 \text{ \AA}^2$) and N_A is the Avogadro constant.

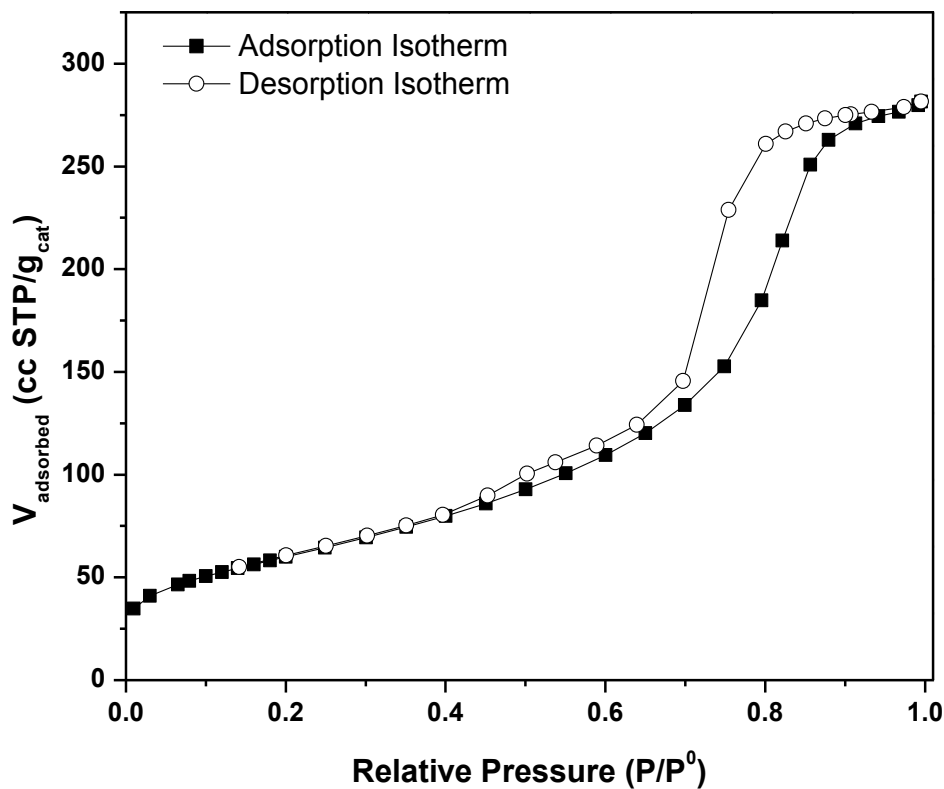


Figure B.1. Isotherm linear plot for calcined 6.5wt.%Pd/Al₂O₃ catalyst

B.2 XRD

X-Ray Diffraction analysis was used to identify the bulk crystalline phases present in the catalysts. The structure of crystalline materials, crystallite size, and degree of crystallinity are determined by XRD. When an X-ray beam hits a crystalline material it is diffracted and the distance between the two different planes of the crystal is described by Bragg's law.

$$n\lambda = 2d \sin\theta$$

B.6

where n is the order of the diffracted beam, λ is the X-ray wavelength, d is the distance between two planes of atoms (d-spacing), and θ is the angle of reflection. d-spacing is calculated by knowing θ and λ . By comparing the obtained data with the standard reference patterns, the material can be identified.

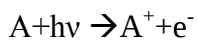
The crystallite size of a material can be determined from the Scherrer equation.

$$L = \frac{k\lambda}{(\beta \cos \theta)} \quad \text{B.7}$$

L is the crystallite size, k is an instrument constant (usually 1), λ is the X-ray wavelength (1.7902 Å), β is the width of the peak (full width at half maximum-FWHM), and θ is the angle of reflection. If an amorphous material is present in a sample, a broad peak will be observed in the XRD pattern.

B.3 XPS

X-ray photoelectron spectroscopy is a surface technique which is used to measure the oxidation state of the active species and the interaction between a metal and the oxide support. In addition, the detection of small crystallites or thin films which is difficult by XRD, can be determined by XPS. In this technique, an electron from the surface of the catalyst is excited when photons from an X-ray source hit it. When the X-ray photon with the energy of $h\nu$ hits the surface of the catalyst, an electron with the binding energy of E_B is adsorbed on the surface that causes the emission of the core electron of the catalyst with a specific amount of kinetic energy of E_k .



$$E_k = h\nu - E_B$$

By measuring E_k and having $h\nu$, the binding energy (E_B) can be determined. The electron emitted from each component has a specific amount of binding energy. So, E_B is used to demonstrate the atom that the electron comes from and also the oxidation state of that atom. For instance, in Pd/Al₂O₃ catalyst, X-ray hits the surface of the catalyst and the electrons of both palladium and Al₂O₃ leave the surface with different signals. The intensity of each signal depends on the number of electrons that escape the sample of palladium versus Al₂O₃. This intensity demonstrates the indication of concentration of Pd on the surface versus Al₂O₃ on the surface. If the Pd/Al₂O₃ ratio is high, it indicates high dispersion of Pd and if this ratio is low, we have low Pd dispersion on the surface of the catalyst.

B.4 CO Chemisorption

Gas adsorption is commonly used to determine the dispersion of metals for fresh and used catalysts. Metal dispersion is defined as the number of metal atoms on the surface of the catalyst which are exposed to the adsorbate species divided by the total number of metal atoms in the catalyst.

$$\text{Dispersion} = \frac{N_s(\text{surface metal atoms})}{N_s(\text{total number of metal atoms})}$$

CO is of the most common used gas for metal dispersion for different types of supported catalysts. In this technique, an inert gas passed through a bed of catalyst which is kept at a specific temperature. Then a pulse of CO is injected into the inert gas. The adsorbed CO is measured by having the amount of CO injected into the system and measuring the amount of gas which is not adsorbed. When the monolayer coverage is obtained, no more CO is adsorbed on the surface from the gas. The amount of adsorbed CO represents the number of metal surface atoms. Unfortunately, the dispersion obtained based on CO adsorption is not

consistent because a CO molecule is able to bind with more than one metal atom. Hence, it may not give the actual sites of the catalyst exposed to the reaction species.

A Micromeritics AutoChemII 2920 analyzer was used for CO pulse chemisorption of the reduced catalysts in order to determine the dispersion of active sites. In the analysis, the oxidized catalyst was purged in a $50 \text{ cm}^3(\text{STP}).\text{min}^{-1}$ flow rate of Ar (Praxair, UHP) at 200°C for 2h in order to remove moisture. The catalyst was then cooled to 100°C and held for 1h. After degas, a $50 \text{ cc}.\text{min}^{-1}$ flow rate of 9.5(v/v)% H_2/Ar (Praxair) at 100°C was fed to the catalyst for 1h, and then cooled to 25°C in He [88]. The purpose of flowing H_2/Ar is to partially reduce the catalyst so that a thin layer of PdO is transformed to Pd^0 that is able to adsorb CO, without affecting the size of the supported PdO particle. The CO uptake was measured by passing pulses of 9.93 (v/v)% CO/He (Praxair) at 25°C over the partially reduced catalyst. The CO pulse injection continued until no additional chemisorption was observed. The CO uptake was measured using a thermal conductivity detector (TCD).

The CO chemisorption analysis for the co-2.9Ce/6.5Pd/ Al_2O_3 catalyst is described below:

Table B.1. Properties of co-2.9Ce/6.5Pd/ Al_2O_3 catalyst used for CO chemisorption analysis

Sample mass (g)	0.1167
Active loop volume at 108.4°C (cc STP)	4.04×10^{-2}
Peak area at zero CO uptake	7.94×10^{-3}
Fc (volume-to-area factor) (cc/peak area)	5.09
Stoichiometry factor	1
Pd molecular weight (g/ μmol)	106.42×10^{-6}

Table B.2. Cumulative volume of co-2.9Ce/6.5Pd/Al₂O₃ catalyst during CO chemisorption analysis

Peak Number	Quantity Adsorbed μmol/g	Peak Area _n	ΔArea _n	Volume Adsorbed (cc STP)	Cumulative Quantity (cc STP)
1	-	0	7.94E-03	4.04E-02	4.04E-02
2	-	0	7.94E-03	4.04E-02	8.09E-02
3	46.37	0	7.94E-03	4.04E-02	1.21E-01
4	15.12	1.80E-04	7.76E-03	3.95E-02	1.61E-01
5	14.03	7.90E-04	7.15E-03	3.64E-02	1.97E-01
6	13.75	9.40E-04	7.00E-03	3.56E-02	2.33E-01
7	13.69	9.80E-04	6.96E-03	3.54E-02	2.68E-01
8	12.89	1.42E-03	6.52E-03	3.32E-02	3.01E-01
9	10.86	2.54E-03	5.40E-03	2.75E-02	3.29E-01
10	9.91	3.06E-03	4.88E-03	2.48E-02	3.54E-01
11	8.82	3.67E-03	4.27E-03	2.17E-02	3.76E-01
12	6.45	4.97E-03	2.97E-03	1.51E-02	3.91E-01
13	4.45	6.08E-03	1.86E-03	9.46E-03	4.00E-01
14	1.47	7.72E-03	2.18E-04	1.11E-03	4.01E-01

The total CO uptake is calculated is as follow:

$$\text{CO uptake} = \frac{\text{chemisorption volume}}{\text{STP volume} \times \text{mass of catalyst}} \quad \text{B.8}$$

$$\text{CO uptake} = \frac{4.01 \times 10^{-1} \text{ cm}^3 (\text{STP})}{22414 \times 10^{-6} \frac{\text{cm}^3}{\mu\text{mol}} \times 0.1167 \text{ g}_{\text{cat}}} = 153.30 \frac{\mu\text{mol}}{\text{g}_{\text{cat}}}$$

$$\text{Metal dispersion (\%)} = \frac{\text{CO uptake} \times \text{metal molecular weight}}{\text{metal wt.\%}} \times 100 \quad \text{B.9}$$

$$\text{Pd dispersion (\%)} = \frac{153.30 \frac{\mu\text{mol}}{\text{g}_{\text{cat}}} \times 106.42 \times 10^{-6} \frac{\text{g}_{\text{Pd}}}{\mu\text{mol}}}{0.065 \frac{\text{g}_{\text{Pd}}}{\text{g}_{\text{cat}}}} \times 100 = 25.1\%$$

Appendix C: MFC and MS Calibration

C.1 MFC Calibration

Mass flow controllers were used to direct the flow rate of CH₄/Ar, He, O₂, and Ar gases to the reactor separately. Each MFC was calibrated for the wide range of flow rate using a bubble flow meter. Tables C.1 and C.2 present the 9.97(v/v)%CH₄/Ar and He MFC calibration results.

Table C.1. CH₄/Ar calibration using a bubble flow meter

Set Point %	Volume cc	Time s	Flow rate cc(STP).min ⁻¹
10	5	38.0	7.3
20	10	34.7	15.9
30	10	24.1	22.9
40	15	26.6	31.1
60	15	17.0	48.8

Table C.2. He calibration using a bubble flow meter

Set Point %	Volume cc	Time s	Flow rate cc(STP).min ⁻¹
30	5	34.4	8.0
40	5	25.8	10.7
50	5	20.6	13.4
60	5	17.2	16.0
65	5	15.7	17.6
75	5	13.7	20.1
85	5	12.3	22.4

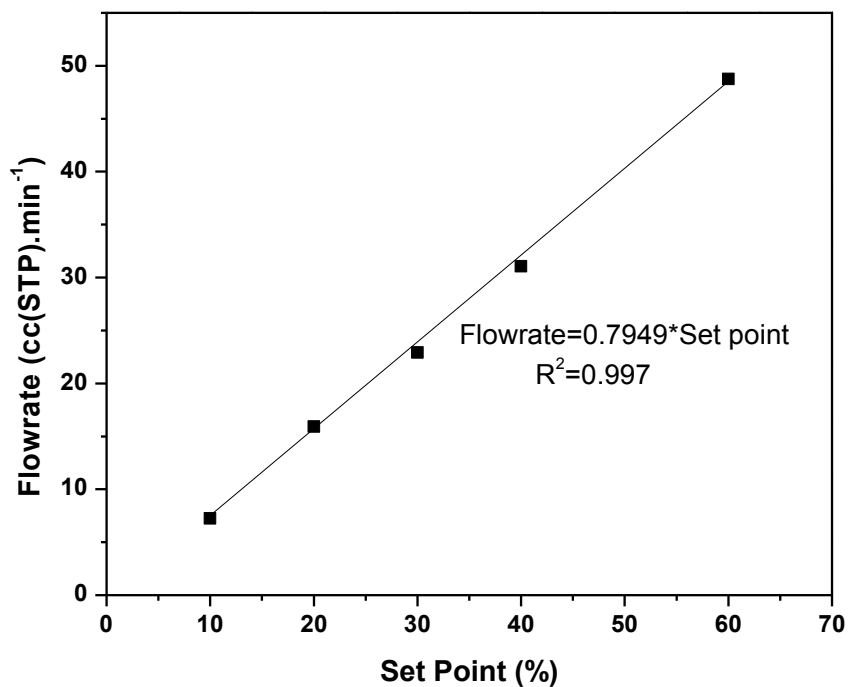


Figure C.1. MFC Calibration equation obtained for 9.97(v/v)%CH₄/Ar

Table C.3. Calibration equations obtained from the data presented in Tables C.1-C.2

Gas	Calibration equation	R ²
CH ₄ /Ar	Flow rate=0.7949×SP	0.997
He	Flow rate=0.2673×SP	0.999
O ₂	Flow rate=2.525×SP	0.995
Ar	Flow rate=7.112×SP	0.996

C.2 MS Calibration

To calculate CH₄ conversion, the change in the concentration of CH₄ and CO₂ during the reaction needs to be measured over time. Therefore, the MS is calibrated for CH₄ and CO₂. For both TPO and TOS experiments the signal intensities of CH₄ and CO₂ based on the mass signal of He are recorded.

Table C.4 presents the change in $\frac{I_{CH_4}}{I_{He}}$ ratio as a function of $\frac{Y_{CH_4}}{Y_{He}}$ molar fraction in a constant flow rate of He and O₂ at 185 sccm and 60 sccm, respectively.

Table C.4. MS calibration for 9.97%CH₄/He using 185 sccm He and 50 sccm O₂

I_{He}	I_{CH_4}	I_{CH_4}/I_{He}	Y_{CH_4}/Y_{He}
Torr	Torr		
1.01×10^{-4}	3.00×10^{-7}	0.0033	0.000000
5.66×10^{-5}	1.80×10^{-6}	0.0318	0.002371
5.94×10^{-5}	2.17×10^{-6}	0.0356	0.003240
5.83×10^{-5}	2.80×10^{-6}	0.0480	0.004145
5.46×10^{-5}	3.24×10^{-6}	0.0593	0.005280
5.50×10^{-5}	3.80×10^{-6}	0.0691	0.006582
5.86×10^{-5}	5.10×10^{-6}	0.0870	0.008223

Figure C.2 presents the calibration equation for $\frac{I_{CH_4}}{I_{He}}$ as a function of $\frac{Y_{CH_4}}{Y_{He}}$ molar ratio.

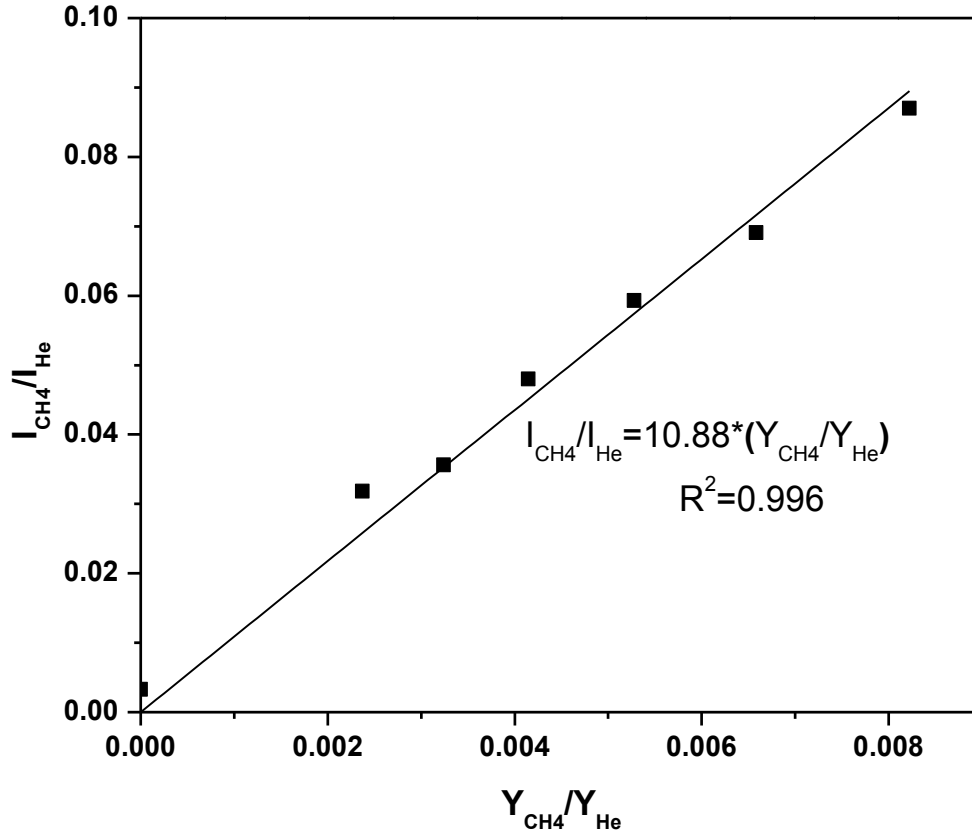


Figure C.2. MS Calibration equation for CH₄

C.3 Liquid Pump Calibration

In a wet-TOS experiment with 5vol.% H₂O in the feed (with the total inlet flow rate of 300 sccm) , the flow rate of H₂O is 15 sccm.

$$\frac{15 \text{ sccm}}{22414 \text{ cc/mol}} \times 18.02 \frac{\text{g}}{\text{mol}} = 0.012 \frac{\text{g}}{\text{min}}$$

$$\frac{0.012 \text{ g/min}}{1 \text{ g/cc}} \times \frac{(273+25)\text{K}}{273 \text{ K}} = 0.013 \frac{\text{cc}}{\text{min}}$$

In order to obtain 15 cm³(STP).min⁻¹ in gas feed, 0.013 cm³.min⁻¹ of H₂O in liquid phase in ambient temperature needs to be injected to the system.

Table C.5 shows the calibration for Harvard Apparatus Syringe Pump (Model 44) at 25°C.

Table C.5. Harvard apparatus syringe pump (Model 44) calibration

Infuse Rate cc.min ⁻¹	H ₂ O Collected cc	Time min	Flow rate cc.min ⁻¹
0.002	1.1	720	0.0015
0.005	2.8	720	0.0039
0.010	7.0	720	0.0097
0.020	13.8	720	0.0190

Appendix D: Error Analysis

In order to confirm the repeatability of the characterization, the standard deviation (SD) is reported for BET, CO chemisorption, XPS, and XRD analyses. The standard deviation is calculated in Equation D.1.

$$SD = \sqrt{\frac{\sum_{i=1}^k S_{t_{ij}}}{\sum n_j - k}} \quad D.1$$

S_{t_j} is the summation of the squares of each variable (y_j) and the average ($\bar{y}$):

$$S_{t_j} = \sum_{j=1}^n (y_j - \bar{y})^2 \quad D.2$$

n is the number of repeats and k is the number of S_{t_j} .

Table D.1. Catalyst preparation repeatability

Sample	Pd Content wt. %
6.5Pd/Al ₂ O ₃ -Batch#1	6.49
6.5Pd/Al ₂ O ₃ -Batch#2	6.97
Average	6.73
S_{t1}	0.11
co-2.9Ce/6.5Pd/Al ₂ O ₃ -Batch#1	6.68
co-2.9Ce/6.5Pd/Al ₂ O ₃ -Batch#1	6.90
Average	6.79
S_{t2}	0.02
SD	0.26

Table D.2. BET analysis repeatability

Sample	Surface Area $\text{m}^2.\text{g}^{-1}$	Pore Size nm	Pore Volume $\text{cm}^3.\text{g}^{-1}$
3.4Pd/Al ₂ O ₃ -Run#1	216	8.3	0.45
3.4Pd/Al ₂ O ₃ -Run#2	225	8.4	0.47
Average	220	8.4	0.46
S _t 1	46.2	1.8×10^{-4}	2.23×10^{-4}
9.5Ce/Al ₂ O ₃ -Run#1	191	8.5	0.41
9.5Ce/Al ₂ O ₃ -Run#2	191	8.5	0.41
Average	191	8.5	0.41
S _t 2	0.2	3.9×10^{-4}	1.25×10^{-8}
SD	4.8	1.7×10^{-2}	1.1×10^{-2}

Table D.3. CO Uptake analysis repeatability

Sample	CO Uptake $\mu\text{mol}.\text{g}_{\text{cat}}^{-1}$	Pd Dispersion %
6.5Pd/Al ₂ O ₃ -Run#1	204	33.5
6.5Pd/Al ₂ O ₃ -Run#2	198	32.4
Average	201	32.9
S _t 1	18	0.6
co-9.5Ce/6.5Pd/Al ₂ O ₃ -Run#1	228	36.5
co-9.5Ce/6.5Pd/Al ₂ O ₃ -Run#2	242	38.1
Average	235	37.3
S _t 2	98	1.3
SD	7.6	0.9

Table D.4. XPS analysis repeatability

Sample	Pd at. %	Ce at. %	O at. %	Al at. %
3.4Pd/Al ₂ O ₃ -Run#1	0.41	-	62.25	37.35
3.4Pd/Al ₂ O ₃ -Run#2	0.37	-	63.65	35.97
Average	0.39	-	62.95	36.66
S _{t1}	4.94×10 ⁻⁴	-	0.99	0.94
seq-5Ce/3.4Pd/Al ₂ O ₃ -Run#1	1.02	0.13	61.98	36.88
seq-5Ce/3.4Pd/Al ₂ O ₃ -Run#2	1.08	-	63.30	35.62
Average	1.05	0.13	62.64	36.25
S _{t2}	0.002	-	0.87	0.78
seq-17Ce/3.4Pd/Al ₂ O ₃ -Run#1	1.31	0.51	62.00	36.17
seq-17Ce/3.4Pd/Al ₂ O ₃ -Run#2	1.26	0.46	62.13	36.16
Average	1.28	0.49	62.07	36.17
S _{t3}	0.001	0.002	0.01	0.00
co-14Ce/3.4Pd/Al ₂ O ₃ -Run#1	1.78	0.85	64.89	32.48
co-14Ce/3.4Pd/Al ₂ O ₃ -Run#2	1.08	0.69	63.06	35.16
Average	1.43	0.77	63.98	33.82
S _{t4}	0.25	0.01	1.67	3.60
6.5Pd/Al ₂ O ₃ -Run#1	0.99	-	61.63	37.38
6.5Pd/Al ₂ O ₃ -Run#2	1.04	-	63.48	35.48
6.5Pd/Al ₂ O ₃ -Run#3	0.85	-	61.84	37.30
Average	0.96	-	62.32	36.72
S _{t5}	0.02	-	2.04	2.30
SD	0.21	0.07	0.96	1.23

Table D.5. XRD analysis repeatability

Sample	Obs. Max	d (@ Obs. Max)	FWHM	Crystallite Size (nm)
6.5Pd/Al ₂ O ₃ - Run#1	39.50	2.65	1.92	5.68
6.5Pd/Al ₂ O ₃ - Run#2	39.50	2.65	1.76	6.18
6.5Pd/Al ₂ O ₃ - Run#3	39.43	2.65	1.91	5.71
Average	39.48	2.65	1.86	5.86
SD	0.04	0.00	0.09	0.28
Error (%)	0.10	0.09	4.69	4.85

Appendix E: Reaction System

E.1 CH₄ Conversion Calculation

In order to measure the initial activity and loss of activity CH₄ conversion needs to be calculated during both TPO and TOS experiments. To calculate the CH₄ conversion, the total mole balance of carbon, e.g. ($n_{\text{CH}_4} + n_{\text{CO}_2}$) is calculated. The mass signal intensities (Y_i) are monitored by a quadrupole mass spectrometer showing the relative intensities of both CH₄ and CO₂ to the He intensity. A constant He flow rate (20 cc(STP).min⁻¹) was fed to the system so the change in signal intensities of CH₄ and CO₂ during the reaction can be recorder based on the He signal intensity. Prior to the reaction, the reactant gas feed consists of CH₄, O₂, and He passes through the catalyst bed and the MS in order to measure the relative signal intensities of the reactants at the beginning of the reaction. However, a small amount of CO₂ is observed by MS, indicating the CO₂ from the environment. Therefore, the exact amount of CO₂ as a product of the reaction is obtained by subtracting the CO₂ of the environment from the measured CO₂ at each specific time by MS. For this purpose, the mass signal intensities are recorded for 15 min at ambient temperature and the relative intensities are recorded.

$$I_{\text{rei}} = \frac{I_i}{I_{\text{He}}}, i=\text{CH}_4 \text{ or } \text{CO}_2 \quad \text{E.1}$$

During the TPO reaction, the change in signal intensities of CH₄ and CO₂ are recorded every 40 s to be consistent with the reaction temperature recording with the same time step. For the TOS experiments, with a constant reaction temperature, the change in signal intensities of each component are recorded every 40 s for 24h.

