The Impact of CeO_2 Loading on the Activity and Stability of PdO/γ-AlOOH/γ-Al_2O_3 Monolith Catalysts for CH_4 Oxidation

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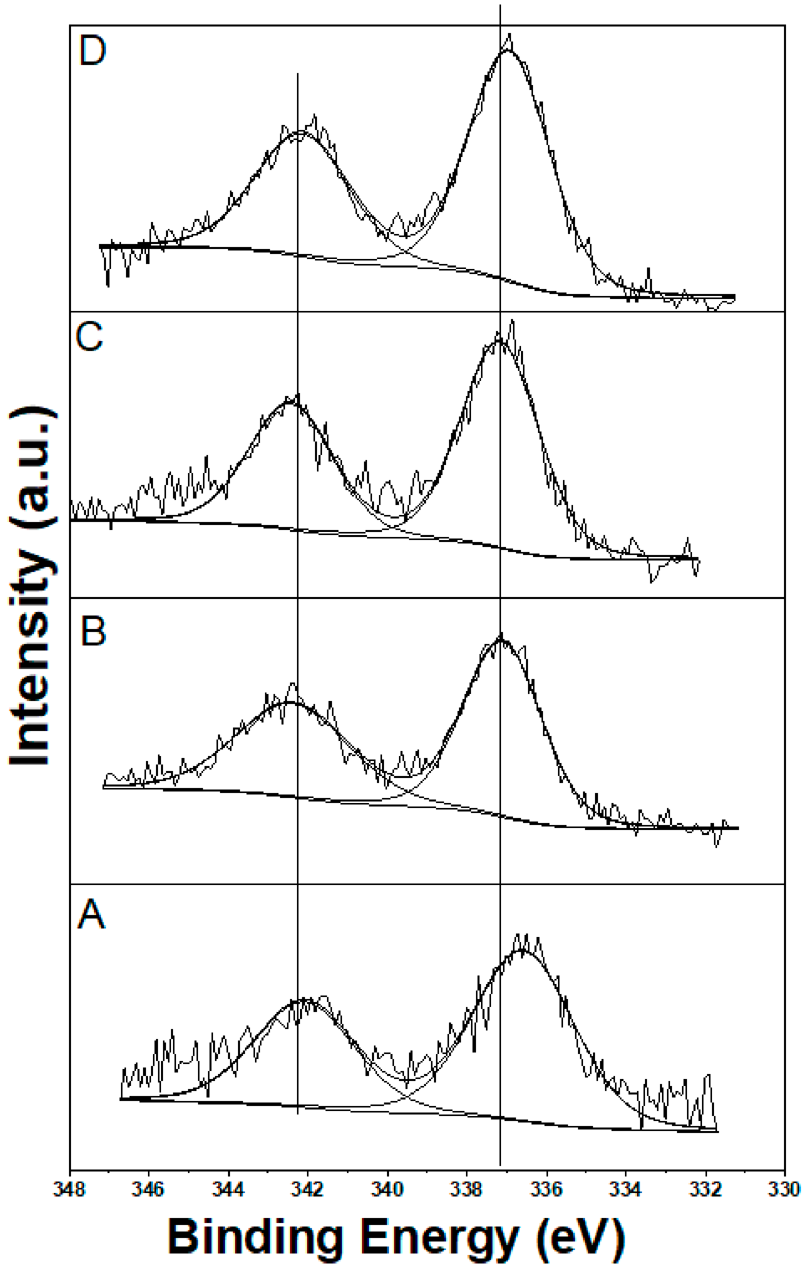

Figure S1: XPS Pd 3d spectra measured for catalysts: A – Pd0Ce; B- Pd1Ce; C: Pd2Ce; D:Pd4Ce.

