The effect of milling parameters on the mechanochemical preparation of Pd-CeO_2 methane oxidation catalysts

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SUPPLEMENTARY MATERIAL

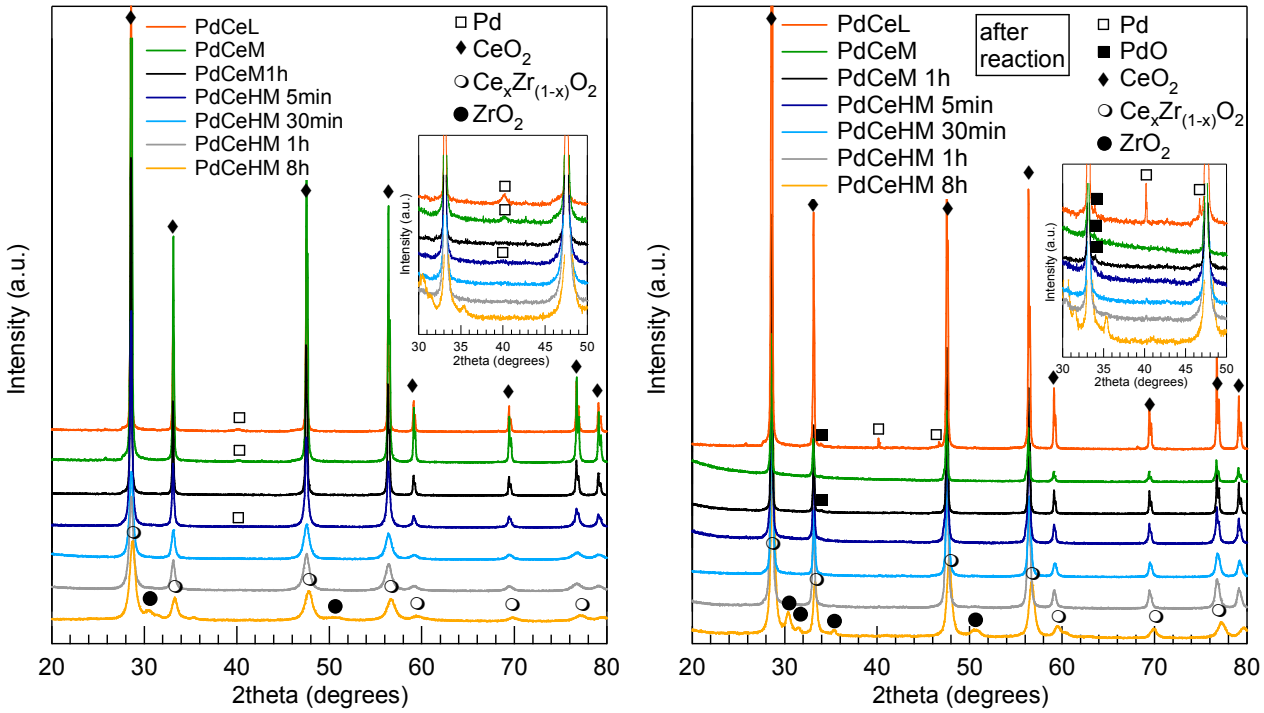


Fig. S1: XRD spectra of milled samples, as prepared (left) and after reaction (right). Inset: focus on the Pd-PdO 2theta range.