As shown in Appendix C.2, the relative flow rate of each component is calculated using the calibration equation presented in Figure C.2.

$$Y_{re_i} = AI_{re_i} \quad E.2$$

$$Y_{re_i} = \frac{Y_i}{Y_{He}} \quad E.3$$

The flow rate of component i (e.g. CH₄ or CO₂) is calculated considering the He flow rate, Y_{He}, remains unchanged during the reaction.

Corrected Y_{CO₂} is calculated as below:

$$Y_{CO_2})_{corrected} = Y_{CO_2} - Y_{CO_2}^0 \quad E.4$$

where Y_{CO₂}⁰ is the CO₂ flow rate at ambient temperature.

To measure the CH₄ conversion, total carbon mole balance should be calculated.

$$\sum n_c = n_{CH_4} + n_{CO_2} \quad E.5$$

As the reaction stoichiometry of complete oxidation of CH₄ shows, the volume basis corresponds to the mole basis, so the CH₄ conversion is calculated as below:

$$C \text{ flow})_{total} = CH_4 \text{ flow} + CO_2 \text{ flow} \quad E.6$$

$$X_{CH_4} = \frac{C \text{ flow})_{total} - CH_4 \text{ flow}}{C \text{ flow})_{total}} \times 100 \quad E.7$$

Details of CH₄ conversion calculations in a TPO experiment for 6.5Pd/Al₂O₃ catalyst using 0.1 g catalyst with 5°C.min⁻¹ from ambient temperature to 450°C are reported in Table E.1.

Table E.1. CH₄ conversion calculation for 6.5Pd/Al₂O₃ catalyst during TPO experiment. Reaction condition: GHSV=180,000 cm³(STP).g_{cat}⁻¹.h⁻¹,

1000 ppm CH₄, 20(v/v)% O₂, and the balance He and Ar

T °C	I _{He} Torr	I _{CH₄} Torr	I _{CO₂} Torr	I _{CH₄} /I _{He}	I _{CO₂} /I _{He}	Y _{CH₄} /Y _{He}	Y _{CO₂} /Y _{He}	He flow cc(STP).min ⁻¹	CH ₄ flow cc(STP).min ⁻¹	CO ₂ flow cc(STP).min ⁻¹	C flow) _{total} cc(STP).min ⁻¹	X mol.%
60.1	6.85E-09	4.77E-10	8.09E-11	6.96E-02	-2.12E-04	1.50E-02	-2.48E-05	20	3.01E-01	-4.96E-04	0.3	-0.17
64.9	6.84E-09	4.76E-10	8.07E-11	6.96E-02	-2.17E-04	1.50E-02	-2.55E-05	20	3.00E-01	-5.09E-04	0.3	-0.17
71.1	6.81E-09	4.72E-10	8.07E-11	6.92E-02	-1.87E-04	1.49E-02	-2.19E-05	20	2.99E-01	-4.38E-04	0.3	-0.15
75.3	6.84E-09	4.72E-10	8.18E-11	6.90E-02	-7.22E-05	1.49E-02	-8.46E-06	20	2.98E-01	-1.69E-04	0.3	-0.06
79.6	6.81E-09	4.68E-10	8.06E-11	6.87E-02	-2.03E-04	1.48E-02	-2.38E-05	20	2.96E-01	-4.76E-04	0.3	-0.16
83.9	6.82E-09	4.67E-10	8.16E-11	6.84E-02	-6.12E-05	1.48E-02	-7.17E-06	20	2.95E-01	-1.43E-04	0.3	-0.05
88.3	6.75E-09	4.62E-10	8.11E-11	6.85E-02	-1.66E-05	1.48E-02	-1.95E-06	20	2.96E-01	-3.90E-05	0.3	-0.01
92.5	6.73E-09	4.60E-10	8.05E-11	6.84E-02	-6.96E-05	1.48E-02	-8.16E-06	20	2.95E-01	-1.63E-04	0.3	-0.06
96.5	6.71E-09	4.55E-10	7.99E-11	6.79E-02	-1.10E-04	1.46E-02	-1.29E-05	20	2.93E-01	-2.58E-04	0.29	-0.09
100.4	6.75E-09	4.56E-10	8.04E-11	6.76E-02	-1.19E-04	1.46E-02	-1.39E-05	20	2.92E-01	-2.78E-04	0.29	-0.1
104	6.76E-09	4.55E-10	7.98E-11	6.72E-02	-2.21E-04	1.45E-02	-2.59E-05	20	2.90E-01	-5.18E-04	0.29	-0.18
107.5	6.70E-09	4.51E-10	8.03E-11	6.74E-02	-3.72E-05	1.45E-02	-4.36E-06	20	2.91E-01	-8.72E-05	0.29	-0.03
110.8	6.69E-09	4.50E-10	7.94E-11	6.72E-02	-1.67E-04	1.45E-02	-1.95E-05	20	2.90E-01	-3.91E-04	0.29	-0.13
114	6.66E-09	4.45E-10	7.97E-11	6.69E-02	-5.18E-05	1.44E-02	-6.07E-06	20	2.89E-01	-1.21E-04	0.29	-0.04
117	6.69E-09	4.47E-10	7.91E-11	6.67E-02	-2.04E-04	1.44E-02	-2.39E-05	20	2.88E-01	-4.77E-04	0.29	-0.17
119.9	6.63E-09	4.43E-10	7.99E-11	6.67E-02	2.30E-05	1.44E-02	2.69E-06	20	2.88E-01	5.38E-05	0.29	0.02
122.7	6.66E-09	4.42E-10	8.00E-11	6.63E-02	-1.07E-06	1.43E-02	-1.26E-07	20	2.86E-01	-2.52E-06	0.29	0
125.5	6.64E-09	4.38E-10	8.14E-11	6.61E-02	2.46E-04	1.43E-02	2.88E-05	20	2.85E-01	5.76E-04	0.29	0.2
128.2	6.68E-09	4.36E-10	8.22E-11	6.53E-02	2.72E-04	1.41E-02	3.18E-05	20	2.82E-01	6.37E-04	0.28	0.23
130.9	6.60E-09	4.32E-10	8.38E-11	6.55E-02	6.69E-04	1.41E-02	7.84E-05	20	2.83E-01	1.57E-03	0.28	0.55
133.6	6.58E-09	4.32E-10	8.67E-11	6.56E-02	1.15E-03	1.42E-02	1.35E-04	20	2.83E-01	2.69E-03	0.29	0.94

T	I _{He}	I _{CH₄}	I _{CO₂}	I _{CH₄} /I _{He}	I _{CO₂} /I _{He}	Y _{CH₄} /Y _{He}	Y _{CO₂} /Y _{He}	He flow	CH ₄ flow	CO ₂ flow	C flow) _{total}	X
°C	Torr	Torr	Torr					cc(STP).min ⁻¹	cc(STP).min ⁻¹	cc(STP).min ⁻¹	cc(STP).min ⁻¹	mol.%
136.4	6.60E-09	4.34E-10	8.88E-11	6.57E-02	1.43E-03	1.42E-02	1.68E-04	20	2.84E-01	3.35E-03	0.29	1.17
139.2	6.60E-09	4.30E-10	8.88E-11	6.51E-02	1.43E-03	1.40E-02	1.68E-04	20	2.81E-01	3.35E-03	0.28	1.18
142.1	6.58E-09	4.27E-10	8.86E-11	6.49E-02	1.43E-03	1.40E-02	1.68E-04	20	2.80E-01	3.36E-03	0.28	1.19
145	6.52E-09	4.25E-10	8.88E-11	6.51E-02	1.59E-03	1.41E-02	1.86E-04	20	2.81E-01	3.72E-03	0.28	1.3
148	6.53E-09	4.23E-10	8.96E-11	6.47E-02	1.69E-03	1.40E-02	1.98E-04	20	2.79E-01	3.96E-03	0.28	1.4
151.1	6.49E-09	4.20E-10	9.05E-11	6.46E-02	1.91E-03	1.39E-02	2.24E-04	20	2.79E-01	4.47E-03	0.28	1.58
154.1	6.48E-09	4.19E-10	9.18E-11	6.47E-02	2.14E-03	1.40E-02	2.51E-04	20	2.79E-01	5.02E-03	0.28	1.77
157.2	6.49E-09	4.15E-10	9.43E-11	6.39E-02	2.50E-03	1.38E-02	2.93E-04	20	2.76E-01	5.86E-03	0.28	2.08
160.3	6.50E-09	4.14E-10	9.61E-11	6.37E-02	2.74E-03	1.37E-02	3.21E-04	20	2.75E-01	6.43E-03	0.28	2.29
163.4	6.54E-09	4.14E-10	9.92E-11	6.33E-02	3.13E-03	1.37E-02	3.67E-04	20	2.73E-01	7.34E-03	0.28	2.62
166.5	6.50E-09	4.08E-10	1.03E-10	6.27E-02	3.83E-03	1.35E-02	4.49E-04	20	2.71E-01	8.99E-03	0.28	3.21
169.6	6.46E-09	4.02E-10	1.05E-10	6.23E-02	4.27E-03	1.34E-02	5.01E-04	20	2.69E-01	1.00E-02	0.28	3.59
172.7	6.42E-09	4.01E-10	1.09E-10	6.25E-02	5.03E-03	1.35E-02	5.89E-04	20	2.70E-01	1.18E-02	0.28	4.19
175.7	6.42E-09	3.97E-10	1.12E-10	6.18E-02	5.41E-03	1.33E-02	6.34E-04	20	2.67E-01	1.27E-02	0.28	4.54
178.8	6.42E-09	3.92E-10	1.15E-10	6.11E-02	5.86E-03	1.32E-02	6.87E-04	20	2.64E-01	1.37E-02	0.28	4.95
181.9	6.39E-09	3.89E-10	1.14E-10	6.09E-02	5.88E-03	1.31E-02	6.89E-04	20	2.63E-01	1.38E-02	0.28	4.98
184.9	6.44E-09	3.91E-10	1.18E-10	6.07E-02	6.28E-03	1.31E-02	7.36E-04	20	2.62E-01	1.47E-02	0.28	5.32
187.9	6.40E-09	3.85E-10	1.20E-10	6.02E-02	6.73E-03	1.30E-02	7.88E-04	20	2.60E-01	1.58E-02	0.28	5.72
191	6.39E-09	3.84E-10	1.22E-10	6.01E-02	7.12E-03	1.30E-02	8.34E-04	20	2.59E-01	1.67E-02	0.28	6.05
194.1	6.43E-09	3.82E-10	1.28E-10	5.94E-02	7.94E-03	1.28E-02	9.31E-04	20	2.56E-01	1.86E-02	0.27	6.77
197.2	6.44E-09	3.78E-10	1.34E-10	5.87E-02	8.85E-03	1.27E-02	1.04E-03	20	2.54E-01	2.08E-02	0.27	7.57
200.2	6.43E-09	3.72E-10	1.42E-10	5.79E-02	1.01E-02	1.25E-02	1.18E-03	20	2.50E-01	2.37E-02	0.27	8.64
203.3	6.42E-09	3.64E-10	1.51E-10	5.67E-02	1.15E-02	1.22E-02	1.35E-03	20	2.45E-01	2.70E-02	0.27	9.93
206.3	6.36E-09	3.56E-10	1.61E-10	5.59E-02	1.33E-02	1.21E-02	1.55E-03	20	2.41E-01	3.11E-02	0.27	11.4
209.4	6.38E-09	3.49E-10	1.74E-10	5.48E-02	1.53E-02	1.18E-02	1.79E-03	20	2.37E-01	3.58E-02	0.27	13.16

T	I _{He}	I _{CH₄}	I _{CO₂}	I _{CH₄} /I _{He}	I _{CO₂} /I _{He}	Y _{CH₄} /Y _{He}	Y _{CO₂} /Y _{He}	He flow	CH ₄ flow	CO ₂ flow	C flow) _{total}	X
°C	Torr	Torr	Torr					cc(STP).min ⁻¹	cc(STP).min ⁻¹	cc(STP).min ⁻¹	cc(STP).min ⁻¹	mol.%
212.5	6.40E-09	3.39E-10	1.87E-10	5.30E-02	1.72E-02	1.14E-02	2.01E-03	20	2.29E-01	4.03E-02	0.27	14.96
215.5	6.39E-09	3.31E-10	2.01E-10	5.17E-02	1.94E-02	1.12E-02	2.27E-03	20	2.23E-01	4.54E-02	0.27	16.9
218.5	6.42E-09	3.24E-10	2.17E-10	5.05E-02	2.18E-02	1.09E-02	2.55E-03	20	2.18E-01	5.10E-02	0.27	18.96
221.5	6.39E-09	3.16E-10	2.32E-10	4.94E-02	2.42E-02	1.07E-02	2.84E-03	20	2.13E-01	5.68E-02	0.27	21.04
224.4	6.35E-09	3.05E-10	2.47E-10	4.80E-02	2.69E-02	1.04E-02	3.15E-03	20	2.07E-01	6.30E-02	0.27	23.31
227.3	6.36E-09	2.94E-10	2.64E-10	4.63E-02	2.95E-02	9.99E-03	3.46E-03	20	2.00E-01	6.93E-02	0.27	25.75
230.3	6.34E-09	2.82E-10	2.82E-10	4.44E-02	3.24E-02	9.59E-03	3.80E-03	20	1.92E-01	7.60E-02	0.27	28.37
233.2	6.33E-09	2.68E-10	3.03E-10	4.23E-02	3.58E-02	9.13E-03	4.20E-03	20	1.83E-01	8.40E-02	0.27	31.5
236.2	6.37E-09	2.58E-10	3.25E-10	4.05E-02	3.90E-02	8.74E-03	4.57E-03	20	1.75E-01	9.15E-02	0.27	34.35
239.2	6.35E-09	2.45E-10	3.47E-10	3.86E-02	4.26E-02	8.32E-03	4.99E-03	20	1.66E-01	9.98E-02	0.27	37.47
242.2	6.34E-09	2.29E-10	3.72E-10	3.62E-02	4.66E-02	7.80E-03	5.46E-03	20	1.56E-01	1.09E-01	0.27	41.18
245.2	6.36E-09	2.17E-10	3.98E-10	3.41E-02	5.06E-02	7.36E-03	5.93E-03	20	1.47E-01	1.19E-01	0.27	44.6
248.3	6.37E-09	2.00E-10	4.24E-10	3.14E-02	5.46E-02	6.78E-03	6.40E-03	20	1.36E-01	1.28E-01	0.26	48.57
251.4	6.33E-09	1.87E-10	4.51E-10	2.95E-02	5.92E-02	6.37E-03	6.94E-03	20	1.27E-01	1.39E-01	0.27	52.17
254.4	6.33E-09	1.68E-10	4.78E-10	2.66E-02	6.34E-02	5.73E-03	7.44E-03	20	1.15E-01	1.49E-01	0.26	56.48
257.4	6.39E-09	1.55E-10	5.06E-10	2.42E-02	6.71E-02	5.23E-03	7.86E-03	20	1.05E-01	1.57E-01	0.26	60.05
260.4	6.37E-09	1.37E-10	5.30E-10	2.15E-02	7.12E-02	4.64E-03	8.35E-03	20	9.28E-02	1.67E-01	0.26	64.28
263.4	6.38E-09	1.20E-10	5.59E-10	1.89E-02	7.56E-02	4.07E-03	8.86E-03	20	8.14E-02	1.77E-01	0.26	68.53
266.4	6.39E-09	1.07E-10	5.86E-10	1.67E-02	7.96E-02	3.60E-03	9.33E-03	20	7.20E-02	1.87E-01	0.26	72.15
269.5	6.38E-09	9.00E-11	6.09E-10	1.41E-02	8.34E-02	3.04E-03	9.78E-03	20	6.09E-02	1.96E-01	0.26	76.26
272.5	6.41E-09	7.77E-11	6.37E-10	1.21E-02	8.73E-02	2.61E-03	1.02E-02	20	5.23E-02	2.05E-01	0.26	79.64
275.6	6.37E-09	5.53E-11	6.58E-10	8.67E-03	9.12E-02	1.87E-03	1.07E-02	20	3.74E-02	2.14E-01	0.25	85.1
278.7	6.40E-09	4.47E-11	6.79E-10	6.99E-03	9.41E-02	1.51E-03	1.10E-02	20	3.02E-02	2.20E-01	0.25	87.97
281.7	6.39E-09	2.96E-11	6.99E-10	4.62E-03	9.73E-02	9.97E-04	1.14E-02	20	1.99E-02	2.28E-01	0.25	91.96
284.7	6.39E-09	2.17E-11	7.14E-10	3.39E-03	9.97E-02	7.32E-04	1.17E-02	20	1.46E-02	2.34E-01	0.25	94.1

T	I _{He}	I _{CH4}	I _{CO2}					He flow	CH ₄ flow	CO ₂ flow	C flow) _{total}	X
°C	Torr	Torr	Torr	I _{CH4} /I _{He}	I _{CO2} /I _{He}	Y _{CH4} /Y _{He}	Y _{CO2} /Y _{He}	cc(STP).min ⁻¹	cc(STP).min ⁻¹	cc(STP).min ⁻¹	cc(STP).min ⁻¹	mol.%
287.7	6.38E-09	1.11E-11	7.27E-10	1.74E-03	1.02E-01	3.74E-04	1.19E-02	20	7.49E-03	2.39E-01	0.25	96.96
290.6	6.37E-09	2.98E-12	7.40E-10	4.67E-04	1.04E-01	1.01E-04	1.22E-02	20	2.02E-03	2.44E-01	0.25	99.18
293.6	6.41E-09	-2.43E-12	7.50E-10	-3.79E-04	1.05E-01	-8.17E-05	1.23E-02	20	-1.63E-03	2.46E-01	0.24	100.67
296.5	6.38E-09	-8.01E-12	7.56E-10	-1.26E-03	1.07E-01	-2.71E-04	1.25E-02	20	-5.42E-03	2.50E-01	0.24	102.22
299.5	6.37E-09	-1.16E-11	7.62E-10	-1.82E-03	1.07E-01	-3.93E-04	1.26E-02	20	-7.86E-03	2.52E-01	0.24	103.22
302.5	6.34E-09	-1.57E-11	7.63E-10	-2.47E-03	1.08E-01	-5.32E-04	1.27E-02	20	-1.06E-02	2.54E-01	0.24	104.38
305.4	6.35E-09	-1.46E-11	7.70E-10	-2.30E-03	1.09E-01	-4.97E-04	1.28E-02	20	-9.94E-03	2.56E-01	0.25	104.04
308.4	6.34E-09	-1.57E-11	7.71E-10	-2.48E-03	1.09E-01	-5.35E-04	1.28E-02	20	-1.07E-02	2.57E-01	0.25	104.35
311.4	6.37E-09	-1.77E-11	7.69E-10	-2.78E-03	1.09E-01	-6.00E-04	1.27E-02	20	-1.20E-02	2.55E-01	0.24	104.94
314.4	6.30E-09	-1.97E-11	7.67E-10	-3.12E-03	1.10E-01	-6.73E-04	1.28E-02	20	-1.35E-02	2.57E-01	0.24	105.53
317.4	6.31E-09	-2.05E-11	7.69E-10	-3.25E-03	1.10E-01	-7.01E-04	1.29E-02	20	-1.40E-02	2.58E-01	0.24	105.76
320.3	6.31E-09	-1.83E-11	7.67E-10	-2.90E-03	1.10E-01	-6.26E-04	1.28E-02	20	-1.25E-02	2.57E-01	0.24	105.12
323.3	6.29E-09	-1.90E-11	7.68E-10	-3.02E-03	1.10E-01	-6.51E-04	1.29E-02	20	-1.30E-02	2.58E-01	0.25	105.31
326.4	6.26E-09	-2.32E-11	7.68E-10	-3.71E-03	1.11E-01	-8.00E-04	1.30E-02	20	-1.60E-02	2.59E-01	0.24	106.58
329.4	6.27E-09	-2.42E-11	7.64E-10	-3.85E-03	1.10E-01	-8.31E-04	1.29E-02	20	-1.66E-02	2.57E-01	0.24	106.91
332.5	6.25E-09	-2.39E-11	7.65E-10	-3.82E-03	1.10E-01	-8.24E-04	1.29E-02	20	-1.65E-02	2.59E-01	0.24	106.81
335.5	6.26E-09	-2.29E-11	7.67E-10	-3.66E-03	1.11E-01	-7.89E-04	1.30E-02	20	-1.58E-02	2.59E-01	0.24	106.48
338.6	6.23E-09	-1.97E-11	7.66E-10	-3.17E-03	1.11E-01	-6.84E-04	1.30E-02	20	-1.37E-02	2.60E-01	0.25	105.55
341.7	6.26E-09	-1.99E-11	7.67E-10	-3.19E-03	1.11E-01	-6.87E-04	1.30E-02	20	-1.37E-02	2.59E-01	0.25	105.61
344.6	6.27E-09	-2.37E-11	7.63E-10	-3.79E-03	1.10E-01	-8.17E-04	1.29E-02	20	-1.63E-02	2.57E-01	0.24	106.79
347.6	6.25E-09	-2.51E-11	7.61E-10	-4.02E-03	1.10E-01	-8.67E-04	1.28E-02	20	-1.73E-02	2.57E-01	0.24	107.24
350.6	6.22E-09	-2.04E-11	7.60E-10	-3.28E-03	1.10E-01	-7.08E-04	1.29E-02	20	-1.42E-02	2.58E-01	0.24	105.8
353.7	6.24E-09	-2.10E-11	7.59E-10	-3.36E-03	1.10E-01	-7.25E-04	1.28E-02	20	-1.45E-02	2.57E-01	0.24	105.98
356.7	6.20E-09	-2.16E-11	7.60E-10	-3.48E-03	1.11E-01	-7.51E-04	1.30E-02	20	-1.50E-02	2.59E-01	0.24	106.15
359.8	6.15E-09	-2.51E-11	7.57E-10	-4.08E-03	1.11E-01	-8.81E-04	1.30E-02	20	-1.76E-02	2.60E-01	0.24	107.26