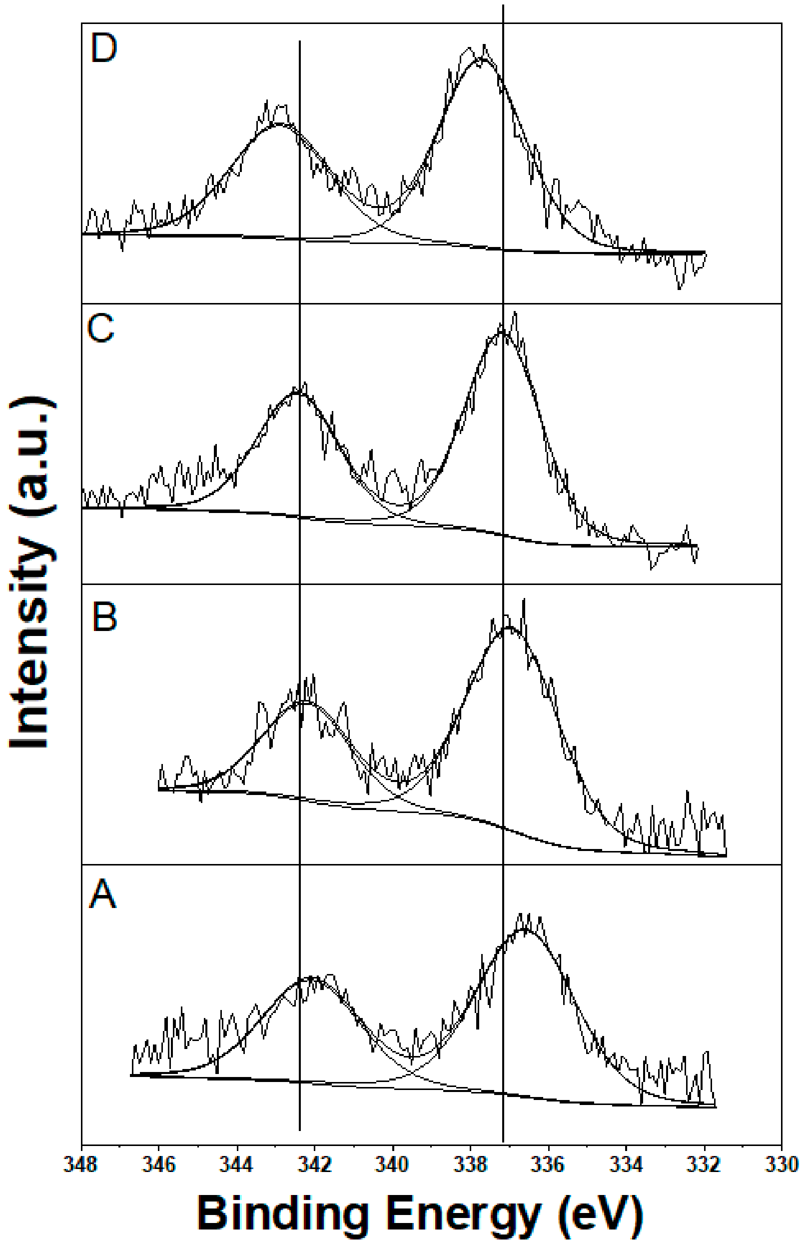

Figure S2 : XPS Pd 3d spectra measured for catalysts: A - Pd0Ce; B - Pd0Ce-used; C - Pd2Ce; D - Pd2Ce-used.