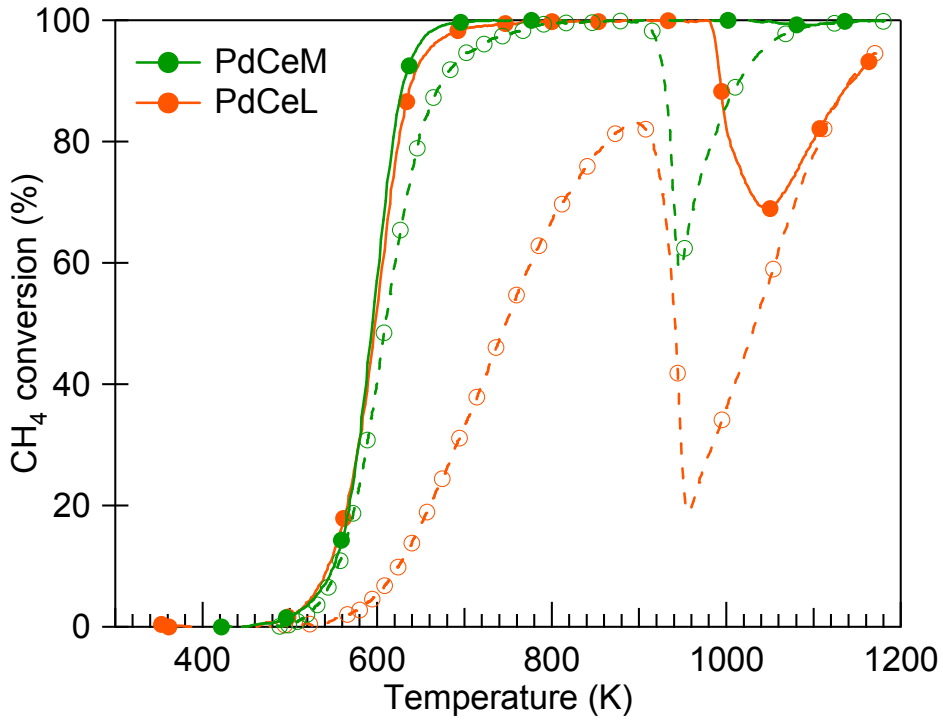


Fig. S2: Methane conversion of PdCeM and PdCeL samples, 1st heating/cooling cycle.

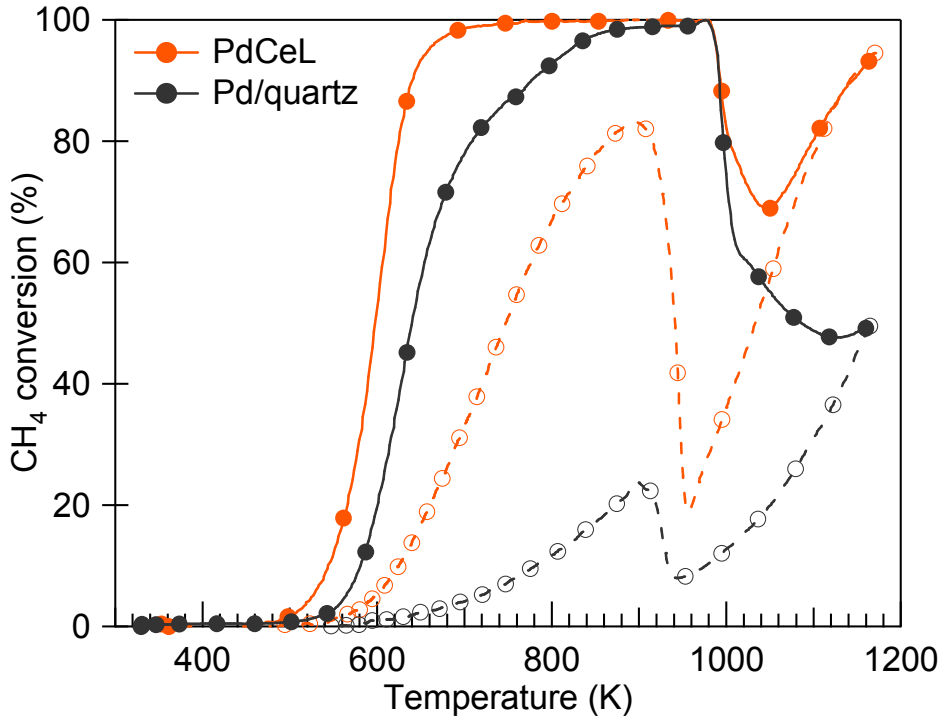


Fig. S3: Methane conversion of PdCeL and unsupported Pd (mixed with quartz), 1st heating/cooling cycle.