T	I _{He}	I _{CH₄}	I _{CO₂}					He flow	CH ₄ flow	CO ₂ flow	C flow) _{total}	X
°C	Torr	Torr	Torr	I _{CH₄} /I _{He}	I _{CO₂} /I _{He}	Y _{CH₄} /Y _{He}	Y _{CO₂} /Y _{He}	cc(STP).min ⁻¹	cc(STP).min ⁻¹	cc(STP).min ⁻¹	cc(STP).min ⁻¹	mol.%
362.9	6.16E-09	-2.47E-11	7.56E-10	-4.01E-03	1.11E-01	-8.65E-04	1.30E-02	20	-1.73E-02	2.59E-01	0.24	107.15
366	6.17E-09	-1.94E-11	7.58E-10	-3.15E-03	1.11E-01	-6.80E-04	1.30E-02	20	-1.36E-02	2.60E-01	0.25	105.52
368.9	6.16E-09	-2.09E-11	7.59E-10	-3.39E-03	1.11E-01	-7.32E-04	1.30E-02	20	-1.46E-02	2.60E-01	0.25	105.96
371.9	6.18E-09	-2.27E-11	7.56E-10	-3.68E-03	1.10E-01	-7.94E-04	1.29E-02	20	-1.59E-02	2.59E-01	0.24	106.54
374.9	6.18E-09	-2.20E-11	7.58E-10	-3.56E-03	1.11E-01	-7.67E-04	1.30E-02	20	-1.53E-02	2.59E-01	0.24	106.3
377.8	6.22E-09	-1.97E-11	7.57E-10	-3.17E-03	1.10E-01	-6.84E-04	1.29E-02	20	-1.37E-02	2.57E-01	0.24	105.62
380.9	6.14E-09	-2.26E-11	7.57E-10	-3.68E-03	1.11E-01	-7.94E-04	1.30E-02	20	-1.59E-02	2.61E-01	0.25	106.48
383.9	6.14E-09	-2.04E-11	7.53E-10	-3.33E-03	1.11E-01	-7.18E-04	1.30E-02	20	-1.44E-02	2.59E-01	0.24	105.86
386.9	6.12E-09	-2.42E-11	7.54E-10	-3.96E-03	1.11E-01	-8.54E-04	1.30E-02	20	-1.71E-02	2.60E-01	0.24	107.02
390	6.13E-09	-2.06E-11	7.52E-10	-3.36E-03	1.11E-01	-7.25E-04	1.30E-02	20	-1.45E-02	2.59E-01	0.24	105.93
393	6.13E-09	-2.34E-11	7.55E-10	-3.81E-03	1.11E-01	-8.23E-04	1.30E-02	20	-1.65E-02	2.60E-01	0.24	106.75
396	6.15E-09	-2.08E-11	7.54E-10	-3.38E-03	1.11E-01	-7.30E-04	1.30E-02	20	-1.46E-02	2.59E-01	0.24	105.96
398.9	6.16E-09	-2.41E-11	7.53E-10	-3.92E-03	1.10E-01	-8.45E-04	1.29E-02	20	-1.69E-02	2.58E-01	0.24	107.01
401.8	6.12E-09	-2.01E-11	7.53E-10	-3.28E-03	1.11E-01	-7.07E-04	1.30E-02	20	-1.41E-02	2.60E-01	0.25	105.75
404.9	6.13E-09	-2.00E-11	7.51E-10	-3.26E-03	1.10E-01	-7.03E-04	1.29E-02	20	-1.41E-02	2.59E-01	0.24	105.75
407.9	6.13E-09	-2.08E-11	7.53E-10	-3.40E-03	1.11E-01	-7.33E-04	1.30E-02	20	-1.47E-02	2.60E-01	0.25	105.97
410.9	6.09E-09	-2.57E-11	7.49E-10	-4.22E-03	1.11E-01	-9.10E-04	1.30E-02	20	-1.82E-02	2.60E-01	0.24	107.53
414	6.08E-09	-2.47E-11	7.51E-10	-4.07E-03	1.11E-01	-8.78E-04	1.31E-02	20	-1.76E-02	2.61E-01	0.24	107.2
417	6.10E-09	-1.95E-11	7.49E-10	-3.20E-03	1.11E-01	-6.90E-04	1.30E-02	20	-1.38E-02	2.60E-01	0.25	105.61
420	6.09E-09	-2.41E-11	7.51E-10	-3.95E-03	1.11E-01	-8.52E-04	1.30E-02	20	-1.70E-02	2.61E-01	0.24	107
422.9	6.15E-09	-1.98E-11	7.50E-10	-3.22E-03	1.10E-01	-6.94E-04	1.29E-02	20	-1.39E-02	2.58E-01	0.24	105.7
425.9	6.07E-09	-2.48E-11	7.50E-10	-4.09E-03	1.11E-01	-8.82E-04	1.31E-02	20	-1.76E-02	2.61E-01	0.24	107.24
428.9	6.10E-09	-2.25E-11	7.52E-10	-3.68E-03	1.11E-01	-7.95E-04	1.30E-02	20	-1.59E-02	2.61E-01	0.24	106.5
432	6.09E-09	-2.27E-11	7.51E-10	-3.73E-03	1.11E-01	-8.04E-04	1.30E-02	20	-1.61E-02	2.61E-01	0.24	106.57
435.1	6.07E-09	-2.15E-11	7.50E-10	-3.54E-03	1.12E-01	-7.63E-04	1.31E-02	20	-1.53E-02	2.61E-01	0.25	106.2

T °C	I _{He} Torr	I _{CH₄} Torr	I _{CO₂} Torr	I _{CH₄} /I _{He}	I _{CO₂} /I _{He}	Y _{CH₄} /Y _{He}	Y _{CO₂} /Y _{He}	He flow cc(STP).min ⁻¹	CH ₄ flow cc(STP).min ⁻¹	CO ₂ flow cc(STP).min ⁻¹	C flow) _{total} cc(STP).min ⁻¹	X mol.%
438.1	6.02E-09	-2.55E-11	7.49E-10	-4.23E-03	1.12E-01	-9.13E-04	1.32E-02	20	-1.83E-02	2.64E-01	0.25	107.45
441.1	6.06E-09	-2.26E-11	7.47E-10	-3.73E-03	1.11E-01	-8.05E-04	1.30E-02	20	-1.61E-02	2.61E-01	0.24	106.59
444.1	6.05E-09	-2.11E-11	7.49E-10	-3.50E-03	1.12E-01	-7.55E-04	1.31E-02	20	-1.51E-02	2.62E-01	0.25	106.11
446.9	6.06E-09	-2.14E-11	7.48E-10	-3.53E-03	1.11E-01	-7.62E-04	1.31E-02	20	-1.52E-02	2.61E-01	0.25	106.2
450	6.03E-09	-2.15E-11	7.45E-10	-3.56E-03	1.12E-01	-7.69E-04	1.31E-02	20	-1.54E-02	2.62E-01	0.25	106.25

Appendix F: Repeatability

F.1 TPO Reaction Repeatability

Table F.1. TPO Reaction Repeatability. GHSV=180,000 cm³(STP).g_{cat}⁻¹.h⁻¹. 1000 ppm CH₄, 20(v/v)% O₂, and the balance He and Ar

Sample	Light-off Temperature (°C)		
	T ₁₀	T ₅₀	T ₉₀
3.4Pd/Al ₂ O ₃ -Run#1	223	278	317
3.4Pd/Al ₂ O ₃ -Run#2	214	268	301
Average	219	273	309
S _t 1	45	45	125
seq-2Ce/3.4Pd/Al ₂ O ₃ -Run#1	222	273	309
seq-2Ce/3.4Pd/Al ₂ O ₃ -Run#2	207	271	307
Average	214	272	308
S _t 2	110	3	3
seq-17Ce/3.4Pd/Al ₂ O ₃ -Run#1	207	262	295
seq-17Ce/3.4Pd/Al ₂ O ₃ -Run#2	226	271	299
seq-17Ce/3.4Pd/Al ₂ O ₃ -Run#3	212	260	294
Average	215	264	296
S _t 3	10	6	3
seq-28Ce/3.4Pd/Al ₂ O ₃ -Run#1	226	283	322
seq-28Ce/3.4Pd/Al ₂ O ₃ -Run#2	221	278	315
Average	223	281	318
S _t 4	11	11	25
SD	6	4	6

F.2 TOS Reaction Repeatability

Table F.2. TOS repeatability. GHSV=180,000 cm³(STP).g_{cat}⁻¹.h⁻¹. 5000 ppm CH₄, 20(v/v)% O₂, and the balance He

Sample		TOS (h)			
		1	6	12	24
		Conversion (mol.%)			
6.5Pd/Al ₂ O ₃ , dry-TOS, 350°C	Run#1	100	95	90	84
	Run#2	100	97	93	87
	Average	100	96	92	86
S _t 1		0	2	4.5	4.5
6.5Pd/Al ₂ O ₃ , wet-TOS, 350°C	Run#1	82	48	45	43
	Run#2	78	49	48	46
	Average	80	49	47	45
S _t 2		8	0.5	4.5	4.5
co-2.9Ce/6.5Pd/Al ₂ O ₃ , dry-TOS, 350°C	Run#1	84	61	53	47
	Run#2	87	64	58	51
	Average	86	63	56	49
S _t 3		4.5	4.5	12.5	8
co-2.9Ce/6.5Pd/Al ₂ O ₃ , wet-TOS, 380°C	Run#1	76	54	53	50
	Run#2	80	52	49	48
	Average	78	53	51	49
S _t 4		8	2	8	2
SD		2	1	3	2

Appendix G: Supplementary Figures and Tables for Chapter 6

The Ce 3d spectra for co-impregnated catalysts are presented in Figure G.1. Because of the low intensity of Ce 3d peaks of the co-2Ce/3.4Pd/Al₂O₃ catalyst, only the Ce 3d spectra of co-14Ce/3.4Pd/Al₂O₃ and co-47Ce/3.4Pd/Al₂O₃ catalysts are shown in Figure G.1 and the B.E.s of Ce 3d for all co-2Ce/3.4Pd/Al₂O₃, co-14Ce/3.4Pd/Al₂O₃, and co-47Ce/3.4Pd/Al₂O₃ catalysts are reported in Table G.2. The two main peaks attributed to 3d_{5/2} and 3d_{3/2} electrons for Ce³⁺ (Ce₂O₃) are located at 885.0 eV (v') and 903.6 eV (u'), respectively for all three catalysts. The three main peaks assigned to 3d_{3/2} for Ce⁴⁺ (CeO₂) occur at 901.0 eV (u), 906.9 eV (u''), and 917.0 eV (u''') for all three catalysts. There are also three peaks for Ce⁴⁺ (CeO₂) 3d_{5/2} identified as v, v'', and v'''. For all co-impregnated catalysts, the v and v''' peak appear at 882.9 eV and 898.7 eV, respectively, however, the peak corresponded to v'' appears at 887.4 eV for co-2Ce/3.4Pd/Al₂O₃ and the B.E. increases to 888.1 eV and 888.4 eV for co-14Ce/3.4Pd/Al₂O₃ and co-47Ce/3.4Pd/Al₂O₃ catalysts, respectively.

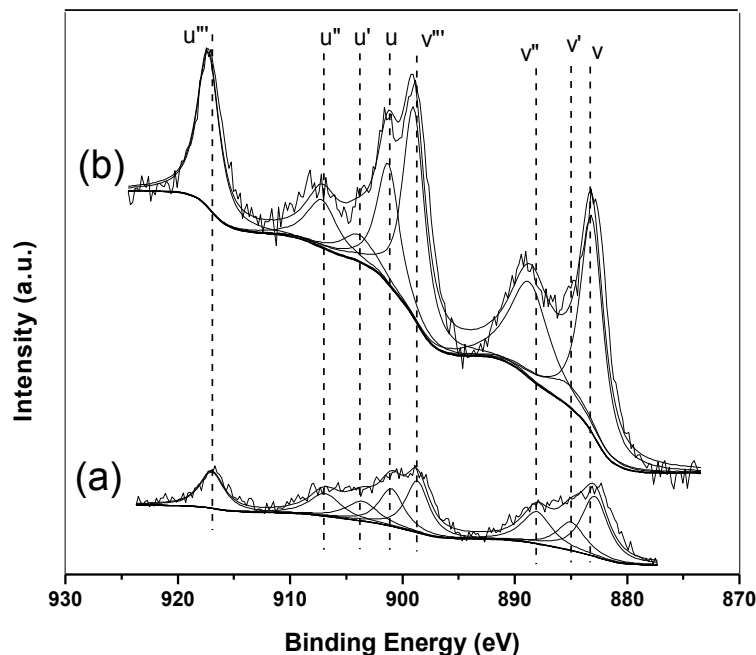


Figure G.1. Ce 3d for co-impregnated catalysts (a) co-14Ce/3.4Pd/Al₂O₃, (b) co-47Ce/3.4Pd/Al₂O₃ catalysts

For the xCe/Al₂O₃ support shown in Figure G.2 the same peaks appear for Ce 3d at the same positions as those for the sequentially impregnated catalysts, except for the v'' and u'' peaks. The peak for Ce⁴⁺ (CeO₂) 3d_{5/2} appears at 887.4 eV (v'') for seq-2Ce/Al₂O₃ support and shifts to 888.7 eV as the Ce loading increases to 52wt.%. Also the peak assigned to Ce⁴⁺ (CeO₂) 3d_{3/2} (u'') appeared at 906.9 eV for 2Ce/Al₂O₃ support and moved to 907.8 eV by increasing the Ce loading to 52wt.%.

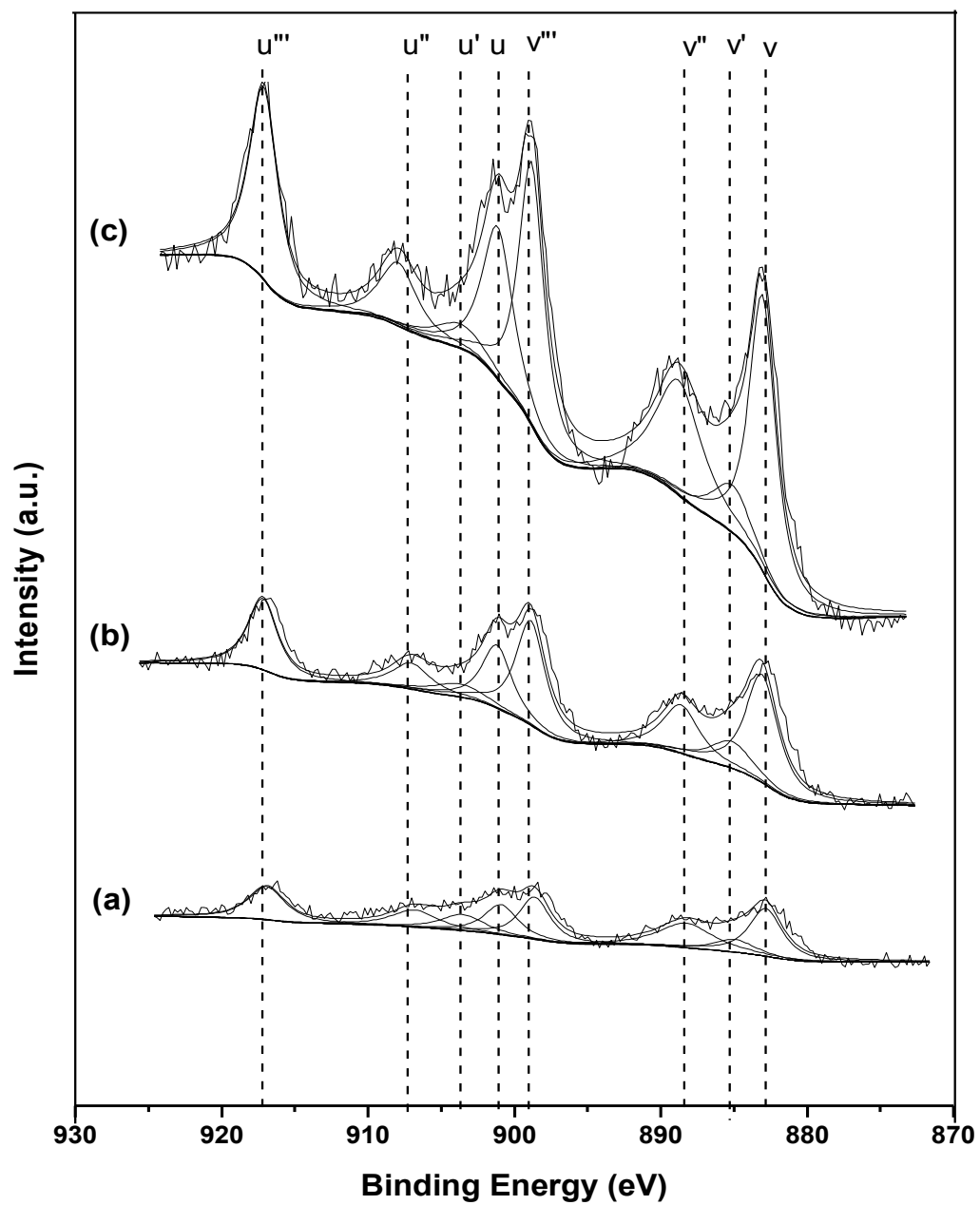


Figure G.2. Ce 3d for (a) 16Ce/Al₂O₃ (b) 26Ce/Al₂O₃, and (c) 52Ce/Al₂O₃ supports

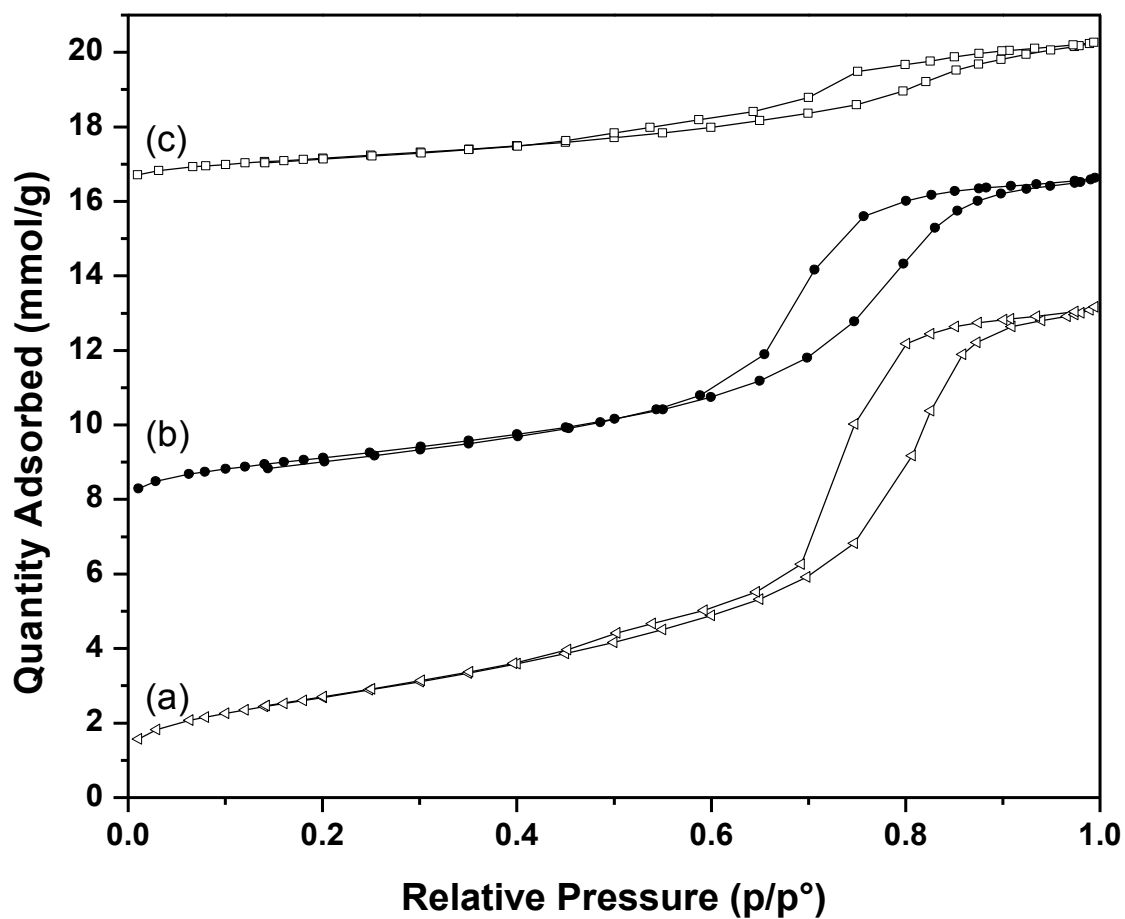


Figure G.3. N_2 adsorption-desorption isotherms for co-impregnated (a) $co-2Ce/3.4Pd/Al_2O_3$, (b) $co-14Ce/3.4Pd/Al_2O_3$, and (c) $co-47Ce/3.4Pd/Al_2O_3$ catalysts

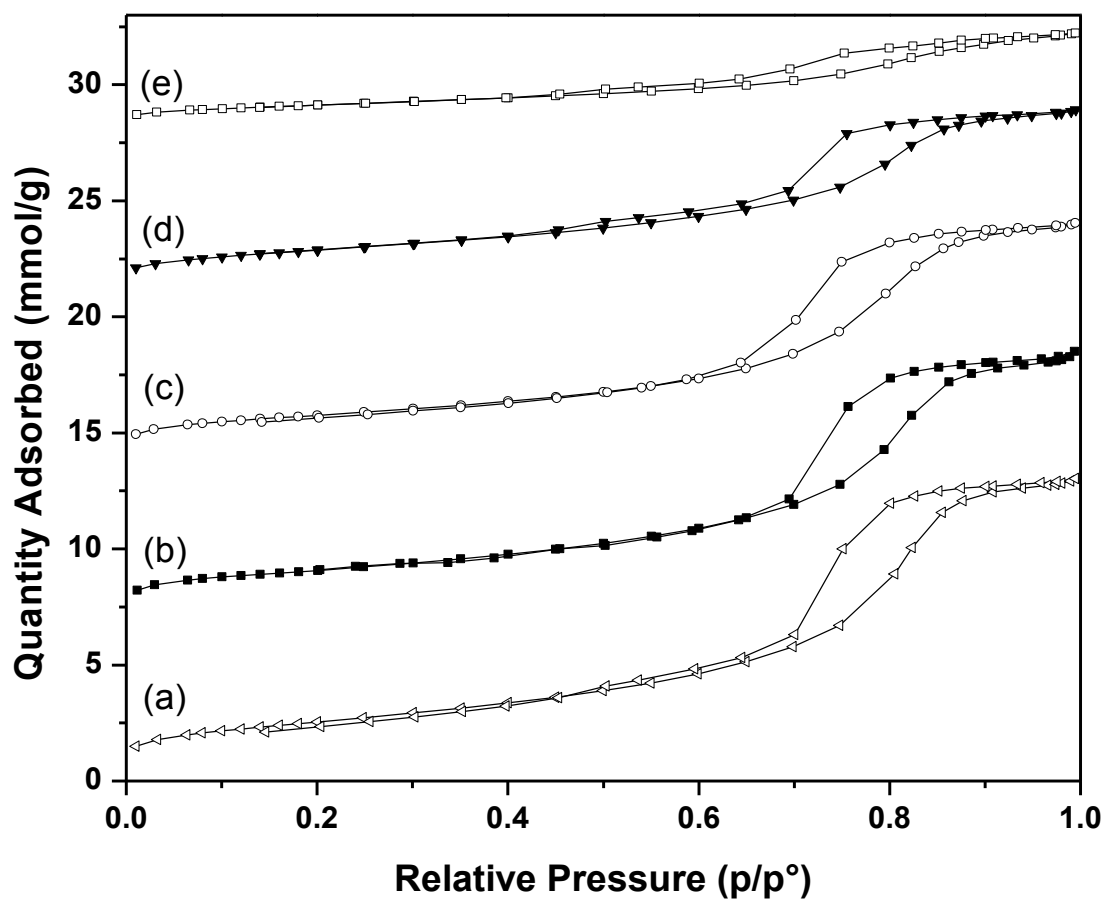


Figure G.4. N₂ adsorption-desorption isotherms for sequentially impregnated (a) seq-2Ce/3.4Pd/Al₂O₃, (b) seq-6Ce/3.4Pd/Al₂O₃, (c) seq-17Ce/3.4Pd/Al₂O₃, (d) seq-28Ce/3.4Pd/Al₂O₃, and (e) seq-57Ce/3.4Pd/Al₂O₃ catalysts