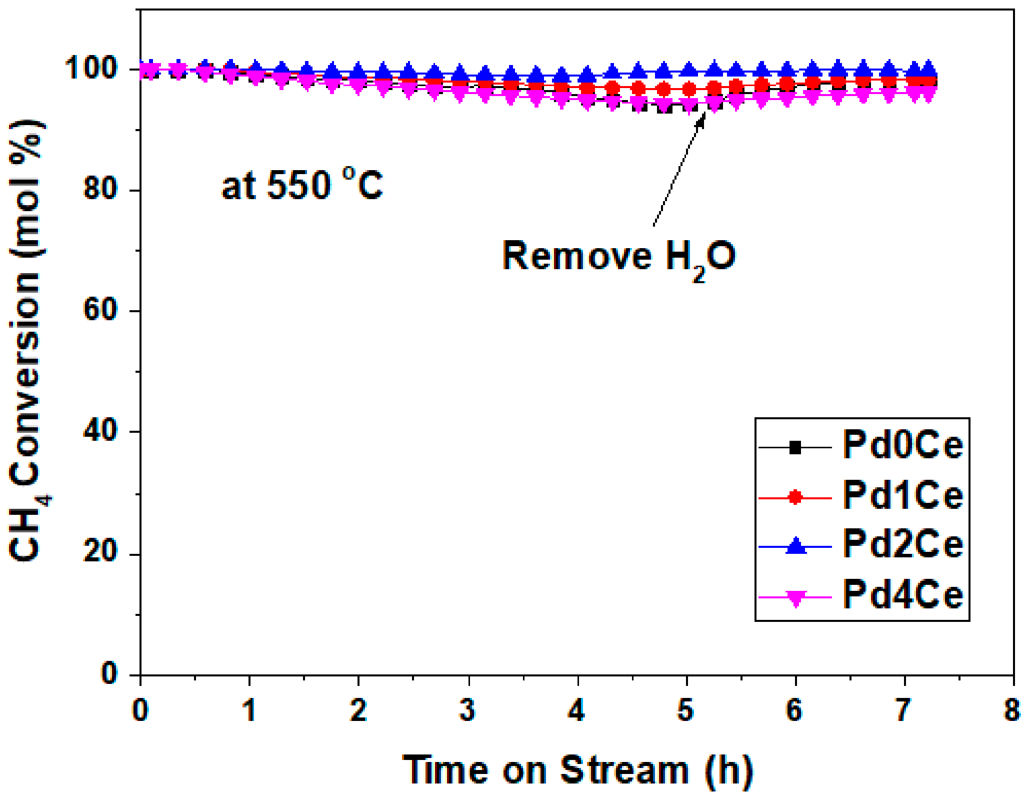

Figure S3: TOS results after adding 10 vol % H_2O to the dry feed gas. Reaction conditions: Total feed gas flow = 1025 cm^3(STP)·min^{-1}, GHSV = 36000 h^{-1}, Feed gas composition: 0.07 vol % CH_4, 8.5 vol % O_2, 0.06 vol % CO, 8 vol% CO_2 and 10 vol % H_2O in N_2 and He at 550 °C.

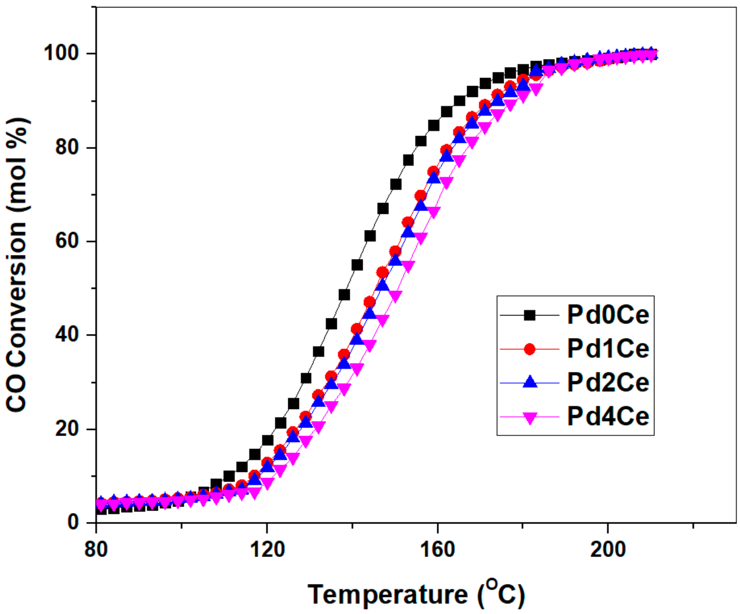

Figure S4: Temperature-programmed oxidation profile for CO conversion as function of temperature for the catalysts. Reaction conditions: Total feed gas flow = 1025 cm^3(STP)·min^{-1}, GHSV of 36000 h^{-1}, Feed gas composition: 0.07 vol % CH_4, 8.5 vol % O_2, 0.06 vol% CO, and 8 vol % CO_2 in N_2 and He.

Heat and Mass transfer effects:

The maximum temperature inside the washcoat is calculated using equation S1 to make sure the assumption of the isothermal condition is valid.

$$T_{max} = T_s - \frac{\Delta H_r D_{eff} C_{CH_4}}{k_p} \qquad S1$$

Table S1 Calculation of the maximum temperature inside the washcoat

Parameter	Definition	Value
T_s	Surface temperature (K)	523
ΔH_r	Heat of reaction at 298 K, (kJ mol^{-1})	-891
D_{eff}	Effective diffusivity, (m^2 s^{-1})	1.67E-07
C_{CH_4}	CH_4 concentration, (mol m^{-3})	0.029
k_p	Thermal conductivity of washcoat, (kJ m^{-1} s^{-1} K^{-1})	0.025
T_{max}	Reaction temperature (K)	523+1.7e-4

From the results T_{max} is equal to T_S; thus, the temperature gradient in the washcoat layer will be small due to the low CH_4 concentration and the thin layer of washcoat.