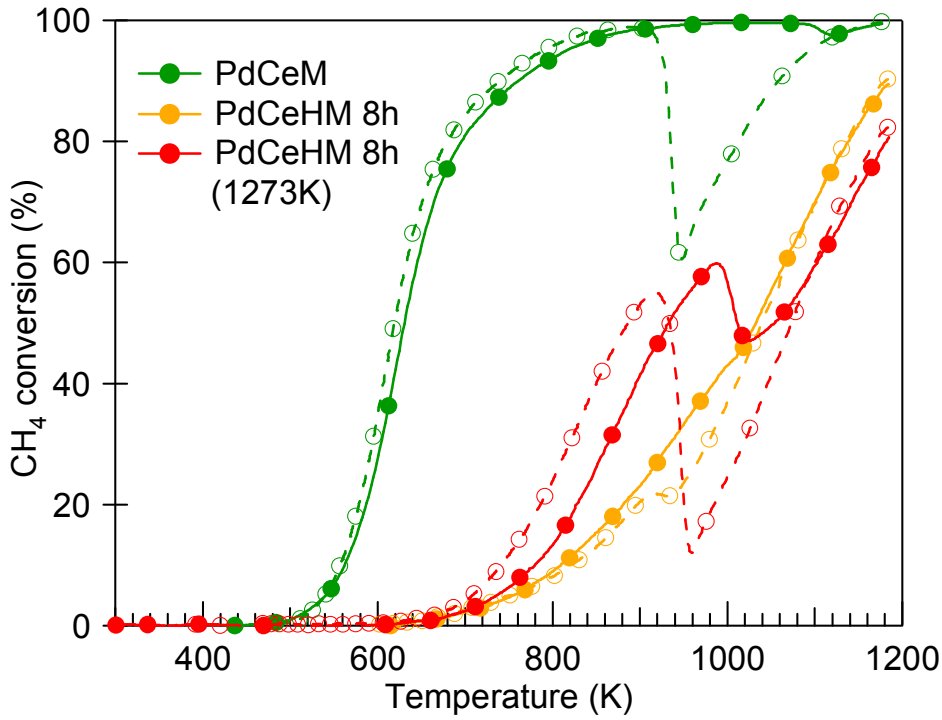


Fig. S4: Catalytic activity of PdCeHM 8h before and after oxidation test (at 1273 K). PdCeM is reported for comparison.

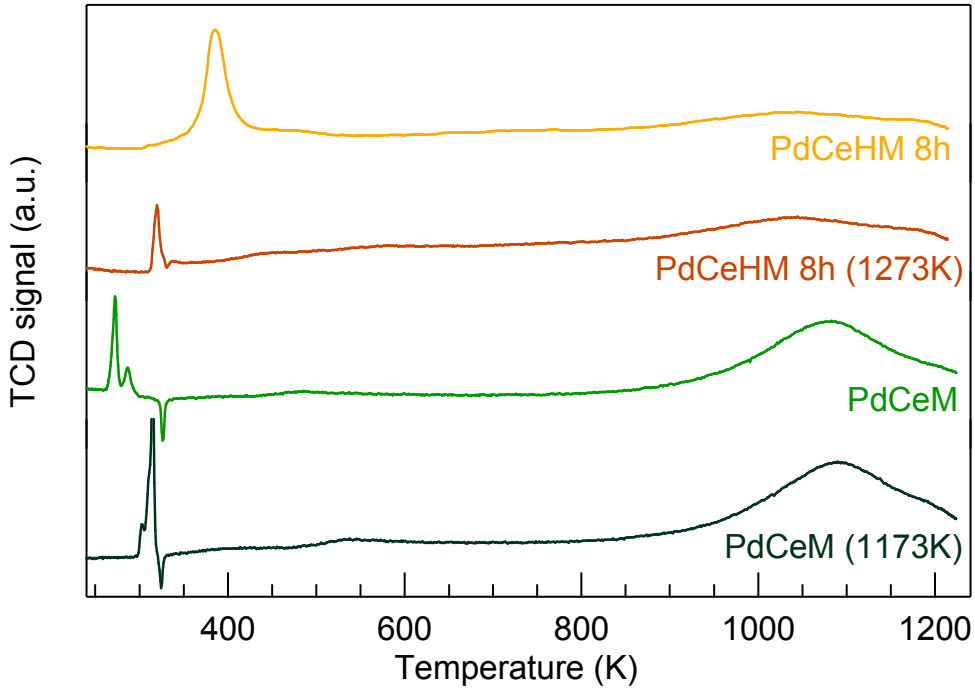
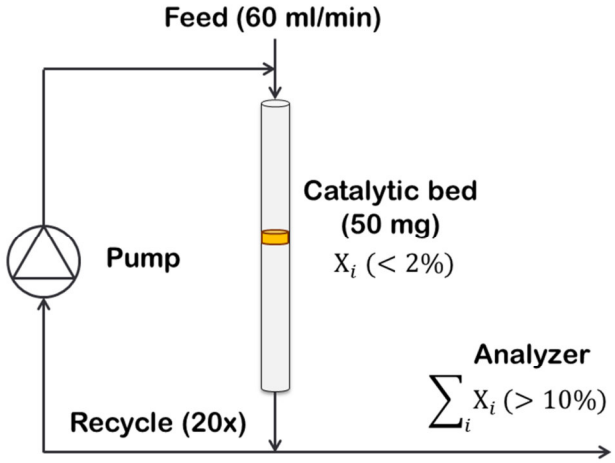