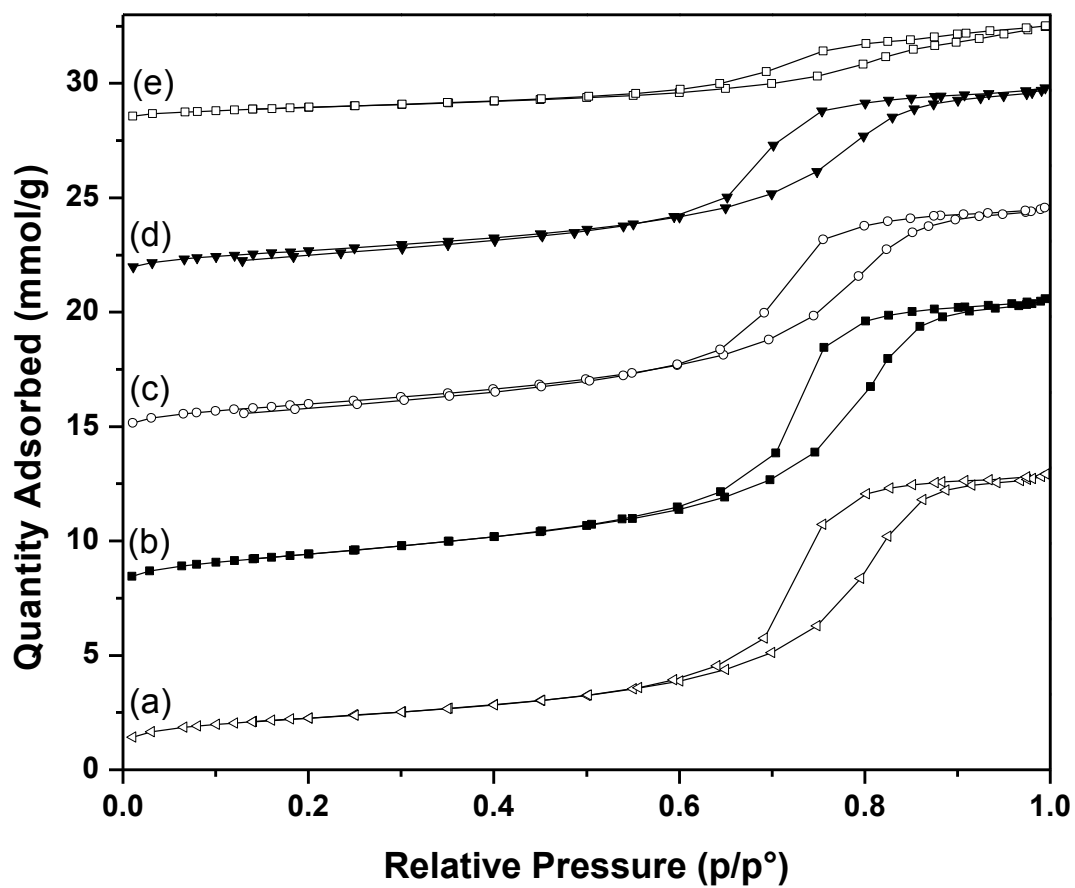


Figure G.5. N_2 adsorption-desorption isotherms for (a) 2Ce/ Al_2O_3 , (b) 5Ce/ Al_2O_3 , (c) 16Ce/ Al_2O_3 , (d) 26Ce/ Al_2O_3 , and (e) 52Ce/ Al_2O_3 supports

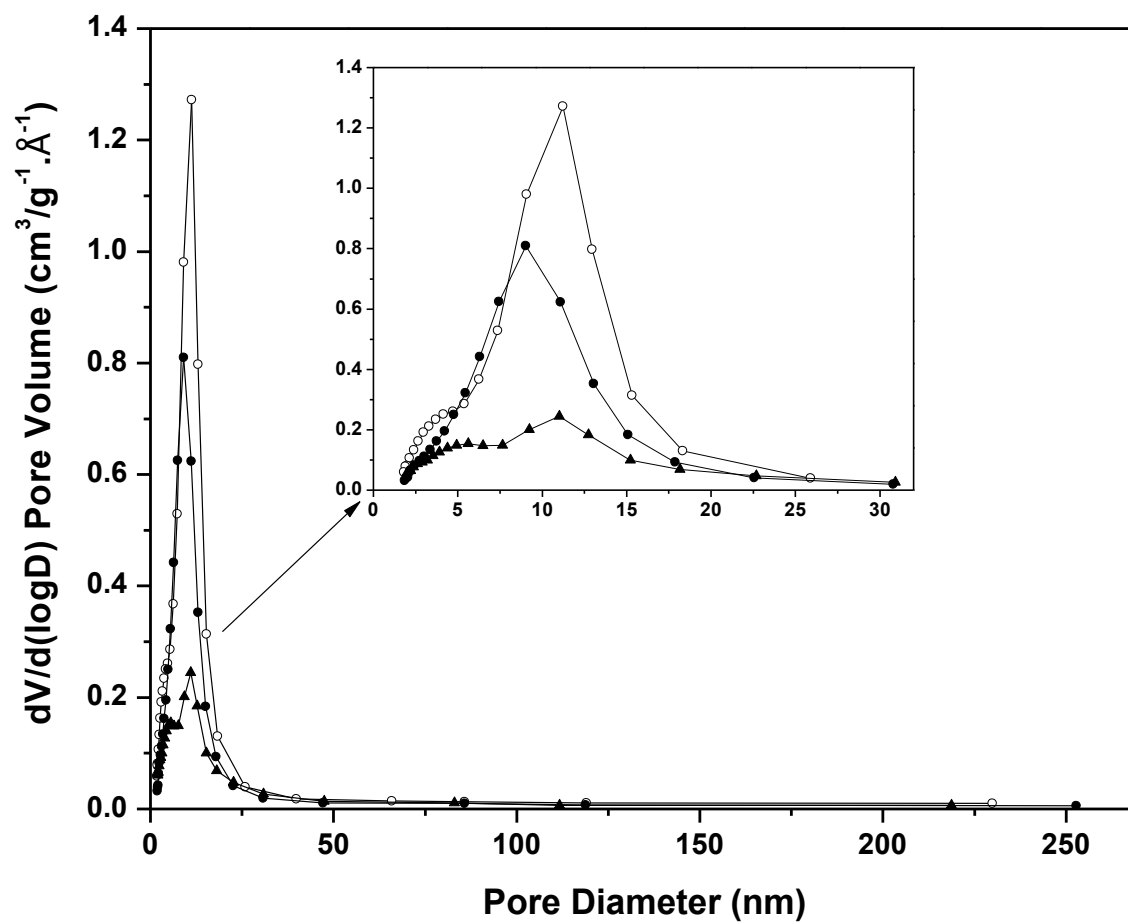


Figure G.6. BJH pore size distribution for co-2Ce/3.4Pd/Al₂O₃ (○), co-14Ce/3.4Pd/Al₂O₃ (■), and co-47Ce/3.4Pd/Al₂O₃ (▲) catalysts

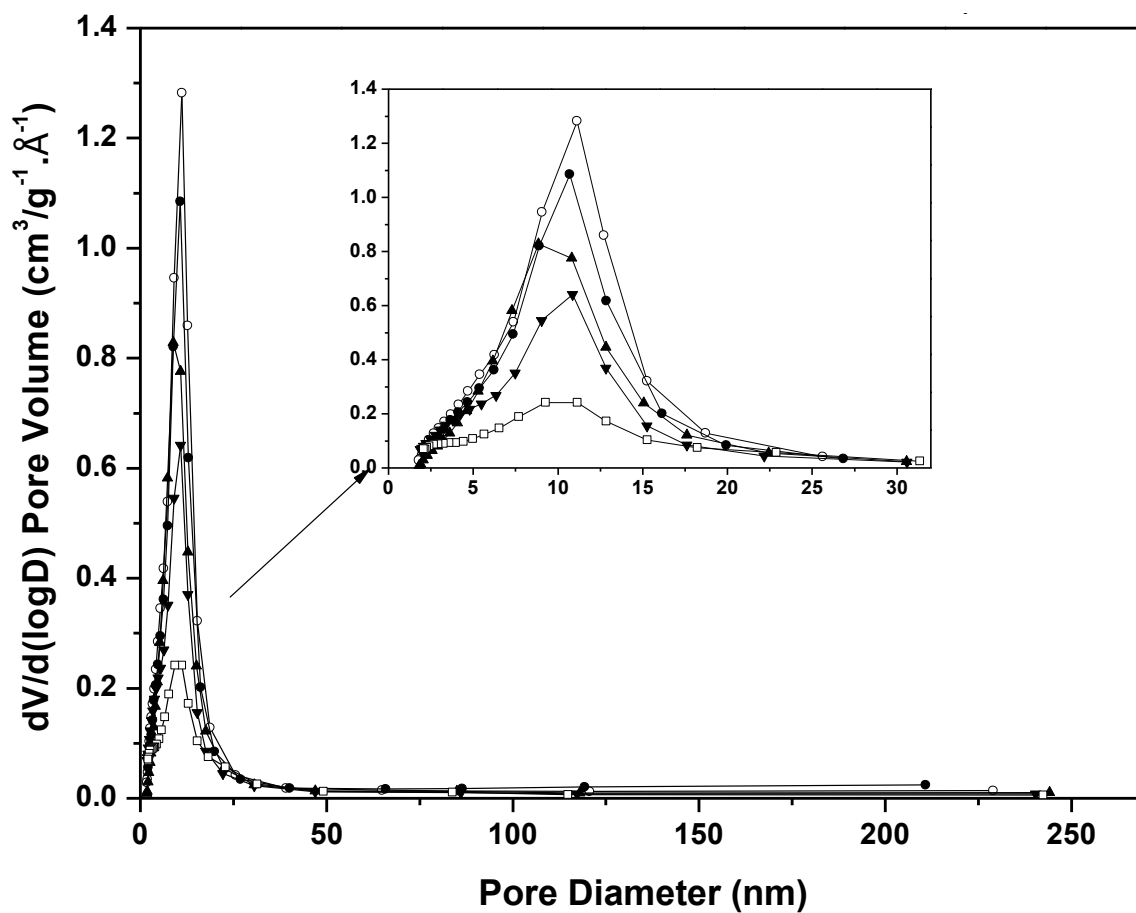


Figure G.7. BJH pore size distribution for (○) seq-2Ce/3.4Pd/Al₂O₃, (●) seq-6Ce/3.4Pd/Al₂O₃, (▲) seq-17Ce/3.4Pd/Al₂O₃, (▼) seq-28Ce/3.4Pd/Al₂O₃, and (□) seq-57Ce/3.4Pd/Al₂O₃ catalysts

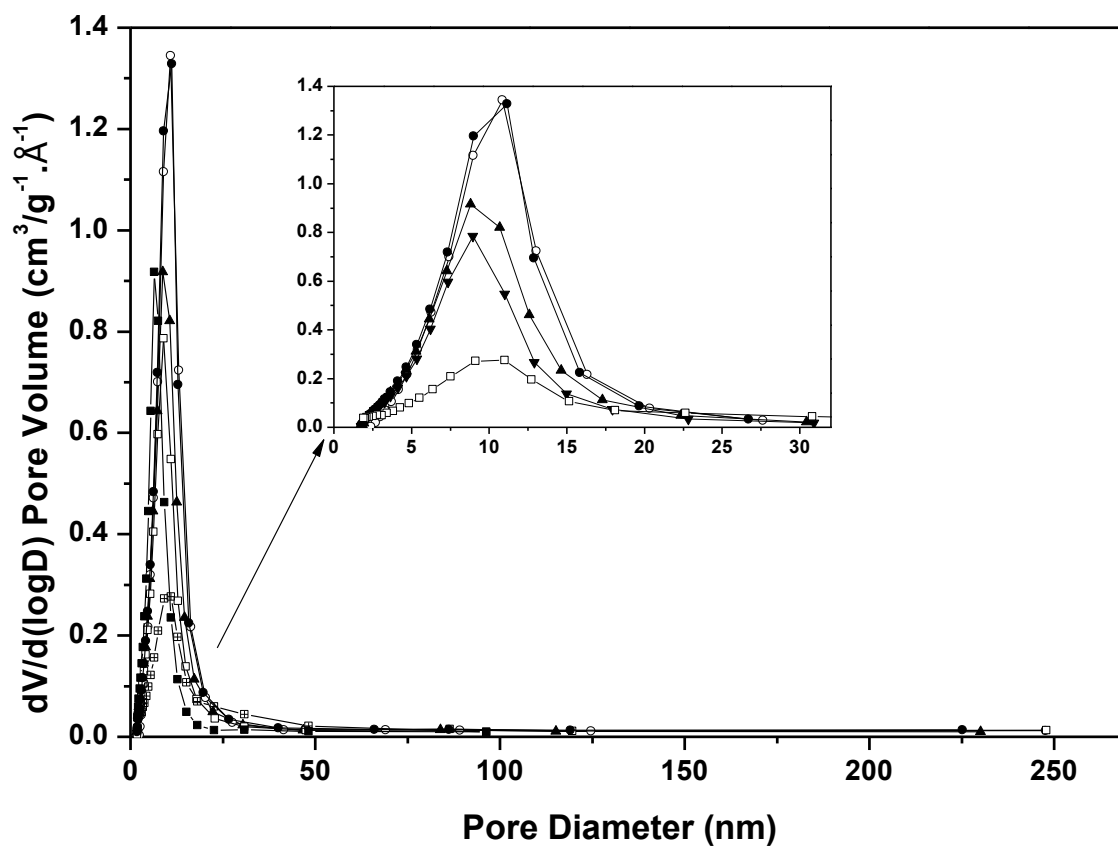


Figure G.8. BJH pore size distribution for (○) 2Ce/Al₂O₃, (●) 5Ce/Al₂O₃, (▲) 16Ce/Al₂O₃, (▼) 26Ce/Al₂O₃, and (□) 52Ce/Al₂O₃ supports

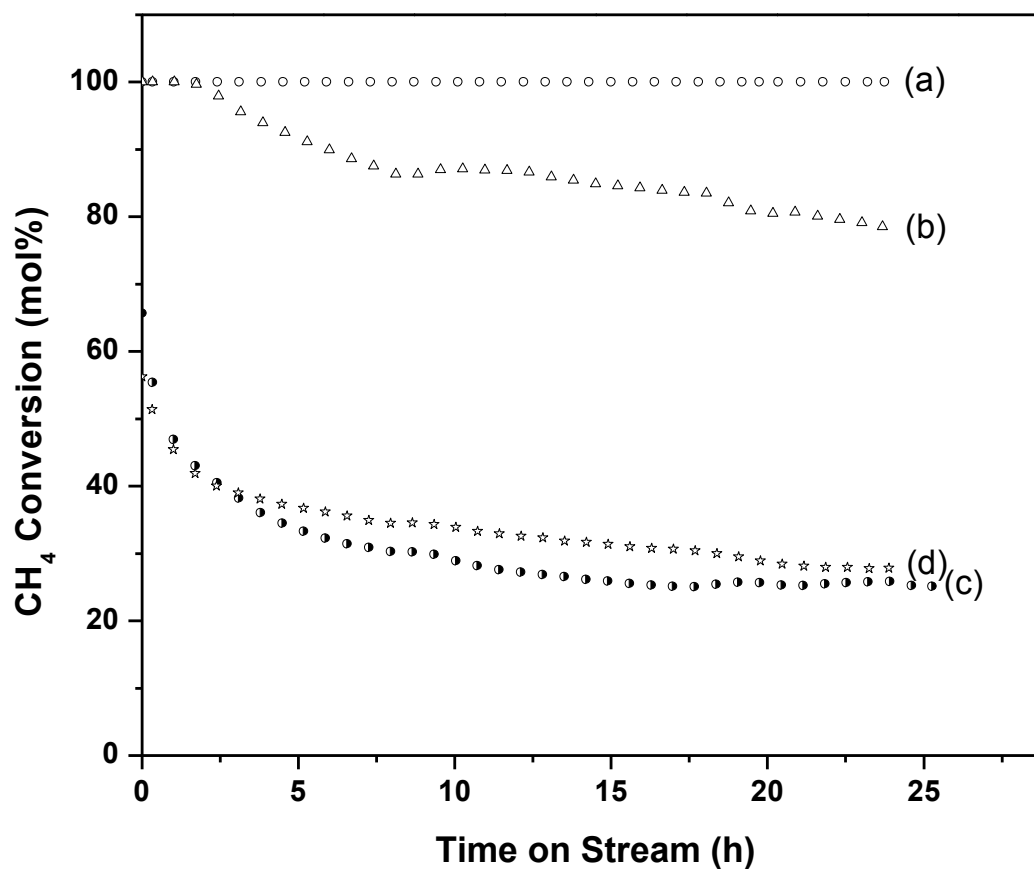


Figure G.9. Dry-TOS results for 3.4Pd/Al₂O₃ (a) and (b) co-2Ce/3.4Pd/Al₂O₃, (c) co-14Ce/3.4Pd/Al₂O₃, and (d) co-47Ce/3.4Pd/Al₂O₃ at 350°C. GHSV=180,000 cm³(STP)·g_{cat}⁻¹·h⁻¹, 1000 ppm CH₄, 20(v/v)% O₂, and the balance He and Ar

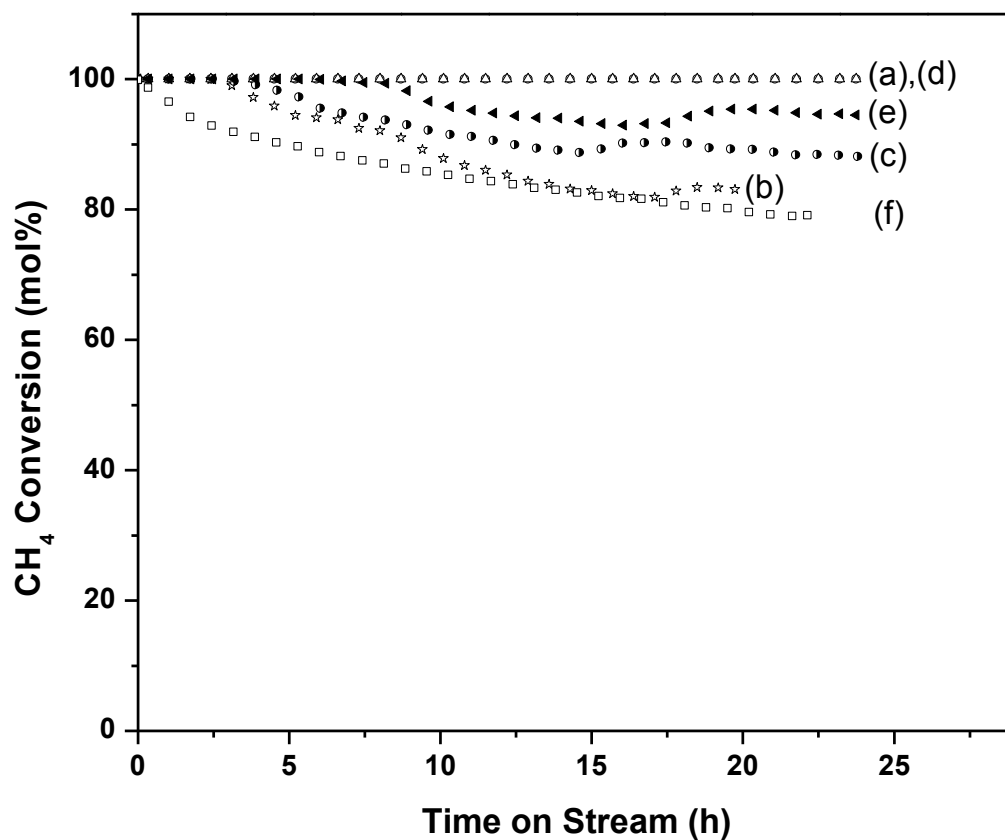


Figure G.10. Dry-TOS results for 3.4Pd/Al₂O₃ (a) and (b) seq-2Ce/3.4Pd/Al₂O₃, (c) seq-6Ce/3.4Pd/Al₂O₃, (d) seq-17Ce/3.4Pd/Al₂O₃, (e) seq-28Ce/3.4Pd/Al₂O₃, and (f) seq-57Ce/3.4Pd/Al₂O₃ at 350°C. GHSV=180,000 cm³(STP).g_{cat}⁻¹.h⁻¹, 1000 ppm CH₄, 20(v/v)% O₂, and the balance He and Ar

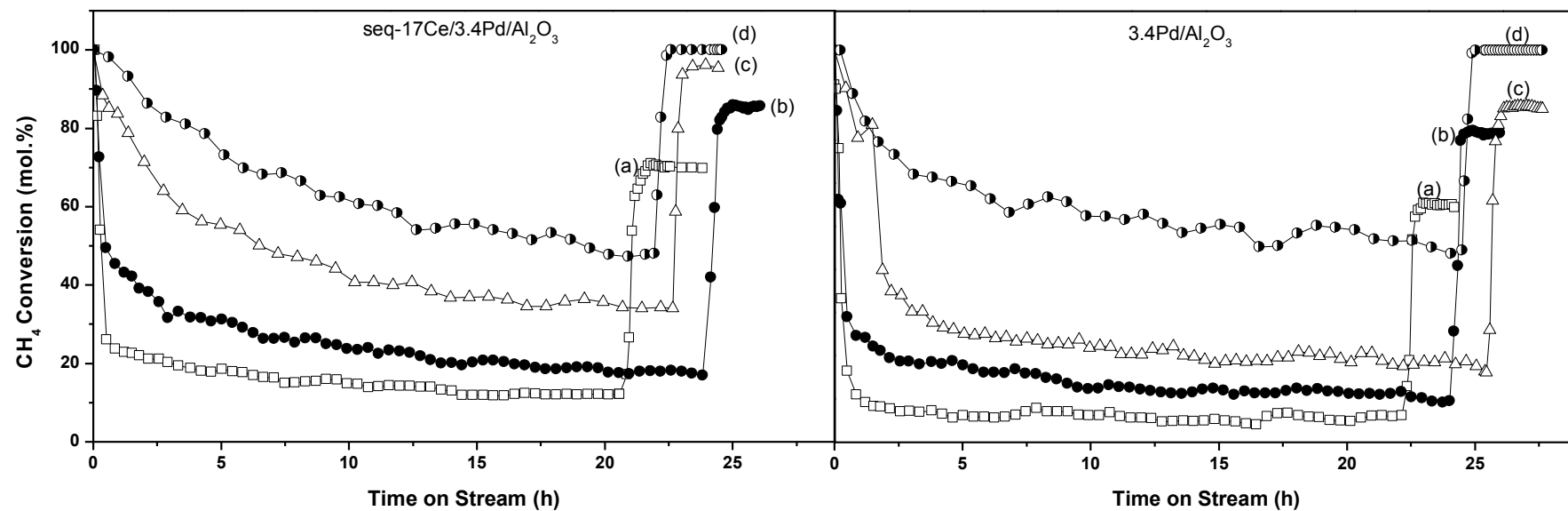


Figure G.11. Wet-TOS results for seq-17Ce/3.4Pd/Al₂O₃ and 3.4Pd/Al₂O₃ catalysts with 2vol.% H₂O. GHSV=180,000 cm³(STP).g_{cat}⁻¹.h⁻¹, 1000 ppm CH₄, 20(v/v)% O₂, and the balance He and Ar. (a) T=310°C, (b) T=330°C, (c) T=350°C, and (d) T=370°C