External Mass Transfer Calculation:

$$Open\ Frontal\ Area\ (OFA) = \frac{(l - t_w)^2}{l^2} \qquad S2$$

$$Geometric\ Surface\ \ Area\ (GSA) = \frac{4(l - t_w)}{l^2} \qquad S3$$

where l = width of channel in inches and t_w = thickness of the wall in inches

$$Hydraulic\ diameter\ (d_h) = \frac{4\ OFA}{GSA} \qquad S4$$

Washcoat Reynolds number is calculated as follows:

$$Re = \frac{d_h u \rho_g}{\mu} \qquad S5$$

Where L_c is the washcoat thickness, μ is the dynamic gas viscosity, and ϵ_d is the washcoat porosity, ρ_g the gas density and u_s the superficial gas velocity are defined as:

$$\rho_g = \frac{PM_{wfeed}}{RT} \qquad S6$$

$$u = \frac{v_0}{A} \qquad S7$$

Schmidt number is given by:

$$Sc = \frac{\mu}{\rho_g D_{CH_4,He}} \qquad S8$$

In a gas phase system with Re < 2000 and 0.4 < ϵ_d < 0.79, j_D factor is calculated

$$j_D \epsilon_d = 0.35 Re^{-0.359} \qquad S9$$

The Sherwood number is calculated as follows

$$Sh = j_D Re Sc^{\frac{1}{3}} \qquad S10$$

The external mass transfer coefficient (k_c) is calculated as follows:

$$k_c = \frac{D_{CH_4,He} Sh}{L_c} \qquad S11$$

Mears criterion is calculated as follows

$$C_M = \frac{r_{CH_4}^m \rho_{wash} L_c}{k_c C_{CH_4}} \qquad S12$$

The mass transfer from the bulk gas phase to the surface of the washcoat is negligible if C_M is < 0.15. C_M is obtained as 0.0002 in this study which indicates the absence of external heat transfer limitations since C_M is < 0.15

Table **Error! No text of specified style in document.**1 Details of calculations for Mears criterion factor for Pd0Ce at 523 K

Parameter	Definition	Value
T	Reaction temperature (K)	523
P	Total pressure (Pa)	101325
R	Gas constant ($Pa.m^3.mol^{-1}.K^{-1}$)	8.314
M_{wfeed}	Feed molecular weight ($kg.kmol^{-1}$)	34
$F^o_{CH_4}$	Feed CH_4 molar flow ($mol.s^{-1}$ (STP))	5.35e-7
OFA	Open frontal area (m^2/ m^2)	0.75
GSA	Geometric surface area (m/ m^2)	3.04
d_h	Hydraulic diameter (m)	0.98
r_t	Radius of reactor (m)	4.6e-3
A_c	Cross sectional area of the reactor (m^2)	6.4e-5
u_s	Superficial gas velocity ($m.s^{-1}$)	0.26
ε_b	Washcoat porosity	0.67
$D_{CH_4,He}$	Binary bulk diffusivity, (m^2 s^{-1})	1.04e-04
ρ_g	Gas density ($kg.m^3$)	0.78
μ	Gas dynamic viscosity ($kg.m^{-1}.s^{-1}$)	3.87e-5
Re	Reynolds Number	5.13
Sc	Schmidt Number	0.5
j_D	j_D factor	0.29
S_h	Sherwood number	1.15
k_c	External mass transfer coefficient, (m s^{-1})	3.43
C_{CH_4}	CH_4 concentration, (mol m^{-3})	0.029
$-r^m_{CH_4}$	CH_4 oxidation reaction rate ($mol.kgcat^{-1}.s^{-1}$)	3.06E-04
ρ_{wash}	Washcoat density ($kg.m^3$)	1340
C_M	Mears criterion factor	0.0002