

Supplementary information to

Stabilizing Pd-cerium oxide-aluminum oxide catalysts for methane combustion by reduction pretreatments†

Anil C. Banerjee^{a,*}, Laura Proaño^b, Alexis Alvarez^a, Imani Rogers^a, Jihyeon Park^a, Maddison Montgomery^a, Mehmet Z. Billor^c, Bert M. Weckhuysen^d, Matteo Monai^{d,*}

^a Department of Chemistry, Columbus State University, Columbus, GA 31907, United States

^b Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States

^c Department of Geosciences, Auburn University, Auburn, AL 36849, United States

^d Inorganic Chemistry and Catalysis Group, Debye Institute for Nanomaterials Science and Institute for Sustainable and Circular Chemistry, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands

* E-mail: banerjee_anil@columbusstate.edu, m.monai@uu.nl; Tel: +17065693030

† Electronic supplementary information (ESI) available: Hydrogen temperature programmed reduction of Pd/Ce/Al-F and Ce/Pd/Al-F catalysts (Fig.S1), calculated hydrogen consumption during hydrogen temperature programmed reduction (Table S1), ignition-extinction curves of Pd/Ce/Al-R catalyst (Fig.S2), ignition-extinction curves of Ce/Pd/Al-R catalyst (Fig.S3), ignition-extinction profile of Pd/Ce/Al-R and Ce/Pd/Al-R catalysts (Table S2), at.% Pd, PdO, PdOx in Pd 3d XPS spectra of Pd/Ce/Al and Ce/Pd/Al catalysts (Table S3), at.% Ce(III) and Ce(IV) in Ce 3d XPS spectra of Pd/Ce/Al and Ce/Pd/Al catalysts (Table S4), effect of aging and reduction on stability of the as- prepared catalysts (Table S5), mass transfer limitations data for Pd/Ce/Al and Ce/Pd/Al catalysts (Table S6 and S7), mass transfer limitations calculations. See DOI: ----

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Table S1. Calculated hydrogen consumption (μmol H₂/g) during hydrogen temperature programmed reduction (TPR).

Fig. S2. Ignition-extinction curves of Pd/CeO_x-γ-Al₂O₃-R (Pd/CeAl-R) catalyst.

Fig. S3. Ignition-extinction curves of CeO_x/Pd-γ-Al₂O₃-R (Ce/PdAl-R) catalyst.

Table S2. Ignition-Extinction profile of Pd/CeO_x-γ-Al₂O₃-R (Pd/CeAl-R) and CeO_x/Pd-γ-Al₂O₃-R (Ce/PdAl-R) catalysts.

Table S3. Atomic % of Pd, PdO and PdOx based on deconvolutions of 3d5/2 peak in the Pd 3d X-ray photoelectron spectroscopy (XPS) spectra.

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Table S6. Mass transfer limitations data for Pd/CeO_x-γAl₂O₃ (Pd/Ce/Al), CeO_x/Pd-γAl₂O₃ (Ce/Pd/Al) catalysts [Figs.7A and 7C, R=reduced; a=aged].

Table S7. Internal mass transfer limitations data for Pd/CeO_x/Al₂O₃ (Pd/Ce/Al) and CeO_x/Pd/Al₂O₃ (Ce/Pd/Al) catalysts [Figs.2B, F=fresh, R=Reduced].