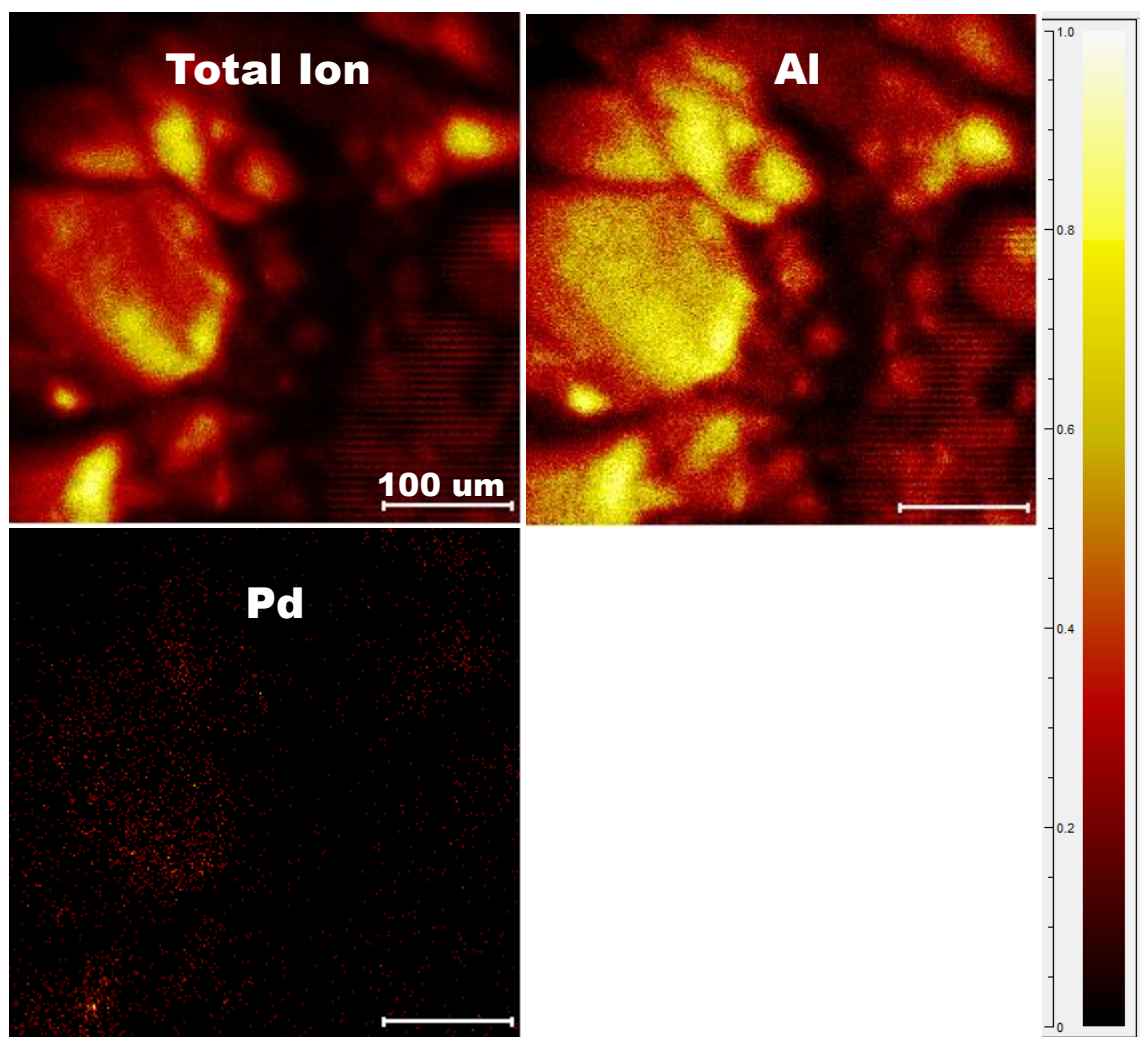


Figure G.12. ToF-SIMS analysis for 3.4Pd/Al₂O₃ catalyst

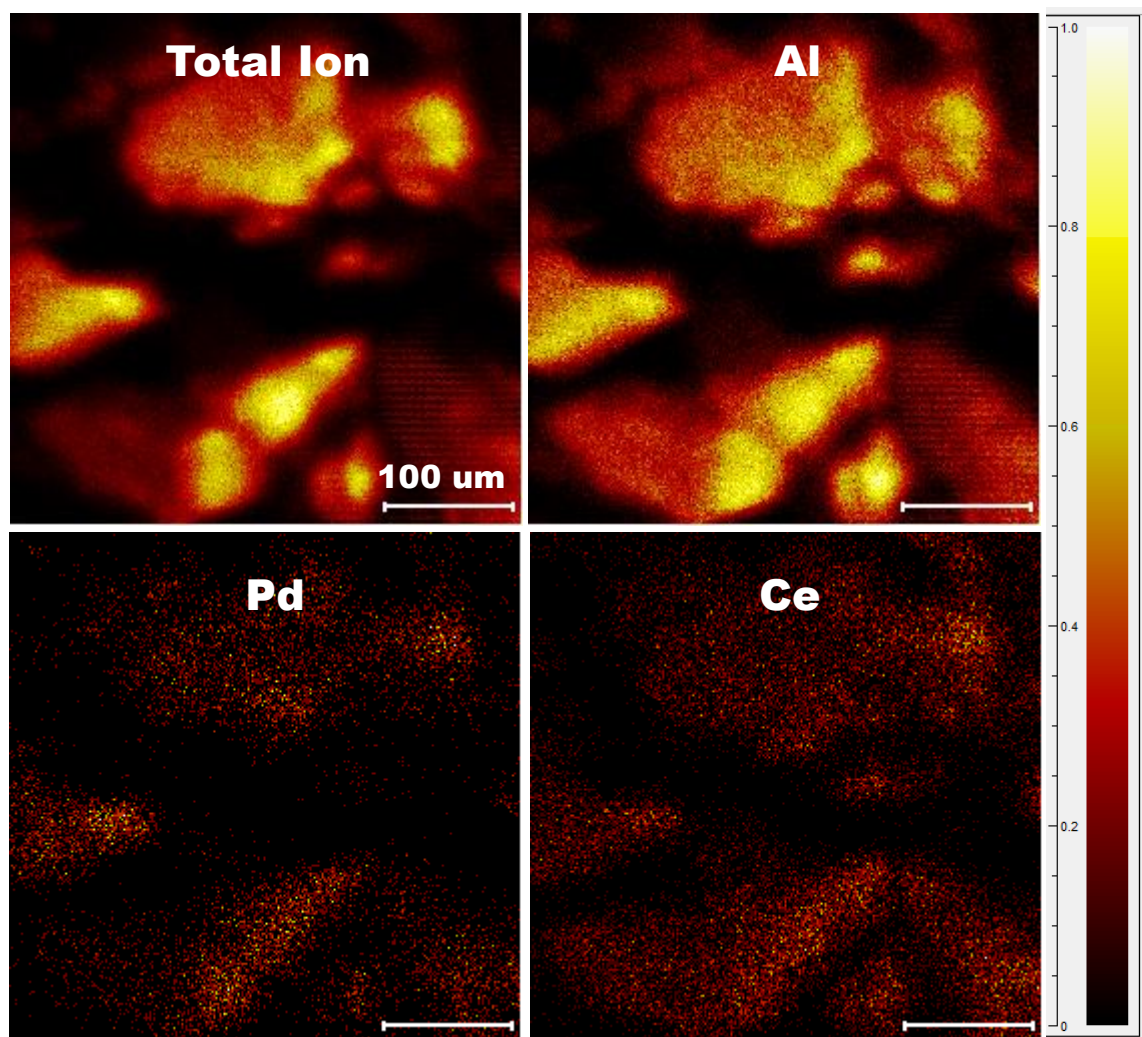


Figure G.13. ToF-SIMS analysis for co-14Ce/3.4Pd/Al₂O₃ catalyst

Table G.1. Properties of calcined catalysts prepared by co-impregnation and sequentially impregnation

Catalyst	methods		
	BET		
	SA	Pore Size	Pore Volume
	m ² /g	nm	cm ³ /g
3.4Pd/Al ₂ O ₃	215	8.3	0.45
co-2Ce/3.4Pd/Al ₂ O ₃	218	8.2	0.45
co-14Ce/3.4Pd/Al ₂ O ₃	170	7.7	0.33
co-47Ce/3.4Pd/Al ₂ O ₃	93	6.2	0.14
seq-2Ce/3.4Pd/Al ₂ O ₃	205	8.6	0.44
seq-6Ce/3.4Pd/Al ₂ O ₃	166	9.3	0.38
seq-17Ce/3.4Pd/Al ₂ O ₃	143	9.5	0.34
seq-28Ce/3.4Pd/Al ₂ O ₃	152	7.1	0.27
seq-57Ce/3.4Pd/Al ₂ O ₃	91	6.3	0.14
2Ce/Al ₂ O ₃	180	9.8	0.44
5Ce/Al ₂ O ₃	196	9.4	0.46
16Ce/Al ₂ O ₃	161	9.0	0.36
26Ce/Al ₂ O ₃	137	8.7	0.29
52Ce/Al ₂ O ₃	76	7.8	0.15

Table G.2. Light-off temperatures for 3.4Pd/Al₂O₃, co-impregnated and sequentially impregnated catalysts. GHSV=180,000 cm³(STP).g_{cat}⁻¹.h⁻¹, 1000 ppm CH₄, 20(v/v)% O₂, and the balance He and Ar

Catalyst	T ₁₀ °C	T ₅₀ °C	T ₉₀ °C
3.4Pd/Al ₂ O ₃	219	273	309
co-2Ce/3.4Pd/Al ₂ O ₃	221	278	314
co-14Ce/3.4Pd/Al ₂ O ₃	254	334	395
co-47Ce/3.4Pd/Al ₂ O ₃	263	351	446
seq-2Ce/3.4Pd/Al ₂ O ₃	214	271	307
seq-6Ce/3.4Pd/Al ₂ O ₃	225	276	310
seq-17Ce/3.4Pd/Al ₂ O ₃	215	264	296
seq-28Ce/3.4Pd/Al ₂ O ₃	223	281	318
seq-57Ce/3.4Pd/Al ₂ O ₃	227	288	332

Table G.3. Ce 3d peaks and $\frac{\text{Ce}^{3+}}{\text{Ce}^{3+}+\text{Ce}^{4+}}$ ratio for co-impregnated catalysts with different loadings of Ce

Catalyst	Ce 3d _{5/2}				Ce 3d _{3/2}				$\frac{\text{Ce}^{3+}}{\text{Ce}^{3+} + \text{Ce}^{4+}}$
	Ce ⁴⁺	Ce ³⁺	Ce ⁴⁺	Ce ⁴⁺	Ce ⁴⁺	Ce ³⁺	Ce ⁴⁺	Ce ⁴⁺	
	eV	eV	eV	eV	eV	eV	eV	eV	%
co-2Ce/3.4Pd/Al ₂ O ₃	882.9	885.0	887.4	898.7	901.0	903.6	906.9	917.0	37.8
co-14Ce/3.4Pd/Al ₂ O ₃	882.9	885.0	888.1	898.7	901.0	903.6	906.9	917.0	18.4
co-47Ce/3.4Pd/Al ₂ O ₃	882.9	885.0	888.4	898.7	901.0	903.6	906.9	917.0	8.5

Table G.4. Ce 3d peaks and $\frac{\text{Ce}^{3+}}{\text{Ce}^{3+}+\text{Ce}^{4+}}$ ratio for xCe/Al₂O₃ supports with different loadings of Ce

Catalyst	Ce 3d _{5/2}				Ce 3d _{3/2}				$\frac{\text{Ce}^{3+}}{\text{Ce}^{3+} + \text{Ce}^{4+}}$
	Ce ⁴⁺	Ce ³⁺	Ce ⁴⁺	Ce ⁴⁺	Ce ⁴⁺	Ce ³⁺	Ce ⁴⁺	Ce ⁴⁺	
	eV	eV	eV	eV	eV	eV	eV	eV	%
2Ce/Al ₂ O ₃	882.9	885.0	887.4	898.7	901.0	903.6	906.9	917.0	32.1
5Ce/Al ₂ O ₃	882.9	885.0	887.4	898.7	901.0	903.6	906.9	917.0	27.7
16Ce/Al ₂ O ₃	882.9	885.0	888.3	898.7	901.0	903.6	906.9	917.0	14.4
26Ce/Al ₂ O ₃	882.9	885.0	888.5	898.7	901.0	903.6	906.9	917.0	12.0
52Ce/Al ₂ O ₃	882.9	885.0	888.7	898.7	901.0	903.6	907.8	917.0	8.9

Appendix H: Mass Transfer Effects

H.1 Internal Mass Transfer Calculation

In order to determine if the kinetic model is controlled by internal mass transfer, the theoretical calculations are presented in this appendix. Table H.1 presents the physical properties of the catalyst bed for 6.5Pd/Al₂O₃ catalyst. d_{pore} , the average pore size of the catalyst is calculated as follows:

$$d_{\text{pore}} = \frac{4V_0}{S_{\text{BET}}} \quad \text{H.1}$$

ε_p , particle porosity is the ratio of the catalyst pore volume to the total volume of the catalyst that is defined in Equation H.2.

$$\varepsilon_p = \frac{V_0}{V_0 + 1/\rho_s} \quad \text{H.2}$$

The bed density, ρ_{bed} , is calculated as the mass of catalyst per total volume of the catalyst bed. The bed volume is the total bed of both catalyst and SiC diluent.

$$\rho_{\text{bed}} = \frac{W_{\text{cat}}}{V_{\text{bed}}} \quad \text{H.3}$$

$$\rho_{\text{bSiC}} = \frac{m}{V_{\text{bed}}} \quad \text{H.4}$$

m is the total mass of bed as:

$$m = W_{\text{cat}} + W_{\text{SiC}} \quad \text{H.5}$$

$$\varepsilon_{\text{bSiC}} = 1 - \frac{\rho_{\text{bSiC}}}{\rho_{\text{solid}}} \quad \text{H.6}$$

ρ_{solid} is defined as the total density of both porous catalyst and non-porous SiC:

$$\rho_{\text{solid}} = \frac{\rho_{\text{cat}}V_{\text{cat}} + \rho_{\text{SiC}}V_{\text{SiC}}}{V_{\text{cat}} + V_{\text{SiC}}} \quad \text{H.7}$$

Table H.1. Physical properties of catalyst bed consists of 6.5Pd/Al₂O₃

Parameter	Definition	Value
W_{cat}	Catalyst mass (g)	0.0833
W_{SiC}	Mass of SiC (g)	2.1
L_{bed}	Length of bed (cm)	4.2
d_{bed}	Internal diameter of bed (cm)	0.703
V_{bed}	Volume of bed (cm ³)	1.63
m	mass of bed (g)	2.1833
S_{BET}	BET surface area (m ² .g ⁻¹)	2.180×10 ⁵
V_0	Total pore volume of catalyst (cm ³ .g ⁻¹)	0.433
d_{pore}	Pore size (cm)	7.89×10 ⁻⁷
ρ_s	6.5%Pd/Al ₂ O ₃ density (g.cm ⁻³)	4.13
ρ_{bed}	Bed density (g.cm ⁻³)	0.051
ρ_{SiC}	SiC density (g.cm ⁻³)	3.21
ρ_{cat}	Catalyst density (g.cm ⁻³) density of both pores of catalyst and solid particles	1.488
ρ_{bSiC}	Catalyst bed (g.cm ⁻³) density of both catalyst and SiC	1.337
ε_p	Particle porosity	0.64
d_p	Particle diameter (cm)	2.220×10 ⁻²
τ^a	Tortuosity factor	3
σ^a	Constriction factor	0.8
$\varepsilon_{\text{bSiC}}$	Bed porosity	0.57

^a Typical values obtained from [92]

Table H.2 presents the reaction operating condition for TOS experiment using 5000 ppmv CH₄, 20(v/v)% O₂, and the balance He for GHSV=180,000 cm³(STP).g_{cat}⁻¹.h⁻¹. The effective diffusivity, D_{eff} , is calculated at T=330°C and P=1 atm. σ_i , the Lennard-Jones characteristic length for component i (i=He or CH₄) is defined in Equation H.8 [89].

$$\sigma_i = 2.44 \left(\frac{T_{c_i}}{P_{c_i}} \right)^{1/3} \quad \text{H.8}$$

$$\sigma_{\text{CH}_4-\text{He}} = \frac{1}{2} (\sigma_{\text{CH}_4} + \sigma_{\text{He}}) \quad \text{H.9}$$

$$\frac{\varepsilon_i}{k} = 0.77 T_{c_i} \quad \text{H.10}$$

$$\frac{\varepsilon_{\text{CH}_4-\text{He}}}{k} = \sqrt{\frac{\varepsilon_{\text{CH}_4}}{k} \times \frac{\varepsilon_{\text{He}}}{k}} \quad \text{H.11}$$

$$T^* = \frac{T}{\frac{\varepsilon_{\text{CH}_4-\text{He}}}{k}} \quad \text{H.12}$$

$$\Omega_{\text{D}_{\text{CH}_4-\text{He}}} = \frac{1.06036}{T^{*0.15610}} + \frac{0.19300}{\exp(0.47635T^*)} \quad \text{H.13}$$

$$D_{\text{CH}_4-\text{He}} = \frac{0.0018583}{P\sigma_{\text{CH}_4-\text{He}}^2\Omega_{\text{D}_{\text{CH}_4-\text{He}}}} \sqrt{T^3\left(\frac{1}{M_{\text{wCH}_4}} + \frac{1}{M_{\text{wHe}}}\right)} \quad \text{H.14}$$

where P is in atm, T is in K, and $D_{\text{CH}_4-\text{He}}$ is in $\text{cm}^2.\text{s}^{-1}$.

$$D_{\text{CH}_4-\text{He}}^{\text{eff}} = \frac{\varepsilon_p\sigma}{\tau} D_{\text{CH}_4-\text{He}} \quad \text{H.15}$$

$$D_K = \frac{8d_{\text{pore}}}{3} \sqrt{\frac{RT}{2\pi M_{\text{wfeed}}}} \quad \text{H.16}$$

where T is in K, M_{wfeed} in kg.mol^{-1} , and d_{pore} in m.

$$D_K^{\text{eff}} = \frac{\varepsilon_p\sigma}{\tau} D_K \quad \text{H.17}$$

$$\frac{1}{D_{\text{eff}}} = \frac{1}{D_{\text{CH}_4-\text{He}}^{\text{eff}}} + \frac{1}{D_K^{\text{eff}}} \quad \text{H.18}$$

Equations H.8-H.18 are presented in [87,89,92].

Table H.2. Operating condition for TOS experiment using 6.5Pd/Al₂O₃ catalyst

Parameter	Definition	Value
T	Reaction temperature (K)	603
P	Total pressure (Pa)	101325
R	Gas constant (Pa.m ³ .mol ⁻¹ .K ⁻¹)	8.314
y _{CH4}	CH ₄ volume fraction (-)	0.005
y _{O2}	O ₂ volume fraction (-)	0.200
y _{He}	He volume fraction (-)	0.793
Mw _{He}	He molecular weight (g.mol ⁻¹)	4
P _{cHe}	He critical pressure (kPa)	229
T _{cHe}	He critical temperature (K)	5.2
Mw _{CH4}	CH ₄ molecular weight (g.mol ⁻¹)	16.04
P _{cCH4}	CH ₄ critical pressure (kPa)	4640
T _{cCH4}	CH ₄ critical temperature (K)	190.7
Mw _{feed}	Feed molecular weight (g.mol ⁻¹)	9.65
P _{CH4} ⁰	Feed CH ₄ partial pressure (Pa)	506.62
v ₀	Total volumetric flow rate (m ³ .s ⁻¹) at T=330°C	9.20E-06
F _{CH4} ⁰	Feed CH ₄ molar flow (mol.s ⁻¹ (STP))	9.29E-07
r _t	Radius of reactor (m)	3.52E-03
A	Cross sectional area of the reactor (m ²)	3.88E-05
V	Superficial gas velocity (m.s ⁻¹) at T=330°C	0.237
G	Superficial mass velocity (kg.m ⁻² .s ⁻¹)	0.046
(ε/k) _{He}	He Lennard-Jones energy/Boltzmann's constant (-)	4.00
σ _{He}	He Lennard-Jones characteristic length (Å)	3.22
(ε/k) _{CH4}	CH ₄ Lennard-Jones energy/Boltzmann's constant (-)	146.84
σ _{CH4}	CH ₄ Lennard-Jones characteristic length (Å)	3.93
(ε/k) _{CH4-He}	Lennard-Jones energy/Boltzmann's constant (-)	24.25
σ _{CH4-He}	Lennard-Jones characteristic length (Å)	3.57
T*	(-)	24.87
Ω	Collision integral (-)	0.64
τ	Tortuosity factor (-)	3
σ	Constriction factor (-)	0.8
D _{CH4-He}	Binary bulk diffusivity (m ² .s ⁻¹)	1.87E-04
D _{CH4-He} ^{eff}	Bulk effective diffusivity (m ² .s ⁻¹)	3.20E-05
D _K	Knudsen diffusivity (m ² .s ⁻¹)	6.06E-06
D _K ^{eff}	Effective Knudsen diffusivity (m ² .s ⁻¹)	1.03E-06
D _{eff}	Effective diffusivity (m ² .s ⁻¹)	1.00E-06

Applying the calculated D_{eff} value into kinetic equations in Chapters 4 and 5, η values were obtained in the range of 0.24-0.86 emphasizing the internal mass transfer control.

H.2 External Mass Transfer Calculation

Particle Reynolds number is calculated as follows:

$$\text{Re} = \frac{\rho_g d_p u_s}{\mu(1-\varepsilon_{\text{bSiC}})} \quad \text{H.19}$$

where d_p is the particle diameter, μ is the dynamic gas viscosity, and $\varepsilon_{\text{bSiC}}$ is the bed porosity.

ρ_g , the gas density and u_s the superficial gas velocity are defined as below:

$$\rho_g = \frac{PM_{\text{wfeed}}}{RT} \quad \text{H.20}$$

$$u_s = \frac{v_0}{A} \quad \text{H.21}$$

Schmidt number is calculated using Equation H.22.

$$\text{Sc} = \frac{\mu}{\rho_g D_{\text{CH}_4-\text{He}}} \quad \text{H.22}$$

The external mass transfer coefficient (k_c) is calculated using Equation H.23. The Sherwood number is obtained using Equations H.24-H.25.

$$\text{Sh} = \frac{k_c d_p}{D_{\text{CH}_4-\text{He}}} \quad \text{H.23}$$

In a gas phase system with $\text{Re} < 2000$ and $0.416 < \varepsilon_{\text{bSiC}} < 0.788$, j_D factor is calculated using Equation H.24 [125].

$$j_D \varepsilon_{\text{bSiC}} = 0.357 \text{Re}^{-0.359} \quad \text{H.24}$$

$$j_D = \frac{\text{Sh}}{\text{ReSc}^{1/3}} \quad \text{H.25}$$

Finally, Mears criterion is calculated as follows:

$$C_M = \frac{-r_{CH_4}^m \rho_{bSiC} d_p n}{2k_c C_{CH_4}}$$

H.26

The calculated numbers are reported in Table H.3.

Table H.3. Details of calculations for Mears criterion factor for 6.5Pd/Al₂O₃ catalyst at T=330°C

Parameter	Definition	Value
T	Reaction temperature (K)	603
P	Total pressure (Pa)	101325
M _{wfeed}	Feed molecular weight (g.mol ⁻¹)	9.65
R	Gas constant (Pa.m ³ .mol ⁻¹ .K ⁻¹)	8.314
v ₀	Total volumetric flow rate (m ³ .s ⁻¹)	9.20E-06
A	Cross sectional area of the reactor (m ²)	3.88E-05
d _p	Particle diameter (m)	2.22E-04
u _s	Superficial gas velocity (m.s ⁻¹) at T=330°C	0.237
ε _{bSiC}	Bed porosity (-)	0.57
D _{CH₄-He}	Binary bulk diffusivity (m ² .s ⁻¹)	1.87E-04
ρ _g	Gas density (kg.m ³)	1.95E-01
μ	Gas dynamic viscosity (kg.m ⁻¹ .s ⁻¹)	3.22E-05
Re	Reynolds Number (-)	0.74
Sc	Schmidt Number (-)	0.88
j _D	j _D factor (-)	0.67
Sh	Sherwood Number (-)	0.49
k _c	External mass transfer coefficient (m.s ⁻¹)	0.417
C _{CH₄}	Bulk concentration of CH ₄ (mol.m ⁻³)	0.101
-r _{CH₄} ^m	CH ₄ reaction rate (mol.kg ⁻¹ .s ⁻¹)	6.21E-03
ρ _{bSiC}	Catalyst bed density of both catalyst and SiC (kg.m ⁻³)	1.337E+03
n	Order of CH ₄ oxidation reaction (-)	1
C _M	Mears criterion factor (-)	0.02

For C_M < 0.15 the mass transfer from the bulk gas phase to the surface of the catalyst is negligible. In our study, is obtained as 0.02, indicating no external mass transfer control.

H.3 Pressure Drop Calculation over Catalyst Bed

$$\frac{dP}{dW} = - \frac{G}{\rho_g d_p} \left(\frac{1}{\varepsilon_{bSiC}^3} \right) \left[\frac{150(1-\varepsilon_{bSiC})\mu}{d_p} + 1.75G \right] \frac{1}{A \rho_{bSiC}} \quad H.27$$

where G and A are defined as superficial mass velocity ($\text{kg.m}^{-2}.\text{s}^{-1}$) and cross sectional area of the reactor (m^2).

So, ΔP over the entire catalyst bed is 2.4 kPa.

Appendix I: CH₄ Oxidation over PdO-ZrO_x/Al₂O₃ in the Presence of H₂O

I.1 Catalyst Properties

The Pd content measured by AAS analysis was obtained 3.4wt.% as an average loading for all catalysts. Figure I.1 shows the effect of different Zr loadings on the Pd/Al and Zr/Al surface composition, measured by XPS. As the Zr bulk composition increases (reported as the Zr to Al atom ratio i.e. (Zr/Al)_b), the (Zr/Al)_s increases. A higher amount of Zr in the catalyst causes more blockages of alumina pores consequently more Zr stays on the surface [126]. To identify the crystal size of ZrO₂ at different Zr loadings, a XRD analysis was performed. Almost the same quantity of Pd appears on the surface of 0wt.% and 1.5wt.%Zr-catalysts. Since the Zr loading is very low, not many Al₂O₃ pores are blocked [127]. Thus the conditions for Pd to enter into the pores or to stay on the surface are very similar in both catalysts. The slight decrease of Pd on the surface (1.5wt%Zr) is maybe due to the coverage through ZrO₂, so that not all of the Pd could be detected on the surface. Increasing the Zr ratio to 25wt.% leads to a high dispersion of Pd on the surface (higher (Pd/Al)_s). Amaira et al., Souza and Gou argued that the Zr particles block the Al₂O₃ pores and prevent the penetration of Pd particles into the pores [126,128,129].

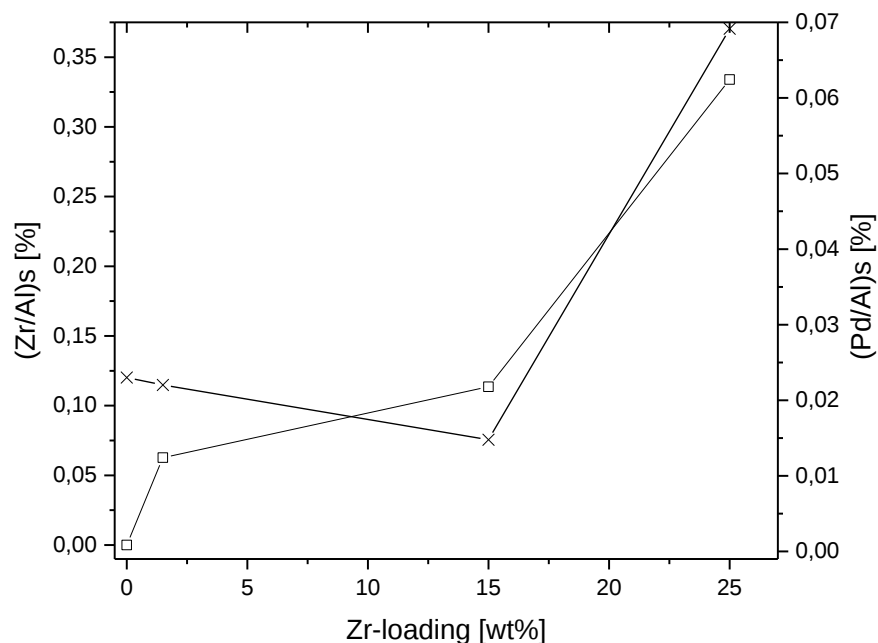


Figure I.1. XPS analysis, Zr on the surface (square), Pd on the surface (cross)

(Pd/Al)_s decreased as the Zr loading increased from 0wt.% to 15wt.% which is due to some Pd blockage caused by Zr. However, higher loading of Zr (25wt.%) caused the opposite effect that can be explained by blocking Al₂O₃ pores due to high Zr loading (see explanation before).

Figure I.2 shows the XRD analysis for 3.4Pd/Al₂O₃ and sequential impregnated catalysts with different loadings of Zr. Major peaks were found at $2\theta=35.55^\circ$ and 59.96° and 71.55° for tetragonal ZrO₂ and at $2\theta=39.49^\circ$ and 64.55° for tetragonal PdO, respectively.

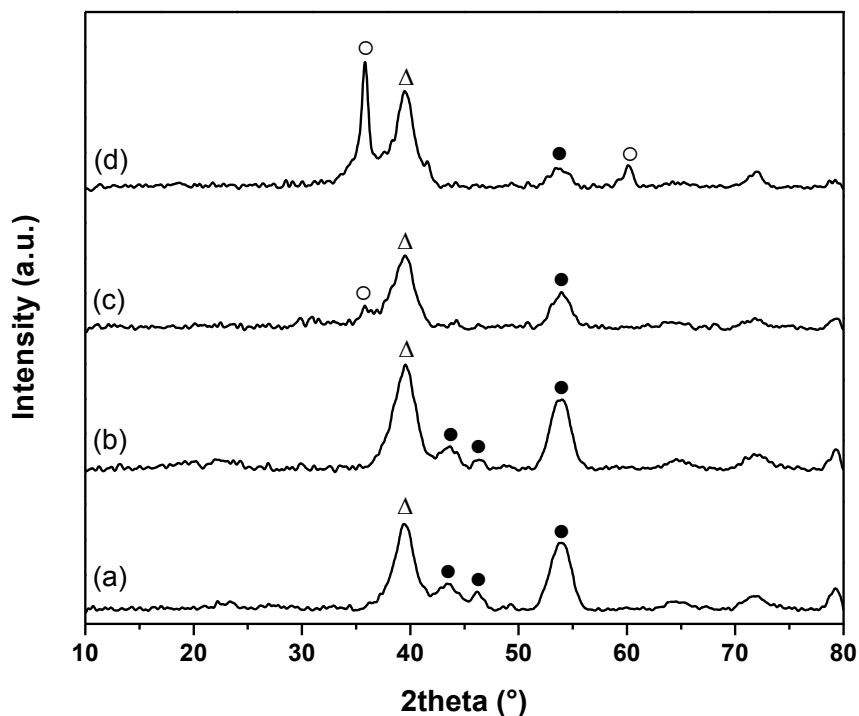


Figure I.2. XRD patterns for 3.4Pd/Al₂O₃ (a) and sequential impregnated catalysts with different loadings of Zr: (b) seq-1.5Zr/3.4Pd/Al₂O₃, (c) seq-15Zr/3.4Pd/Al₂O₃, (d) and seq-25Zr/3.4Pd/Al₂O₃. Δ PdO, ● Al₂O₃, ○ ZrO₂

Table I.1 shows the crystal size of PdO and of ZrO₂. The PdO crystal size does not change by adding different loadings of Zr as it is measured between 6-7 nm for all catalysts. The ZrO₂ crystal size measured for the seq-25Zr/3.4Pd/Al₂O₃ catalyst that shows ZrO₂ crystals are 2.8 bigger than PdO crystals.

Table I.1. Properties of calcined 3.4Pd/Al₂O₃ and sequential impregnated catalysts with different loadings of Zr

	BET	Pore	Pore	PdO	ZrO ₂
	SA ^a	Volume ^a	Size ^a	Crystallite Size ^b	Crystallite Size ^b
Catalysts	m ² /g	cm ³ /g	nm	nm	nm
3.4Pd/Al ₂ O ₃	215	0.45	8.3	7	-
seq-1.5Zr/3.4Pd/Al ₂ O ₃	192	0.41	8.5	6	-
seq-15Zr/3.4Pd/Al ₂ O ₃	139	0.31	8.6	6	-
seq-25Zr/3.4Pd/Al ₂ O ₃	83	0.18	8.6	7	17

^a Determined by N₂ adsorption at 77K

^b PdO (1 0 1) and ZrO₂ (111) obtained by XRD

I.2 Catalyst Activities

Figure I.3 shows the TPO results for the 3.4Pd/Al₂O₃ and sequential impregnated catalysts with different loadings of Zr.

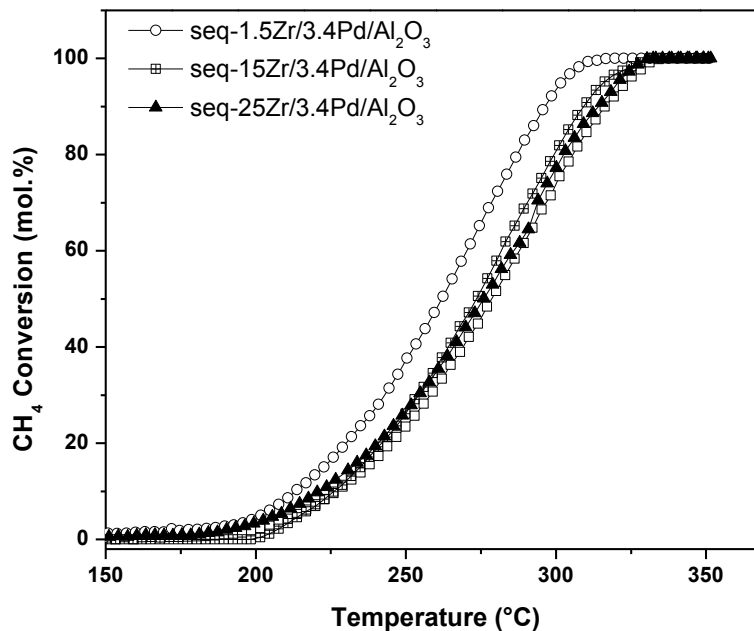


Figure I.3. Temperature Programmed Oxidation profile. Effect of different loadings of Zr on the initial activity of 3.4Pd/Al₂O₃ as a function of temperature. GHSV=180,000 cm³(STP).g_{cat}⁻¹.h⁻¹, 1000 ppm CH₄, 20(v/v)% O₂, and the balance He and Ar

The seq-1.5Zr/3.4Pd/Al₂O₃ catalyst shows the highest initial activity. Increasing the Zr content resulted in less active catalysts as the loading of Zr increased. The light-off temperatures corresponding to 10%, 50%, and 90% CH₄ conversion are shown in Table I.2. Since the standard deviation for T₅₀ for seq-15Zr/3.4Pd/Al₂O₃, seq-25Zr/3.4Pd/Al₂O₃, and 3.4Pd/Al₂O₃ catalysts is between 2.5 and 6.9°C, no significant different between the initial activity of the three catalysts can be observed.

Table I.2. Light-off temperatures for 3.4Pd/Al₂O₃ and sequential impregnated catalysts with different loadings of Zr

Catalyst	T ₁₀	T ₅₀	T ₉₀
	°C	°C	°C
3.4Pd/Al ₂ O ₃	226±5	277±2.5	316.2±2
seq-1.5Zr/3.4Pd/Al ₂ O ₃	214±5	262.4±5	295.6±5
seq-15Zr/3.4Pd/Al ₂ O ₃	226±1	274.1±4	310.2±8
seq-25Zr/3.4Pd/Al ₂ O ₃	221±4	276±7	315.2±7

Effect of H₂O concentration on the stability of Zr-supported catalysts in CH₄ oxidation was performed using 2vol.% and 5vol.% H₂O into the feed stream. Figures I.4 and I.5 show the wet-TOS results at 350°C for 3.4P/Al₂O₃ and sequential catalysts with different loadings of Zr.

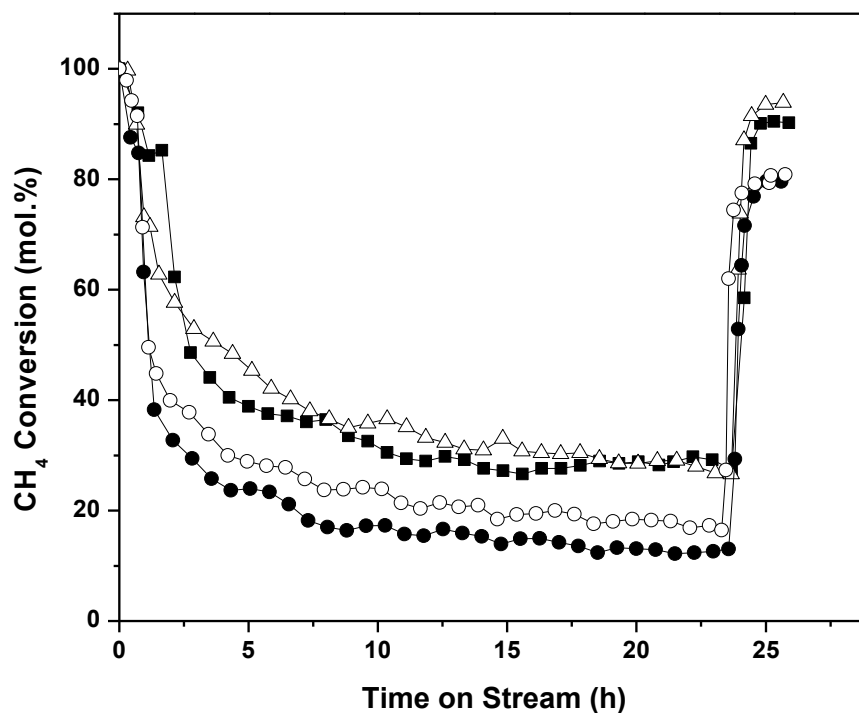


Figure I.4. Wet-TOS results for (■) 3.4Pd/Al₂O₃, (△) seq-1.5Zr/3.4Pd/Al₂O₃, (●) seq-15Zr/3.4Pd/Al₂O₃, and (○) seq-25Zr/3.4Pd/Al₂O₃ catalysts at 350 °C with 2vol. % H₂O. GHSV=180,000 cm³(STP).g_{cat}⁻¹.h⁻¹, 1000 ppm CH₄, 20(v/v)% O₂, and the balance He and Ar

All catalysts showed a fast decrease in CH₄ conversion once H₂O was injected. An exponential decrease followed by a linear decrease was observed for all catalysts. seq-1.5Zr/3.4Pd/Al₂O₃ catalyst showed the highest activity over 24h compared to seq-15Zr/3.4Pd/Al₂O₃ and seq-25Zr/3.4Pd/Al₂O₃ catalysts.

However, the performance of the 3.4%Pd catalyst is very close to 1.5%Zr and after 20h both catalysts showed the same conversion at around 27 mol%. The CH₄ conversion for 15%Zr and 25%Zr is much lower than for 1.5%Zr and 3.4%Pd. At t=24h, the difference in CH₄ conversion is about 15mol% and 11mol%, respectively. Upon removing H₂O from the system, an increase of catalytic activity can be seen for every catalyst. 1.5%Zr and 3.4%Pd

regain high conversion (94 mol% and 90 mol% conversion, respectively), whereas 15%Zr and 25%Zr only achieve 80 mol% of conversion after removing H₂O.

Further experiments with 5vol.% H₂O were done to better understanding the impact of H₂O on different supports. The results are shown in Figure I.5.

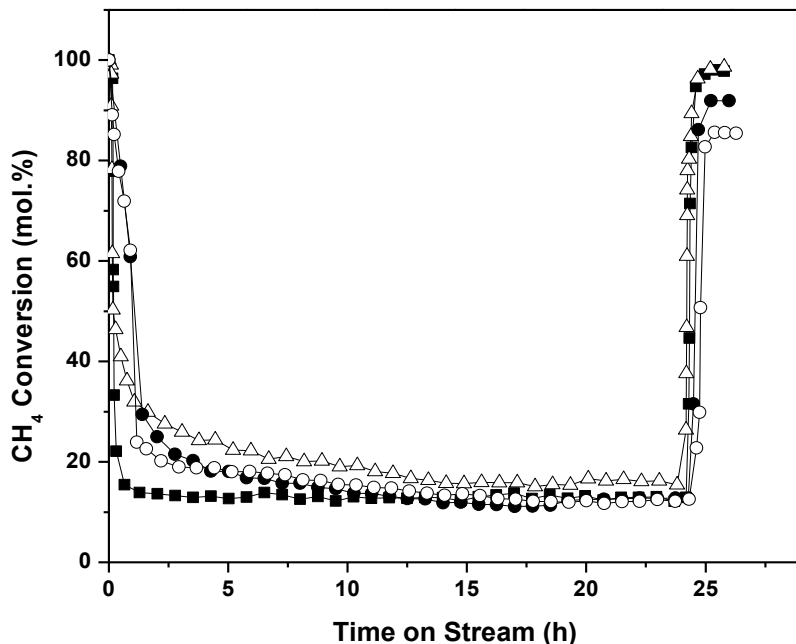


Figure I.5. Wet-TOS results for (■) 3.4Pd/Al₂O₃, (Δ) seq-1.5Zr/3.4Pd/Al₂O₃, (●) seq-15Zr/3.4Pd/Al₂O₃, and (○) seq-25Zr/3.4Pd/Al₂O₃ catalysts at 350°C with 5vol.% H₂O. GHSV=180,000 cm³(STP).g_{cat}⁻¹.h⁻¹, 1000 ppm CH₄, 20(v/v)% O₂, and the balance He and Ar

With 5vol.% H₂O, the sequential catalysts show a better stability than 3.4Pd/Al₂O₃ catalyst in the following order: 1.5Zr/3.4Pd/Al₂O₃ > 15Zr/3.4Pd/Al₂O₃ > 25Zr/3.4Pd/Al₂O₃ for the first 5h. The CH₄ conversion for both seq-15Zr/3.4Pd/Al₂O₃ and seq-25Zr/3.4Pd/Al₂O₃ catalysts reached to 18% after 5h and continued to drop to 12% from t=5h to t=24h. In the case of 3.4Pd/Al₂O₃ catalyst a fast decrease in CH₄ conversion was observed in the first 2h. Then the conversion remained constant at 12% from t=2h to t=24h. The seq-15Zr/3.4Pd/Al₂O₃ and

seq-25Zr/3.4Pd/Al₂O₃ catalysts were more stable than 3.4Pd/Al₂O₃ catalyst only at the beginning of TOS experiment, as all three catalysts reached the same conversion at t=24h. The seq-1.5Zr/3.4Pd/Al₂O₃ catalyst showed highest activity for the whole 24h TOS, however, it was more significant for the first 10h. Upon removing H₂O, the CH₄ conversion reached to 98% for 3.4Pd/Al₂O₃ and seq-1.5Zr/3.4Pd/Al₂O₃ catalysts, 92% and 85% for seq-15Zr/3.4Pd/Al₂O₃ and seq-25Zr/3.4Pd/Al₂O₃ catalysts, respectively.

Experiments were performed with 10vol.% extra water at 425°C simulating the real condition in a catalytic converter (10-15vol.% water vapor, < 500°C). This setting was chosen, since no deactivation could be detected neither with 5vol.% extra water at 425°C nor with 10vol.% extra water at 450°C. After 24h the water feeding was stopped. The aim was to investigate the faster oxygen mobility of ZrO₂ at high temperatures published in the literature [17,130]. Figure I.6 presents the results for 3.4%Pd with 1.5%Zr, 15% Zr and 25% =Zr at this condition. 3.4%Pd shows with 78 mol% of CH₄ conversion (after 24 hours) the highest catalytic activity and the slowest deactivation during the stability test. The conversion of CH₄ for the catalysts with Zr content decreases in the following order: 1.5% Zr > 15% Zr > 25% Zr. After removing the water, all catalysts immediately regain 100 mol% of conversion.

This outcome is unexpected, since ZrO₂ is well known for its high thermal stability and for its high oxygen mobility at higher temperatures [17,130]. Moreover Ciuparu published that the effect of support becomes significant having temperatures of 700K (or above) [130]. However, in the experiment faster deactivation and lower conversion occurs for the ZrO₂ supported catalysts than for 3.4%Pd catalyst. Consequently other aspects like structural properties have an influence on the catalytic activity at higher temperature. Amairia and

Souza argued that the surface area of the catalyst decreases having a higher Zr loading due to the ZrO_2 blockage of the pores. Smaller surface area leads to a lower catalytic activity [127,129]. By looking at Figure I.6 it can be seen that the catalytic activity matches with the decreasing magnitude of surface areas (from 3.4%Pd to 3.4%Pd/25%Zr). Sintering occurs for all catalysts, but having a bigger surface area more palladium active sites are available and losing some of them is less effective than for catalysts with a smaller surface area.

Considering the result with 2vol.% water at 350°C (Figure I.4), a further suggestion can be made. At this setting 3.4%Pd was as good as 1.5%Zr and better than 15%Zr and 25%Zr. The reason is mentioned to be due to low water inhibition and good oxygen exchange of the catalyst with the gas phase. The oxygen exchange rate of the support with PdO is slower, thus the support effect is not significant at this condition. The same behavior can cause the results with 10vol.% water at 425°C. At this temperature the water amount (10vol.%) may be low as well as the hydroxyl coverage of palladium active sites. The oxygen exchange between gas phase and catalyst is fast, making the oxygen mobility of the support negligible. Consequently the larger surface area of 3.4%Pd leads to the better catalytic activity seen in Figure I.6. To verify this explanation, further investigation with higher amounts of water has to be done. The activity of 3.4%Pd should decrease more than the activities of the ZrO_2 supported catalysts.

I.3 Discussion

The higher initial activity of seq-1.5Zr/3.4Pd/ Al_2O_3 catalyst than 3.4Pd/ Al_2O_3 catalyst is consistent with the results reported in the literature [128,129]. Gou et al. showed the highest catalytic activity was found with a Zr content of 2wt.% and the activity decreased by

increasing the Zr loading ($> 10\text{wt.}\%$) [128]. ZrO_2 is reported to have the oxygen mobility three times higher than Al_2O_3 [131] and a small amount of ZrO_2 may enhance the oxygen exchange and consequently improve the catalytic activity.