Mass transfer limitations calculations

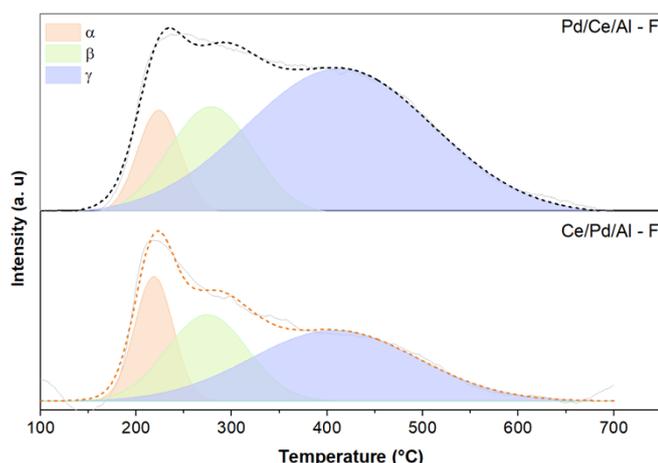


Fig. S1. Hydrogen temperature programmed reduction (TPR) data of Pd/CeO_x-γ-Al₂O₃ (Pd/Ce/Al) and CeO_x/Pd-γ-Al₂O₃ (Ce/Pd/Al) catalysts. Peaks α correspond to peaks with reduction temperature < 250 °C; peaks β correspond to peaks with reduction temperature between 250 and 500 °C; peaks γ correspond to peaks with reduction temperature > 500 °C; calculated hydrogen uptakes (μmol H₂/g) corresponding to these peaks are given in Table S1; [F=fresh].

Table S1 Calculated hydrogen consumption (μmol H₂/g) during hydrogen temperature programmed reduction (TPR). Pd/CeO_x-γ Al₂O₃ (Pd/Ce/Al); CeO_x/Pd-γ-Al₂O₃ (Ce/Pd/Al). [F=fresh].

Catalyst	α (±5.0)	β (±9.7)	γ (±7.6)	Total
Pd/Ce/Al-F	87.0	174.8	530.1	792.0
Ce/Pd/Al-F	34.8	50.6	86.1	171.5

Calculated H₂ uptake for stoichiometric PdO reduction based on 4.5 wt. % Pd loading was of 424 μmol H₂/g; Peaks α correspond to peaks with reduction temperature < 250 °C; Peaks β correspond to peaks with reduction temperature between 250 and 500 °C; Peaks γ correspond to peaks with reduction temperature > 500 °C.

Discussion of TPR Results

The TPR profiles (Fig. S1) were deconvoluted into three gaussian peaks. The first peak (α) located at temperatures below 250 °C could be assigned to the reduction of PdO_x or PdO

loosely bound to the surface. The second peak (β) located between 250-500 °C could be attributed to the reduction of strongly adsorbed PdO on the surface of the support and or to the surface reduction of Ce^{4+} to Ce^{3+} . Peaks (γ) at temperature higher than 500 °C were assigned to reduction of bulk cerium (IV) oxide. The calculated H_2 uptake for the Pd/CeAl-F catalyst exceeded the stoichiometric amount of H_2 needed for PdO reduction (424 $\mu\text{mol } H_2/\text{g}$ based on 4.5 wt.% Pd loading) (Table S1), which could be attributed to H_2 spillover from Pd to the support or activation of Al_2O_3 by reduction with hydrogen and strong metal support interactions between the Pd species and reduced Al_2O_3 - CeO_2 support. For the Ce/PdAl-F catalyst the calculated H_2 consumption was lower than the theoretical H_2 consumption (Table 1) and this could be due to the embedment or encapsulation of PdO particles on CeO_2 .