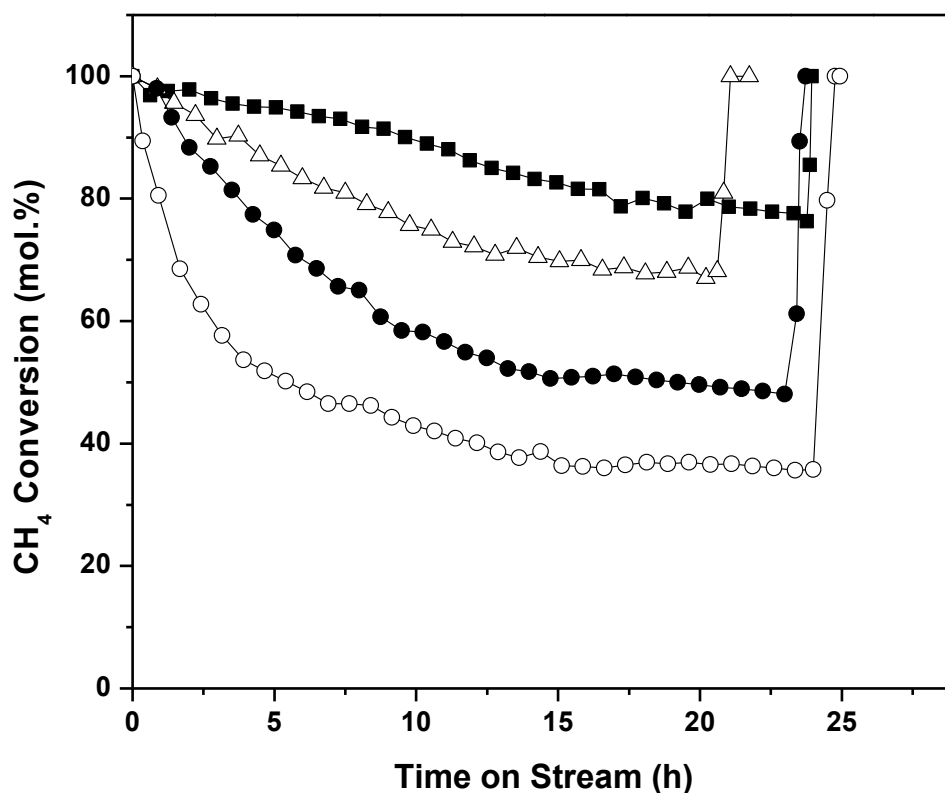


Figure I.6. Wet-TOS results for (■) $3.4\text{Pd}/\text{Al}_2\text{O}_3$, (Δ) $\text{seq-1.5Zr}/3.4\text{Pd}/\text{Al}_2\text{O}_3$, (●) $\text{seq-15Zr}/3.4\text{Pd}/\text{Al}_2\text{O}_3$, and ($\circ$) $\text{seq-25Zr}/3.4\text{Pd}/\text{Al}_2\text{O}_3$ catalysts at 425°C with $10\text{vol.}\% \text{H}_2\text{O}$. $\text{GHSV}=180,000 \text{ cm}^3(\text{STP}).\text{g}_{\text{cat}}^{-1}.\text{h}^{-1}$, 1000 ppm CH_4 , $20(\text{v/v})\% \text{O}_2$, and the balance He and Ar

On the other hand, increasing the Zr content leads to the formation of higher amount of metastable tetragonal ZrO_2 , which decreases the catalytic activity [129,132,133]. The XRD results shown in Figure I.2 confirms the presence of tetragonal ZrO_2 in $\text{seq-25Zr}/3.4\text{Pd}/\text{Al}_2\text{O}_3$ catalyst. The BET results may also play a role in terms of the catalyst activity. The lower

surface area and lower pore volume at higher loadings of Zr explain the lower CH₄ conversion for seq-15Zr/3.4Pd/Al₂O₃ and for seq-25Zr/3.4Pd/Al₂O₃ [127,128].

Increasing the amount H₂O in the feed stream leads to a lower conversion of CH₄. According to Schwartz et al. the accumulation of hydroxyl groups occurs on the surface of the catalyst leads to blockage of the active sites [34]. Having more H₂O in the reaction, more active sites are not available, which causes the lower catalytic activity. On the other hand, Burch et al. [117] claimed that the catalytic deactivation is due to the reaction of H₂O with active palladium and form inactive Pd(OH)₂. Moreover, this reaction is favored at lower temperature (< 450°C), whereas the reverse reaction takes place above 450°C regaining catalytic active sites [117]. As explained in Chapter 5, the formation of Pd(OH)₂ is unlikely in this study. The experiments proved however the partial reversibility of H₂O on the active sites.

Comparing the wet-TOS results of 3.4Pd/Al₂O₃ and seq-1.5Zr/3.4Pd/Al₂O₃ catalysts at different H₂O concentrations leads to a conclusion concerning the impact of ZrO₂. The influence of the support on catalytic activity gets more significant at higher H₂O concentration in the system (i.e. more H₂O inhibition on the surface). 3.4%Pd along with 1.5%Zr were the best catalyst at a low H₂O amount (2vol.%), however 3.4%Pd shows the worst performance at higher H₂O inhibition (5vol.%) (See Figures I.4 and I.5). ZrO₂ is known for its high oxygen mobility (three times higher than Al₂O₃) [131]. Schwartz and Ciuparu published that supports with high oxygen mobility are more resistant to H₂O inhibition confirming our results obtained in the experiments [33,36]. During CH₄ oxidation the active sites get reduced by methane and can get re-oxygenized ($\text{Pd} + \frac{1}{2}\text{O}_2 \rightarrow \text{PdO}$) not

only by the gas phase oxygen but also by the oxygen of the support (lattice oxygen) [34,130]. Yang et al. also reported that a high oxygen mobility of lattice oxygen improves the re-oxidation of the palladium active sites and enhances CH₄ combustion [134]. Since the oxygen exchange of the gas phase with the catalyst is slow at low temperatures [130,135] and is limited by the surface reaction and H₂O inhibition respectively, ZrO₂ partly provides the oxygen for the reaction and consequently improves the catalytic activity. ZrO₂ has the ability to form oxygen vacancies. These vacancies can get refilled quickly by migration of oxygen from the support or the gas phase [34,124]. That is the reason why the catalysts with Zr content show a better performance than 3.4% Pd, when having high hydroxyl coverage on the surface of the catalyst (Figure I.5).

Less H₂O vapor in the system (2vol.%) leads to a better catalytic activity of 3.4%Pd (Figure I.4). The H₂O inhibition is weaker (compared to 5vol.%) at this temperature and affects less the oxygen exchange between the surface of the catalyst and the gas phase. The activity of 3.4%Pd and 1.5%Zr is almost the same for this condition concluding that the effect of support is less significant for a lower amount of H₂O (less H₂O inhibition) in the reaction.

Moreover Ciuparu published that the effect of support becomes significant having temperatures of 700K (or above) [130]. However, in the experiment faster deactivation and lower conversion occurs for the ZrO₂ supported catalysts than for 3.4%Pd catalyst. Consequently other aspects like structural properties have an influence on the catalytic activity at higher temperature. Amairia and Souza argued that the surface area of the catalyst decreases having a higher Zr loading due to the ZrO₂ blockage of the pores. Smaller surface area leads to a lower catalytic activity [127,129].

Considering the result with 2vol.% H₂O at 350°C (Figure I.4), a further suggestion can be made. At this setting 3.4%Pd was as good as 1.5%Zr and better than 15%Zr and 25%Zr. The reason is mentioned to be due to low H₂O inhibition and good oxygen exchange of the catalyst with the gas phase. The oxygen exchange rate of the support with PdO is slower, thus the support effect is not significant at this condition. The same behavior can cause the results with 10vol.% H₂O at 425°C. At this temperature the H₂O amount (10vol.%) may be low as well as the hydroxyl coverage of palladium active sites. The oxygen exchange between gas phase and catalyst is fast, making the oxygen mobility of the support negligible. Consequently the larger surface area of 3.4%Pd leads to the better catalytic activity seen in Figure I.6. To verify this explanation, further investigation with higher amounts of H₂O has to be done. The activity of 3.4%Pd should decrease more than the activities of the ZrO₂ supported catalysts.

One dry experiment (with 1.5%Zr) was performed to identify the influence of temperature on the catalytic activity. Therefore the temperature was changed between 280°C and 330°C. In Figure I.7 the results are presented for four different temperatures.

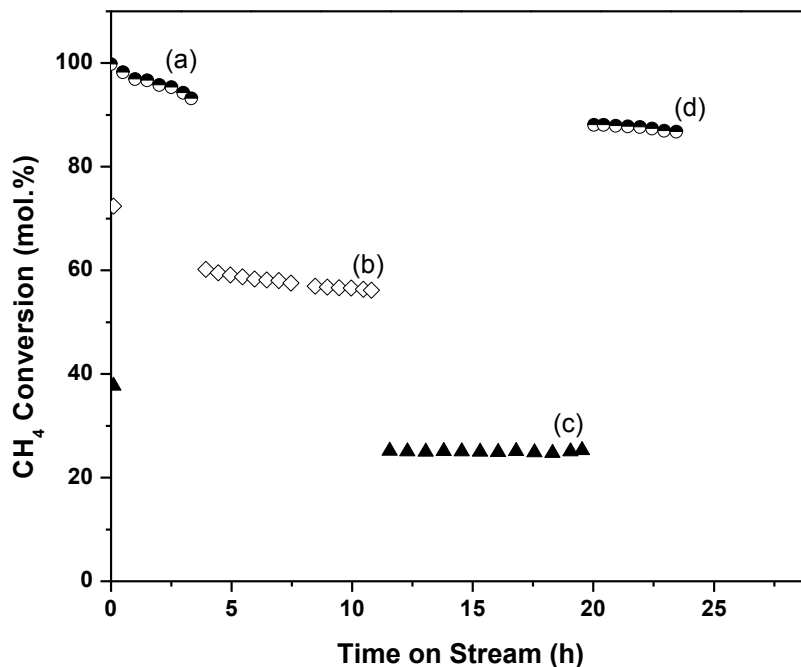


Figure I.7. Dry-TOS results for seq-1.5Zr/3.4Pd/Al₂O₃ catalyst at (a) 310°C, (b) 280°C, (c) 250°C, and (d) 310°C. GHSV=180,000 cm³(STP).g_{cat}⁻¹.h⁻¹, 1000 ppm CH₄, 20(v/v)% O₂, and the balance He and Ar

The deactivation of the catalyst started immediately having reached the temperature of 310°C. The conversion decreased from 99 mol% to 93 mol% while the temperature was kept at T=310°C for about 3h. At the temperature of 280°C the conversion decreased from 60% to 56% after 15h of reaction. For 250°C the conversion stayed constant at 25% for 8h. However, increasing the temperature to 310°C, the deactivation restarted. The deactivation of the catalyst could be due to the sintering caused by temperature. For example, smaller PdO particles combine to bigger PdO particles, which are supposed to be less active. Moreover, pores of alumina melt together that prevents the usability of PdO particles inside the pores and reduces the surface area of the catalyst. All of these effects are irreversible and cause the decrease of conversion over time. More sintering occurs for higher temperature that is why the deactivation restarted, increasing the temperature from 250°C to 310°C. Since H₂O

inhibition occurs below 450°C, the coverage of PdO active sites through hydroxyl groups can also affect the conversion of CH₄ [34]. Thus, higher deactivation of the catalyst at higher temperature could also be due to higher H₂O production during CH₄ oxidation reaction. Hydroxyl groups may adsorb on PdO active sites or sinter the catalyst. Figure I.7 shows clearly the impact of temperature on the catalytic performance. Increasing the temperature leads to higher conversion in CH₄ oxidation. The difference in conversion between 310°C and 250°C is around 60 mol% after a certain time of reaction.

The initial points of 280°C and 250°C obtained from TPO experiments are included in Figure I.7. They represent the maximum achievable conversion when using a fresh catalyst. The strong influence of temperature in CH₄ oxidation can be seen comparing the initial points of conversion at 310, 280, 250°C. They are 99, 72 and 38 mol% of conversion, respectively.

Considering the surface reaction of the catalyst the impact of temperature in CH₄ oxidation is explainable. Beebe et al. studied the adsorption process of CH₄ and showed that one C-H bond breaks leading to adsorbed hydrogen and methyl radicals [136]. Due to the high binding energy of the C-H bond in CH₄ [12], higher temperature favors the activation of CH₄ and the formation of these radicals. Consequently increasing the temperature enhances the adsorption process of CH₄ and the conversion of CH₄ to CO₂ and H₂O on the surface of the catalyst. Another explanation for the less catalytic activity at lower temperature is made by Ciuparu and Au-Yeung [130,135]. They found out that the overall oxygen exchange of the gas phase with the catalyst is very slow at lower temperature. Thus slower oxygen exchange can also cause the decrease of conversion when reducing the temperature.

I.4 Conclusion

The seq-1.5Zr/3.4Pd/Al₂O₃ catalyst demonstrates the highest catalytic activity compared to 3.4Pd/Al₂O₃, 15% Zr and 25% Zr. When comparing the results at 350°C between low amount of H₂O (2vol.%) with high amount of H₂O (5vol.%), it can be concluded that the effect of support gets more significant having more H₂O inhibition. At 2vol.% of H₂O the unsupported and 1.5%Zr supported catalysts, both have with 27mol.% of conversion the highest activity. This can be explained due to the larger surface area of 3.4%Pd and the higher oxygen mobility of ZrO₂ (monoclinic). However, increasing the H₂O vapor to 5vol.% the unsupported catalyst (3.4%Pd) shows the worst performance compared to all ZrO₂ supported catalysts especially during the first 10h. After 24h the 1.5%Zr catalyst was with 16 mol% conversion around 4 mol% better than 3.4%Pd. Thus a higher H₂O amount leads to more hydroxyl blockage of the palladium active sites and limits/decelerates the oxygen exchange from the gas phase to the catalyst. In this condition the oxygen mobility of ZrO₂ (and the oxygen exchange from the support to the surface respectively) helps to improve the conversion of CH₄.

After 24h the feeding of H₂O was stopped in all wet experiments to investigate the reversibility of H₂O inhibition. The conversion went up immediately proving the reversible hydroxyl coverage on the surface of the catalyst. However, the final conversion depends on the H₂O amount utilized in the 24h before. Using more extra H₂O in the experiment, the conversion regains to a higher value. As it was explained before more extra H₂O leads to more hydroxyl coverage of palladium active sites. Due to the coverage more PdO sites are

protected against sintering and stay unused. After removing the H₂O more fresh PdO sites are available again causing a higher final conversion.

The faster oxygen mobility of ZrO₂ at higher temperature could not be proved, because the unsupported catalyst presents the best catalytic activity at 425°C and 10vol.% of H₂O. The catalytic activity at this condition decreases in the following order: 3.4%Pd > 1.5%Zr > 15%Zr > 25% Zr with the corresponding conversions of 76% > 68% > 48% > 35% after 2h. It can be suggested that 10vol.% at 425°C leads to a low H₂O inhibition like 2vol.% H₂O at 350°C. The oxygen exchange between gas phase and catalyst is fast, making the impact of the support negligible. The catalytic activity may depend on the surface area, since the activity decreases in accordance with the decrease of the surface areas (3.4%Pd (215m²/g) > 1.5%Zr (192m²/g) > 15%Zr (139m²/g) > 25%Zr).

Appendix J: The Effect of Second Metal on Pd Catalysts for CH₄ Oxidation (Bimetallic)

The effect of metal oxides added to Pd/Al₂O₃ to improve the hydrothermal stability has been reported by Liu et al. [115] who showed in particular, that the addition of NiO or MgO improved the hydrothermal stability of Pd/Al₂O₃ through the formation of NiAl₂O₄ and MgAl₂O₄ spinel structures. According to the authors, the spinel results in weakened support acidity that suppresses the formation of Pd(OH)₂ during hydrothermal aging.

Pd-bimetallic catalysts have also been studied to improve stability of Pd catalysts for CH₄ oxidation [26,91,100,137]. Pd-bimetallic catalysts are usually less active than Pd alone [43,138–140] simply because they contain less Pd, the most active metal for CH₄ oxidation [29]. The lower activity of the bimetallic compared to Pd alone may also be due to the presence of smaller amounts of PdO as a result of alloy formation between Pd and Pt [43], or the transformation of PdO to Pd metal [141]. According to Ozawa et al. [142] the addition of Pt improves PdO/Al₂O₃ catalyst stability by preventing the growth of PdO and Pd–Pt particles during CH₄ oxidation at high temperature (800°C) [142]. Several studies have reported higher initial activity of Pd-bimetallic catalysts compared to Pd alone [24,26,100,143]. These researchers suggest that the second metal added to Pd dissociates O₂ and the resulting O atoms are adsorbed by Pd, helping to maintain PdO active sites. Ishihara et al. [143] reported T₅₀ for a 1wt.% Pd/Al₂O₃ catalyst to be 533°C, whereas for a Pd–Ni/Al₂O₃ catalyst (Pd:Ni= 9:1) T₅₀ was found to be 380°C. In another study, it was found that the higher dispersion of PdO on a PdO–Pt/ α -Al₂O₃ catalyst (27%) compared to PdO/ α -Al₂O₃ (14%) results in higher initial activity and higher stability of the bimetallic catalyst

[100]. After exposing the PdO/ α -Al₂O₃ catalyst to the reaction feed stream for 6h at 350°C, an increase in average particle size from 8 to 11 nm was observed, whereas the average particle size did not change significantly for the PdO-Pt/ α -Al₂O₃ catalyst [100]. Persson et al. [139] examined a series of Pd-bimetallics supported on Al₂O₃ finding that the metallic phase structure had a significant influence on the catalyst stability. For example, in several bimetallic systems (PdAg, PdCu, PdRh, and PdIr) spinel phases enhanced catalyst stability, whereas formation of Co or Ni aluminate spinels in PdCo and PdNi bimetallics did not improve catalyst stability. Alloy formation in PdPt and PdAu on Al₂O₃ was found to increase hydrothermal stability in the presence of 15% H₂O/air at 1000°C for 10h. In another study by Persson et al. [43], Pd-Pt bimetallic catalysts on various supports (Al₂O₃, ZrO₂) also yielded better thermal stability than monometallic Pd during CH₄ oxidation in dry air (1.5% CH₄ in air at a GHSV 250,000h⁻¹). The stability of the Pd-Pt catalysts was better at lower temperatures (up to 620°C). At temperatures of 520°C and 570°C CH₄ conversion of the Pd-Pt catalysts increased with time-on-stream. Above 620°C (especially at 670°C and 720°C) conversion decreased with time-on-stream. Those catalysts with higher initial activity also showed higher deactivation rates. The deactivation could not be attributed to PdO decomposition because the initial activity test showed that PdO decomposition started at higher temperature (770°C with 1.5vol.% CH₄ in air). The XRD results also confirmed that no PdO decomposition was observed at temperatures below 800°C for the Pd/Al₂O₃.

The amount of second metal added to the Pd can also affect the stability of the bimetallic catalyst. Persson et al. [138] showed that Pd-Pt bimetallic catalysts with Pt:Pd ratios of 0.33:0.67 and 0.5:0.5 were stable catalysts. Time-on-stream experiments for both a 5wt.% Pd/Al₂O₃ and a 2:1Pd:Pt/Al₂O₃ bimetallic with total metal loading of 5wt.% were studied

over a wide range of temperatures (470-720°C) [43]. The temperature was increased from 470°C to 720°C stepwise by 50°C and was held for 1h at each temperature. CH₄ conversion over the Pd/Al₂O₃ and Pd-Pt/Al₂O₃ catalyst decreased during the 1h reaction time at each temperature. However, the decrease in conversion was lower for the bimetallic catalyst compared to the Pd catalyst. The decrease in activity was higher at higher temperatures (670°C and 720°C), especially for the Pd catalyst. In situ XRD spectra of the Pd-Pt bimetallic catalysts are shown in Figure J.1 at room temperature, a sharp peak corresponding to Pd-Pt (111) and a small peak corresponding to PdO (101) are observed for the PdPt-Al₂O₃ catalyst. By increasing the temperature to 300°C, the PdO peak disappears and then reappears at 500°C. The Pd-Pt peak intensity reaches a maximum at 700°C while the PdO peak disappears at this temperature. The formation of Pd-Pt instead of PdO is consistent with deactivation of the bimetallic catalyst at high temperature (700°C).

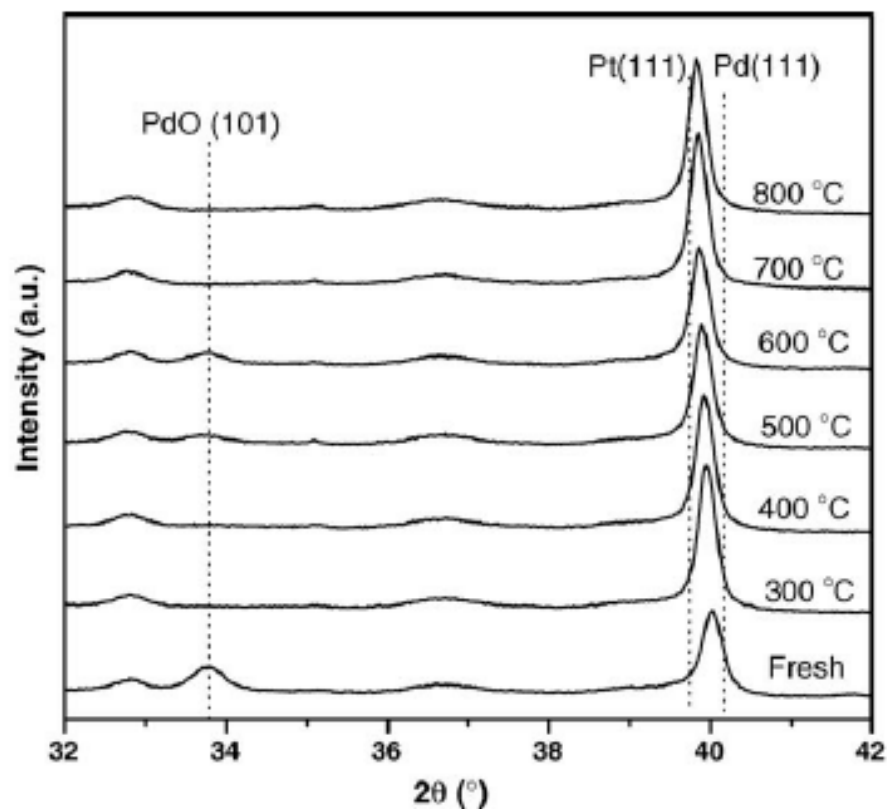


Figure J.1. High-temperature in situ XRD profiles of PdPt-Al₂O₃ during heating [43] (Copyright © 2006 Elsevier)

Steady-state experiments using a 18.7wt.%Pd/Al₂O₃ catalyst with different loadings of Pt (1.6, 3.1 and 3.9wt.%) (Figure J.2) reported by Ozawa et al. [142], also provide some insight into the improved stability of these bimetallic catalysts as Pt content is increased. In this study, reaction temperature was held at 800°C and CH₄ combustion rate was measured over a 10h period using a 1%CH₄ in air feed gas at a GHSV of 1,500,000 mL/(g_{cat}·h). Deactivation rate is shown to decrease as the Pt loading of the Pd-Pt bimetallics increase. For example, the combustion rate for the 18wt.% Pd-3.9wt.% Pt/Al₂O₃ decreased from 710 μmol.s⁻¹.g⁻¹ to 460 μmol.s⁻¹.g⁻¹ after 10h, whereas it decreased to 400 μmol.s⁻¹.g⁻¹ for the 18.4wt.% Pd-1.6wt.% Pt/Al₂O₃ catalyst.