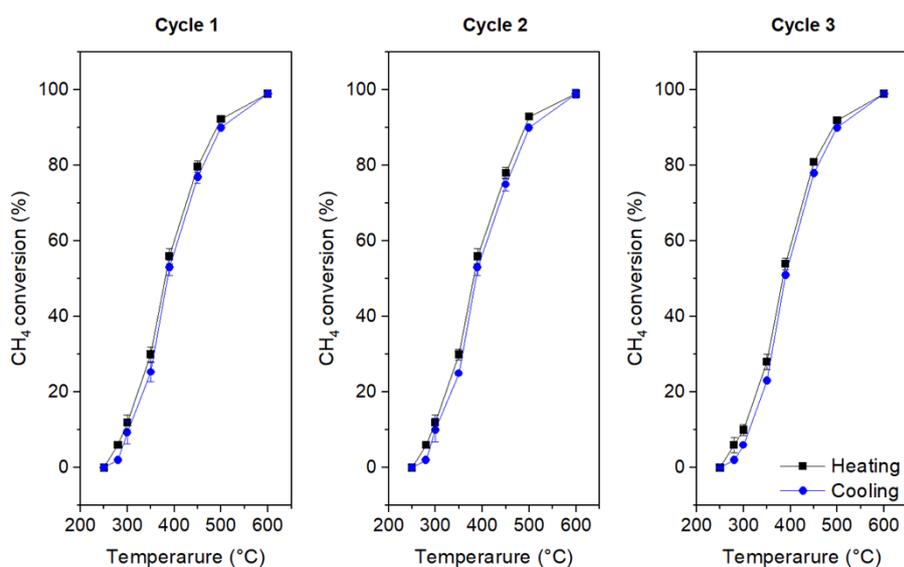


Fig. S2. Ignition-extinction curves of Pd/ CeO_x - γ - Al_2O_3 -R (Pd/CeAl-R) catalyst. Conditions: CH_4 1 vol.%, O_2 4 vol.%, N_2 balance; GHSV 90,000 h^{-1} ; Reaction time, 1 h at each temperature.

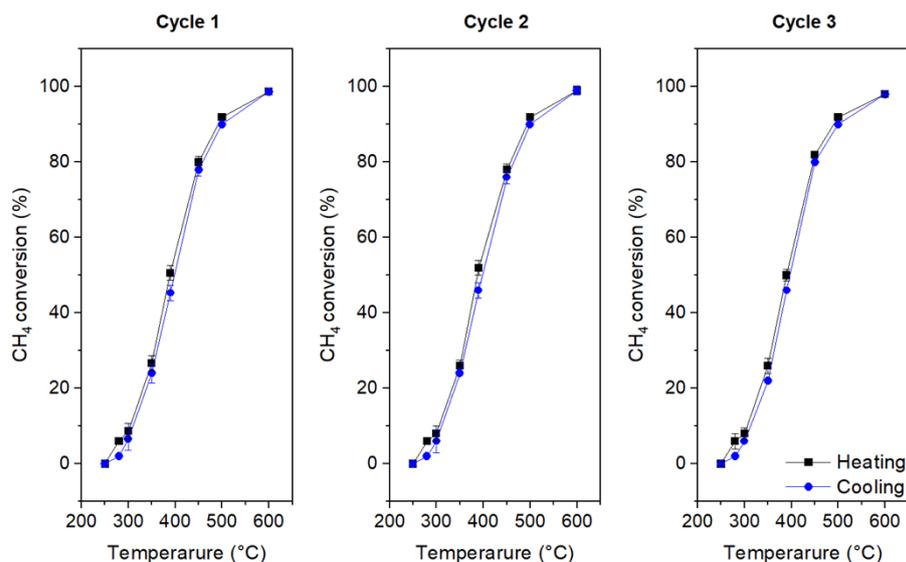


Fig. S3. Ignition-extinction curves of $\text{CeO}_x/\text{Pd}-\gamma\text{-Al}_2\text{O}_3\text{-R}$ (Ce/PdAl-R) catalyst. Conditions: CH_4 1 vol.%, O_2 4 vol.%, N_2 balance; GHSV 90,000 h^{-1} ; Reaction time, 1 h at each temperature.

Table S2. Ignition-Extinction profile of $\text{Pd}/\text{CeO}_x-\gamma\text{-Al}_2\text{O}_3\text{-R}$ (Pd/CeAl-R) and $\text{CeO}_x/\text{Pd}-\gamma\text{-Al}_2\text{O}_3\text{-R}$ (Ce/PdAl-R) catalysts.

Catalyst	T_{ig} ($^{\circ}\text{C}$)	T_{ex} ($^{\circ}\text{C}$)	Hysteresis width ($^{\circ}\text{C}$)
Pd/CeAl-R	280	250	30
Ce/PdAl-R	280	250	30

Data calculated from Figs. S2 and S3. Conditions for experiments: CH_4 1 vol.%, O_2 4 vol.%, N_2 balance; GHSV 90,000 h^{-1} , reaction time, 1 h at each temperature.

Table S3 Atomic % of Pd, PdO and PdOx based on deconvolutions of 3d5/2 peak in the Pd 3d X-ray photoelectron spectroscopy (XPS) data. ^a Pd/CeO_x-γAl₂O₃ (Pd/Ce/Al), CeO_x/Pd-γAl₂O₃ (Ce/Pd/Al) catalysts. [F=fresh; S=spent; R=reduced].

Catalyst	Pd	PdO	PdO _{x, x>2+}
Pd/Ce/Al-F	5	82	12
Pd/Ce/Al-F-S	0	95	5
Pd/Ce/Al-R	100	0	0
Pd/Ce/Al-R-S	4	79	15
Ce/Pd/Al-F	0	90	10
Ce/Pd/Al-F-S	0	95	5
Ce/Pd/Al-R	-	-	-
Ce/Pd/Al-R-S	-	-	-

^a Curve fitting was conducted in the Thermofisher Avantage software until χ^2 reached a value equal or less to 0.8; values are at.%. Due to low intensity of the signals, we refrained from fitting the signals for Ce/Pd/Al-R and Ce/Pd/Al-R-S catalysts.

Table S4 Atomic % Ce (III) and Ce (IV) based on peak deconvolutions in the Ce 3d X-ray photoelectron spectroscopy (XPS) data. ^a Pd/CeO_x- γ Al₂O₃ (Pd/Ce/Al), CeO_x/Pd- γ Al₂O₃ (Ce/Pd/Al) catalysts. [F=fresh; R=reduced].

Catalyst	Ce ³⁺	Ce ⁴⁺
Pd/Ce/Al-F	31	68
Pd/Ce/Al-R	41	58
Ce/Pd/Al-F	35	65
Ce/Pd/Al-R	48	51

^a Curve fitting was conducted in the Thermofisher Avantage software until χ^2 reached a value equal or less to 0.8.

Table S5. Effect of aging and reduction on stability of the as- prepared catalysts . Pd/CeO_x- γ Al₂O₃ (Pd/Ce/Al), CeO_x/Pd- γ Al₂O₃ (Ce/Pd/Al) catalysts. [F=fresh; R=reduced; a=aged].

Catalyst	Methane Conversion %		
	500 °C	700°C	850 °C
Pd/Ce/Al -F	91.8	95.0	97.4
Pd/Ce/Al -R	92.4	96.0	99.6
Pd/Ce/Al -R-a	80.6	93.1	98.0
Pd/Ce/Al -a	78.8	88.6	94.7
Ce/Pd/Al-F	43.1	85.0	96.0
Ce/Pd/Al -R	90.4	95.0	99.7
Ce/Pd/Al -R-a	93.3	97.0	96.5
Ce/Pd/Al -a	78.9	84.7	86.5

Conditions for activity experiments: CH₄ 1 vol.%, O₂ 4 vol/%, N₂ balance; GHSV 90,000 h⁻¹, reaction time, 1 h at each temperature .

Table S6. Mass transfer limitations data for Pd/CeO_x- γ Al₂O₃ (Pd/Ce/Al), CeO_x/Pd- γ Al₂O₃ (Ce/Pd/Al) catalysts[Figs.7A and 7C]. R=reduced; a=aged].

Catalyst	500 °C		700 °C		850 °C	
	C _{w-p}	M _{ext}	C _{w-p}	M _{ext}	C _{w-p}	M _{ext}
Pd/Ce/Al -R-a	6.37	8.31*10 ⁻³	8.26	9.98*10 ⁻³	9.34	1.20*10 ⁻²
Pd/Ce/Al -a	6.23	8.12*10 ⁻³	7.86	9.50*10 ⁻³	9.02	1.16*10 ⁻²
Ce/Pd/Al -R-a	7.37	9.62*10 ⁻³	8.65	1.05*10 ⁻²	9.1	1.17*10 ⁻²

Ce/Pd/Al -a	6.24	8.13*10 ⁻³	7.51	9.08*10 ⁻³	8.24	1.06*10 ⁻²
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C_{w-p} is Weisz-Prater criteria calculated from eq. S1; $C_{w-p} > 1$ indicates internal mass transfer limitations. M_{ext} is Mears' criteria calculated from eq. S3; $M_{ext} < 0.15$ indicates no external mass transfer limitations.