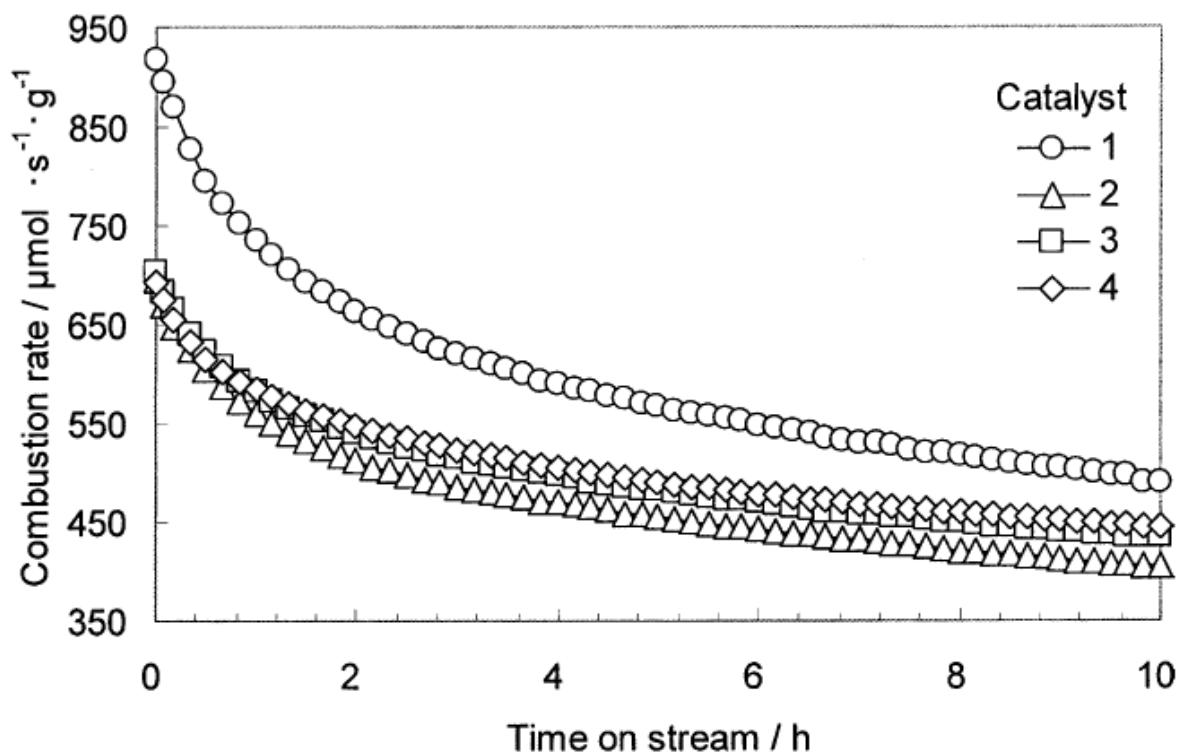


Figure J.2. CH₄ combustion rate at 800°C with time on stream. Combustion conditions: CH₄=1vol.%, air=99vol.%, CH₄/air flow= 450 L.h⁻¹, catalyst weight= 0.3g. Catalyst 1, 2, 3, and 4 represent 18.7wt.% Pd, 18.4wt.%Pd-1.6wt.% Pt, 18.1wt.% Pd-3.4wt.% Pt, and 18.0wt.% Pd-3.9wt.% Pt over Al₂O₃ catalysts [142] (Copyright © 2004 Elsevier)

XRD analysis of the catalysts studied by Ozawa et al. [142] after 10h reaction indicates the PdO to be present in the Pt-doped catalysts while no Pd⁰ is observed. However, Pd⁰ was present in the Pd monometallic catalyst, likely because of the decomposition of PdO at the high temperature of the reaction (800°C). In addition, the crystallite size of the PdO (101) in the Pd catalyst was larger than for the Pd-Pt catalysts. Table J.1 compares changes in PdO particle size and BET surface area before and after 10h reaction for the same Pd and Pd-Pt catalysts. From these data it is clear that the extent of sintering of the Pd catalyst is greater than for the Pd-Pt catalysts. The time-on-stream conversion data reported by Ozawa et al.

[142] (Figure J.2) were fitted to a deactivation equation with two terms, the first representing rapid transformation of PdO to Pd⁰ of the Pd-Pt alloy phase, and the second associated with the slow growth of the PdO crystallite [142]. The deactivation was affected more by the second term suggesting that particle growth of the PdO is the main cause of catalyst deactivation at the chosen reaction conditions [142].

Table J.1. Changes in Pd and Pt-Pd catalyst properties before and after aging (Adapted with permission from [142])

Catalyst, wt % on Al ₂ O ₃		18.7%Pd	18.4%Pd-1.6%Pt	18.1%Pd-3.1%Pt	18.0%Pd-3.9%Pt
BET area, m ² /g	Fresh	56	51	51	52
	Aged	46	46	46	46
PdO size, nm	Fresh	12.5	15.3	15.2	14.7
	Aged	17.9	18.0	16.7	16.2

These results are in a good agreement with the results reported by Yamamoto et al. [137] in which a Pd-Pt bimetallic catalyst was more active for CH₄ conversion (in terms of 50% CH₄ conversion) than Pd and the conversion was maintained following 2500h time-on-stream at 385°C. XRD analyses showed that the crystallite growth as a function of time for both Pd (111) and PdO (101) was faster on the Pd (10 g/l)/Al₂O₃ catalyst than the Pd (10 g/l)-Pt (10 g/l)/Al₂O₃ catalyst. Hence one concludes that the presence of Pt retards the sintering of PdO. Effects of H₂O on deactivation of Pt versus Pt-Pd catalysts have also been reported, at both thermal and hydrothermal aging conditions [24,26,91]. Pieck et al. [24] reported that the T₅₀ of a 0.4%Pt-0.8%Pd/Al₂O₃ catalyst after thermal treatment at 600°C for 4h in wet air (60 cm³.min⁻¹ air flow with 0.356 cm³.h⁻¹ water), was~50°C lower than that obtained over a Pd catalyst. Lapisardi et al. [26] reported that a fresh Pd_{0.93}-Pt_{0.07}/Al₂O₃ catalyst (total metal

loading 2.12wt.% with Pd:Pt molar ratio of 0.93:0.07) was as active as a fresh Pd/Al₂O₃ catalyst in a dry feed [26]. Interestingly, the Pd_{0.93}-Pt_{0.07}/Al₂O₃ catalyst was less affected by addition of 10vol.% steam to the feed stream than the 2.2wt.%Pd/Al₂O₃ catalyst. The T₅₀ for the Pd-Pt bimetallic increased from 320°C to 400°C when 10vol.% steam was added to the feed stream, whereas the corresponding increase in T₅₀ for the Pd/Al₂O₃ catalyst was from 320°C to 425°C. Thus, the Pd-Pt bimetallic, containing only 0.26wt.%Pt was more active and stable than the Pd catalyst for CH₄ oxidation in the presence of steam.

The stability of Pt and Pt-Pd catalysts loaded on a washcoated monolith has also been reported [91]. A feed stream with 4067 ppmv CH₄ in air was reacted over these catalysts as reaction temperature increased from 300°C to 700°C stepwise in 50°C increments. CH₄ conversion was monitored for a period of 1h at each temperature. Subsequently the temperature was decreased to 300°C also in 50°C steps, again holding at each temperature for 1h. The conversion of CH₄ was compared for both heating and cooling cycles. The results showed that the Pt-Pd catalyst was more active than the Pt catalyst. The comparison between the heating and cooling cycles was also done for steam-aged catalysts, in which the catalysts were exposed to the feed stream at 650°C with 5vol.% water for 20h. Table J.2 lists the T₅₀ for both fresh Pt and Pd-Pt catalysts, the steam-aged catalysts during tests in a dry feed and the steam-aged catalysts tested in a wet feed, containing 5wt.%H₂O. The data show that the fresh Pd-Pt catalyst is more active than the fresh Pt catalyst. Higher activities were also observed for steam-aged Pd-Pt catalysts tested in dry or wet feed gas.

Table J.2. T_{50} for fresh and steam aged Pd and Pt-Pd catalysts operated in dry and wet feed. Combustion conditions: 4067 vol. ppm CH_4 ; total flow rate of $234.5 \text{ cm}^3 \cdot \text{min}^{-1}$; 500 mg catalyst; 5vol. % water in wet feed (Adapted with permission from [91])

Temperature at 50% CH_4 conversion (T_{50}), °C			
Catalyst	Fresh	Steam-aged	Steam-aged
	Dry feed	Dry feed	Wet feed
Pt	540	610	610
4:1 Pt-Pd	400	470	535

Appendix K: MATLAB M-files Code

A non-linear regression MATLAB program using Levenberg-Marquardt method written by R. Schragger and A. Jutan and made available through an open-access MATLAB users group was combined with simple MATLAB code containing calculations to solve an ODE using a 4th-order Runge-Kutta algorithm.

Least Square:

```
function [f,p,kvg,iter,corp,covp,covr,stdresid,Z,r2]= ...
    leasqr(x,y,pin,F,stol,niter,wt,dp,dFdp,options)
plotcmd='plot(x(:,1),y,"+",x(:,1),f); shg';
%if (sscanf(version,'%f') >= 4),
vernum= sscanf(version,'%f');
if vernum(1) >= 4,
    global verbose
    plotcmd='plot(x(:,1),y,"+",x(:,1),f); figure(gcf)';
end;
if (exist('OCTAVE_VERSION'))
    global verbose
end;
if(exist('verbose')~=1), %If verbose undefined, print nothing
    verbose(1)=0    %This will not tell them the results
    verbose(2)=0    %This will not replot each loop
end;
if (nargin <= 8), dFdp='dfdp'; end;
if (nargin <= 7), dp=.001*(pin*0+1); end; %DT
if (nargin <= 6), wt=ones(length(y),1); end; % SMB modification
if (nargin <= 5), niter=50; end;
if (nargin == 4), stol=.0001; end;
```

```

y=y(:); wt=wt(:); pin=pin(:); dp=dp(:); %change all vectors to columns
% check data vectors- same length?
m=length(y); n=length(pin); p=pin;[m1,m2]=size(x);
if m1~=m ,error('input(x)/output(y) data must have same number of rows') ,end;
if (nargin <= 9),
    options=[zeros(n,1) Inf*ones(n,1)];
    nor = n; noc = 2;
else
    [nor noc]=size(options);
    if (nor ~= n),
        error('options and parameter matrices must have same number of rows'),
    end;
    if (noc ~= 2),
        options=[options(noc,1) Inf*ones(noc,1)];
    end;
end;
pprec=options(:,1);
maxstep=options(:,2);
% set up for iterations%
f=feval(F,x,p); fbest=f; pbest=p;
r=wt.*(y-f);
sbest=r'*r;
nrm=zeros(n,1);
chgprev=Inf*ones(n,1);
kvg=0;
epsLlast=1;
epstab=[.1 1 1e2 1e4 1e6];
% do iterations%
for iter=1:niter,
    pprev=pbest;
    prt=feval(dFdp,x,fbest,pprev,dp,F);

```

```

r=wt.*(y-fbest);
sprev=sbest;
sgoal=(1-stol)*sprev;
for j=1:n,
    if dp(j)==0,
        nrm(j)=0;
    else
        prt(:,j)=wt.*prt(:,j);
        nrm(j)=prt(:,j)'*prt(:,j);
        if nrm(j)>0,
            nrm(j)=1/sqrt(nrm(j));
        end;
    end
    prt(:,j)=nrm(j)*prt(:,j);
end;
% above loop could ? be replaced by:
% prt=prt.*wt(:,ones(1,n));
% nrm=dp./sqrt(diag(prt'*prt));
% prt=prt.*nrm(:,ones(1,m))';
[prt,s,v]=svd(prt,0);
s=diag(s);
g=prt'*r;
for jjj=1:length(epstab),
    epsL = max(epsLlast*epstab(jjj),1e-7);
    se=sqrt((s.*s)+epsL);
    gse=g./se;
    chg=((v*gse).*nrm);
% check the change constraints and apply as necessary
ochg=chg;
for iii=1:n,
    if (maxstep(iii)==Inf), break; end;

```

```

    chg(iii)=max(chg(iii),-abs(maxstep(iii)*pprev(iii)));
    chg(iii)=min(chg(iii),abs(maxstep(iii)*pprev(iii)));
end;
if (verbose(1) & any(ochg ~= chg)),
    disp(['Change in parameter(s): sprintf('%d ',find(ochg ~= chg)) 'were constrained']);
end;
aprec=abs(pprec.*pbest);
% ss=scalar sum of squares=sum((wt.*(y-f))^2).
if (any(abs(chg) > 0.1*aprec)),%--- % only worth evaluating function if
    p=chg+pprev;                % there is some non-miniscule change
    f=feval(F,x,p);
    r=wt.*(y-f);
    ss=r'*r;
    if ss<sbest,
        pbest=p;
        fbest=f;
        sbest=ss;
    end;
    if ss<=sgoal,
        break;
    end;
end;
end;
epsLlast = epsL;
% if (verbose(2)),
%     eval(plotcmd);
% end;
if ss<eps,
    break;
end
aprec=abs(pprec.*pbest);

```

```

% [aprec chg chgprev]
if (all(abs(chg) < aprec) & all(abs(chgprev) < aprec)),
    kvg=1;
    if (verbose(1)),
        fprintf('Parameter changes converged to specified precision\n');
    end;
    break;
else
    chgprev=chg;
end;
if ss>sgoal,
    break;
end;
end;
% set return values%
p=pbest;
f=fbest;
ss=sbest;
kvg=((sbest>sgoal)|(sbest<=eps))|kvg);
if kvg ~= 1 , disp(' CONVERGENCE NOT ACHIEVED! '), end;
% CALC VARIANCE COV MATRIX AND CORRELATION MATRIX OF
PARAMETERS
% re-evaluate the Jacobian at optimal values%
jac=feval(dFdp,x,f,p,dp,F);
msk = dp ~= 0;
n = sum(msk);      % reduce n to equal number of estimated parameters
jac = jac(:, msk); % use only fitted parameters
%% following section is Ray Muzic's estimate for covariance and correlation
%% assuming covariance of data is a diagonal matrix proportional to
%% diag(1/wt.^2).
if vernum(1) >= 4,

```

```

Q=sparse(1:m,1:m,(0*wt+1)./(wt.^2)); % save memory
Qinv=inv(Q);
else
    Qinv=diag(wt.*wt);
    Q=diag((0*wt+1)./(wt.^2));
end;
resid=y-f; %un-weighted residuals
covr=resid'*Qinv*resid*Q/(m-n); %covariance of residuals
Vy=1/(1-n/m)*covr; % Eq. 7-13-22, Bard %covariance of the data
jtgjinv=inv(jac'*Qinv*jac); %argument of inv may be singular
covp=jtgjinv*jac'*Qinv*Vy*Qinv*jac*jtgjinv;
d=sqrt(abs(diag(covp)));
corp=covp./(d*d');
covr=diag(covr); % convert returned values to compact storage
stdresid=resid./sqrt(diag(Vy)); % compute then convert for compact storage
Z=((m-n)*jac'*Qinv*jac)/(n*resid'*Qinv*resid);
%%% alt. est. of cov. mat. of parm.:(Delforge, Circulation, 82:1494-1504, 1990
%%disp('Alternate estimate of cov. of param. est.')
%%acovp=resid'*Qinv*resid/(m-n)*jtgjinv
%Calculate R^2 (Ref Draper & Smith p.46)%
r=corrcoef(y,f);
if (exist('OCTAVE_VERSION'))
    r2=r^2;
else
    r2=r(1,2).^2;
end
% if someone has asked for it, let them have it
%
if (verbose(2)), eval(plotcmd); end,
if (verbose(1)),
    disp(' Least Squares Estimates of Parameters')

```

```

disp(p')
disp(' Correlation matrix of parameters estimated')
disp(corr)
disp(' Covariance matrix of Residuals' )
disp(covr)
disp(' Correlation Coefficient R^2')
disp(r2)
sprintf(' 95%% conf region: F(0.05)(%.0f,%.0f)>= delta_pvec"*Z*delta_pvec',n,m-n)
Z
n1 = sum((f-y) < 0);
n2 = sum((f-y) > 0);
nrun=sum(abs(diff((f-y)<0)))+1;
if ((n1>10)&(n2>10)), % sufficient data for test?
    zed=(nrun-(2*n1*n2/(n1+n2)+1)+0.5)/(2*n1*n2*(2*n1*n2-n1-n2)...
        /((n1+n2)^2*(n1+n2-1)));
    if (zed < 0),
        prob = erfc(-zed/sqrt(2))/2*100;
        disp([num2str(prob) '% chance of fewer than ' num2str(nrun) ' runs.']);
    else,
        prob = erfc(zed/sqrt(2))/2*100;
        disp([num2str(prob) '% chance of greater than ' num2str(nrun) ' runs.']);
    end;
end;
end
% A modified version of Levenberg-Marquardt
% Non-Linear Regression program previously submitted by R.Schrager.
% This version corrects an error in that version and also provides
% an easier to use version with automatic numerical calculation of
% the Jacobian Matrix. In addition, this version calculates statistics
% such as correlation, etc....
% Errors in the original version submitted by Shrager (now called version 1)

```

```

% and the improved version of Jutan (now called version 2) have been corrected.
% Additional features, statistical tests, and documentation have also been
% included along with an example of usage. BEWARE: Some the the input and
% output arguments were changed from the previous version.
%
% Ray Muzic <rfm2@ds2.uh.cwru.edu>
% Arthur Jutan <jutan@charon.engga.uwo.ca>
dfdp:
function prt=dfdp(x,f,p,dp,func)
% numerical partial derivatives (Jacobian) df/dp for use with leasqr
% -----INPUT VARIABLES-----
% x=vec or matrix of indep var(used as arg to func) x=[x0 x1 ....]
% f=func(x,p) vector initialised by user before each call to dfdp
% p= vec of current parameter values
% dp= fractional increment of p for numerical derivatives
% dp(j)>0 central differences calculated
% dp(j)<0 one sided differences calculated
% dp(j)=0 sets corresponding partials to zero; i.e. holds p(j) fixed
% func=string naming the function (.m) file
% e.g. to calc Jacobian for function expsum prt=dfdp(x,f,p,dp,'expsum')
%-----OUTPUT VARIABLES-----
% prt= Jacobian Matrix prt(i,j)=df(i)/dp(j)
%=====
m=length(x);n=length(p); %dimensions
ps=p; prt=zeros(m,n);del=zeros(n,1); % initialise Jacobian to Zero
for j=1:n
    del(j)=dp(j) .*p(j); %cal delx=fract(dp)*param value(p)
    if p(j)==0
        del(j)=dp(j); %if param=0 delx=fraction
    end
    p(j)=ps(j) + del(j);

```

```

    if del(j)~=0, f1=feval(func,x,p);
        if dp(j) < 0, prt(:,j)=(f1-f)./del(j);
        else
            p(j)=ps(j)- del(j);
            prt(:,j)=(f1-feval(func,x,p))./(2 .*del(j));
        end
    end
    p(j)=ps(j);    %restore p(j)
end
return
Modelmulti:
function f = modelmulti (x,pin)
% Solve a simple system of 2 ODE's - 2 response variables
% find the solution (f) at sepcified x values - corresponding to measured data
% first data point in x corresponds to initial condition
%
global tempK thetaW ncount ya0 PT rhocat Rp tau mPd nx nvar CT;
global verbose
for knt = 1:ncount; % data sets
W0=0.0;
WF=x(knt);
initial = 0;
[W,Xa] = ode45(@P2b, [W0,WF], initial, [],pin,knt);    %x is the solution matrix%
yfinal(knt,:)=Xa(end,:);
end
f = yfinal(:)
pin
end

```

P2B:

```
%USS FBR
% Program contains calculations for odes which are to be solved by ODE45%
function xprime = P2bwet(W,Xa,pin,knt)
global tempK thetaW ncount ya0 PT rhocat Rp tau mPd nx nvar CT Deff
global verbose T
tempK(knt)
Tbar = 603.;
Deff=6.726e-8; % m2/s at 330°C
DeffT=Deff*((tempK(knt)/(273+330))^0.5);
P=PT(knt);
T=tempK (knt);
km1=exp((-pin(1)/8.314)*(1/tempK(knt)-1./Tbar));
km=pin(2)*km1;
Kwater1=exp(-pin(3)/8.314*(1/tempK(knt)-1./Tbar));
Kwater=pin(4)*Kwater1;
k1=km*CT(knt)*CT(knt)*8.314*tempK(knt)*1000*rhocat;% OPTION 1
ratio = k1/DeffT;
thiele=Rp*sqrt(ratio);
eta=(3/thiele)*((1/tanh(thiele))-1/thiele);
% Mina's model
xprime=eta*km*CT(knt)*CT(knt)*ya0(knt)*(1-
Xa)*P/(1+Kwater*ya0(knt)*P*(thetaW(knt)+2*Xa));
```

Multi_realfit:

```
clear all
global tempK thetaW ncount ya0 PT rhocat Rp tau mPd nx nvar CT Deff
global verbose
verbose(1:2) = 1;
```

```

% This program does non-linear regression using the lsqr program...a Levenberg-Marquardt
nonlinear regression%
% Start by generating some phoney data for the test%
% x is the indep variable vector e.g. time measurements
% y is matrix of responses
% columns of y are responses y1, y2 (e.g. mol frac of component 1 and 2)
% rows of y are y values at the value of the indep variable (time) in x
% first row of y is initial value of response
% the program uses the Levenberg-Marquardt method to estimate parameters
% and calc statistics - done in leasqr and dfdp
% these two matlab m-files are designed for single response
% the input data is re-arranged to yield a single response vector y
% the L-M requires the model to be calculated -this is done in modelmulti.m
% and assumes the model is a series of ODEs, with the number of odes equal
% to the number of responses. The ODEs are calculated in ODEfunm. Note that this function
must use the correct model for each y%
% Generate INPUT data
% In this demo the data are generated from the known problem solution
% input number of responses
nvar=1; %This example is single response (conversion versus time)%
% Arbitrary system properties %
% INPUT DATA
format longE
rhocat=1.49e3; % Catalyst density kg/m3
Rp = (2.22e-4/2); % Particle radius, m
measured=xlsread('PdCh4-1.xlsx')
% Order of input file:
% Temp(K)  ThetaW  CONV %  GHSV (ml/g h)  YaO  PT Pd-loading CT
tempK = 273.+ measured(:,1)% reaction T
thetaW = measured(:,2) % water to methane feed molar ratio
conv = measured(:,3)./100.0 %CH4 conv

```

```

ghsv = measured(:,4)./22414./60./60. % units are mol/(g.s)
ya0=measured(:,5) %CH4 inlet mole fraction
ghsvA=ghsv.*ya0
tau=1./ghsvA
PT=measured(:,6) % Total pressure
mPd=measured(:,7) % mass fraction of Pd catalyst
uCT = measured(:,8) % Total sites micromole/g
%Deff = measured(:,9)
CT = uCT./1e6;
[tcount,nnn]= size(tempK)
Xcount=tcount
W0=0.0;
ncount=tcount;
% INPUT DATA - re-formatted%
nx=ncount
y=conv'
newy=y(:)
oldy=reshape(newy,nx,nvar)
x=tau'
newx=x(:);
oldx=x(:);
% plot (tempK,y, 'o')%
%INPUT DATA NOW IN CORRECT COLUMN FORMAT%
y=newy
x=newx
% provide initial parameter guesses%
pin=[1.15E5 17 -40000 1.5E-3]
np=length(pin)
% Begin calculation by calling L-M least squares routine%
[f,p,kvg,iter,corp,covp,covr,stdresid,Z,r2]=leasqr(x,y,pin,'modelmulti');
disp('RESPONSE:')

```

```

if kvg ==1
    disp ('PROBELM CONVERGED')
elseif kvg == 0
    disp('PROBLEM DID NOT CONVERGE')
end
oldf=reshape(f,nx,nvar);
oldr=reshape(y-f, nx, nvar);
disp ('X-values:')
disp (oldx')
disp ('Y-values')
disp(oldy)
disp('f-values - i.e. model calculated responses')
disp(oldf)
disp('Residuals:')
disp (oldr)
disp ('Final SSQ')
disp (stdresid)
disp ('Estimated parameter values are;')
disp (p)
disp ('Covariance of estimated parameters')
disp (covp)
disp('R2 values is:')
disp (r2)
disp (p)
disp (pin)
Calc the eta and theile modulus
Tbar = 603.;
for knt=1:ncount
    tempK(knt)
    Deff=6.726e-8; % m2/s at 330°C
DeffT=Deff*((tempK(knt)/(273+330))^0.5)

```

```

P=PT(knt);
%DeffT=Deff(knt);
T=tempK (knt);
%T=(1./tempK(knt)-1./Tbar)
disp (p(1))
km1=exp((-p(1)/8.314)*(1/tempK(knt)-1./Tbar))
km=p(2)*km1
Kwater1=exp(-p(3)/8.314*(1/tempK(knt)-1./Tbar))
Kwater=p(4)*Kwater1
%k1=km*CT(knt)*CT(knt)*8.314*tempK(knt)*1000*rhocat/(1+Kwater*ya0(knt)*P*(theta
W(knt)+2*f(knt)))
%k1=(km*CT(knt)*CT(knt)*8.314*tempK(knt)*1000*rhocat) % OPTION 1
k1=(km*CT(knt)*CT(knt)*8.314*tempK(knt)*1000*rhocat) % OPTION 1
ratio = k1/DeffT;
thiele=Rp*sqrt(ratio);
TM(knt)=thiele;
EffectFactor(knt)=(3/thiele)*((1/tanh(thiele))-1/thiele);
end
disp ('thiele modulus')
disp (TM)
disp ('Effectiveness factors')
disp (EffectFactor)
% plot (oldx,oldy,'d'), hold, plot (oldx,oldf)
% plot (oldy,oldf, 'o'),hold, plot (oldy,oldy)

```