Table S7. Internal Mass transfer limitations data (C_{w-p}) for Pd/CeO_x- γ Al₂O₃ (Pd/Ce/Al), CeO_x/Pd- γ Al₂O₃ (Ce/Pd/Al) catalysts at 330-390 °C [Fig. 2B] . R=reduced; a=aged].

Temperature (°C)	Pd/Ce/Al-F	Ce/Pd/Al-F	Pd/Ce/Al-R	Ce/Pd/Al-R
250	-	-	0.14	0.14
280	-	-	0.43	0.43
300	-	-	1.01	0.58
330	-	-	-	-
340	0.59	-	-	-
350	0.74	-	-	-
360	-	0.47	-	-
370	0.96	-	-	-
380	-	0.79	-	-
390	-	1.02	-	-

Mass Transfer Limitations (MTL) calculations

The presence of MTL at high temperatures were determined by means of the Weisz-Prater criteria (Eq. S1) and the Mears' criteria (Eq. S2) for internal and external mass transfer limitations, respectively. The calculations were performed for CH₄, since it was the reactant with the lowest concentration.

$$C_{w-p} = \frac{r_{obs} * \rho_p * R_p}{D_e * C_{AS}}$$

S1

Where r_{obs} corresponds to the observed CH₄ reaction rate in (mmol/g_{cat}/s), calculated from the data presented in Table S5, Figs. S2, S3, ρ_p corresponds to the catalyst density with a value of 1.05 g/cm³, R_p is the diameter of the catalyst particle (5.3 * 10⁻³ cm), C_{AS} is the concentration of CH₄ in mmol/cm³ corresponding to 1.5*10⁻⁶. Finally, D_e corresponds to the effective diffusivity, which was estimated from Knudsen diffusivity (Eq. S2)

$$D_e = \frac{d}{3} \sqrt{\frac{8 * R * T}{\pi * M_A}}$$

S2

Where d corresponds to the pore diameter with a value of $1.5 \cdot 10^{-8}$ m, obtained from N_2 physisorption, M_A corresponds to CH_4 molecular weight of 16.0 g/mol, and T corresponds to the reaction temperature in Kelvin. Thus at 500 °C, De and C_{w-p} values of 0.051 cm^2/s and 6.37 were estimated, respectively. The MTL values are tabulated in Table S6 and S7.

For external mass transfer limitations, the Mears' criteria was applied (Eq S3). To estimate the mass transfer coefficient (k_c), Reynolds (Eq S4), Schmidt (Eq S5) and Sherwood (Eq S6) numbers were estimated.

$$M_{ext} = - \frac{r_{obs} * \rho_p * L * n}{k_c * C_{AS}}$$

S3

$$Re = \frac{2 * U * L}{(1 - \phi) * \nu}$$

S4

$$Sc = \frac{\nu}{D_{AB}}$$

S5

$$Sh = Re^{\left(\frac{1}{2}\right)} Sc^{\left(\frac{1}{3}\right)} = \frac{k_c * 2 * L}{D_e}$$

S6

Where U corresponds to the superficial velocity of 0.23 m/s, ϕ is the catalyst porosity, ν is the kinematic viscosity of CH_4 at the temperature of the reaction, at 500 °C this is $9.3 \cdot 10^{-5}$ m^2/s , D_{AB} is the bulk diffusivity of CH_4 in N_2 , which was taken from literature at 300 °C with a value of 0.67 cm^2/s , L is the particle diameter ($5.3 \cdot 10^{-3}$ cm) and n is the order of the reaction estimated to be 1. With this, Mears' parameter was estimated to be between $1.1 \cdot 10^{-2}$ and $8.1 \cdot 10^{-3}$, which is much lower than 0.15 (Table S6).