Fig. S5: TPR profiles of PdCeHM 8h and PdCeM, as prepared and after thermal treatment. Fresh samples were pretreated in air at 623 K for 1 h prior to the reduction test.

INFLUENCE OF MASS AND HEAT TRANSFER LIMITATIONS

To verify the presence of internal and external mass and heat transfer limitations at temperatures below 623 K suitable calculations were carried out on the reaction set-up. As input data, reaction rates were calculated in differential conditions in a recycle reactor[1] at 623 K for the most active samples (PdCeG, PdCeM, PdCeM 1h). A scheme of the recycle reactor set-up is reported in Scheme S1. For the least active samples, conversion data for reaction rate measurements could be extrapolated directly from the light-off curves at 623 K as all values were below 5% CH_4 conversion. The calculated reaction rates are summarized in Table S1.



Scheme S1: Recycle reactor.

Table S1: Calculated reaction rates for all prepared samples.

Sample	Reaction rate ($\mu mol/g_{cat} \cdot s$)	Pd loading (wt%)	Reaction rate ($\mu mol/g_{Pd} \cdot s$)
PdCeL	0.36 [a]	1 [d]	35.7 [a]
PdCeG	1.19	0.8 [c]	205 [b]
PdCeM	1.66	0.8 [c]	208 [b]
PdCeM 1 h	1.69	0.82 [c]	206 [b]
PdCeHM 5 min	0.46 [a]	0.87 [c]	52.6 [a]
PdCeHM 30 min	0.12 [a]	1 [d]	11.6 [a]
PdCeHM 1 h	$9.1 \cdot 10^{-2}$ [a]	1 [d]	9.1 [a]
PdCeHM 8 h	$8.32 \cdot 10^{-3}$ [a]	1 [d]	0.8 [a]

[a] measured in a flow reactor at 623 K (conversion <5%) [b] calculated in differential conditions in a recycle reactor at 623 K. [c] measured by ICP elemental analysis. [d] nominal Pd loading; due to the lower activity of these samples determination of Pd loading by elemental analysis has not been performed.

To evaluate the mass and heat transfer limitations, the criteria in equations (1)-(4) were used.[2] Given the strong positive dependency on reaction rate and particle size, the calculations are reported in the following for the case most susceptible to mass transfer limitations, i.e. PdCeM. The input data are reported in Table S2.

Firstly, the external mass transfer limitations were evaluated by calculating the difference in methane concentration between the gas film surrounding the catalyst particle and the gas bulk. Indeed, for a packed-bed reactor with spherical pellets in steady state conditions the reaction rate can be coupled to the film transport by equation (1)

$$-r'_A = \frac{6\, k_c\, \Delta C_{CH_4}}{\rho_p D_p} \tag{1}$$

where k_c is the mass transfer coefficient ($k_c = ShD_{AB}/D_p$), Sh is the Sherwood number, D_{AB} is the binary gas diffusivity, ρ_p is the pellet density and D_p is the pellet diameter. Re-arranging the terms and introducing the observed rate, the film concentration difference can be written as (2).

$$\Delta C_{CH_4} = \frac{-r'_A(obs)\rho_p {D_p}^2}{6ShD_{AB}} \tag{2}$$

Assuming data values as reported in Table S1, the resulting concentration difference in the film is equal to $\Delta C_{CH_4} = 1.7{\cdot}10^{-10}$ mol/m^3, which is negligible compared to the bulk methane concentration ($C_{A,b}$ = 0.0108 mol/m^3). It can be therefore assumed that no external resistance to mass transport is present.

Concerning the internal mass transfer limitations, the Weisz-Prater method was applied (3)

$$C_{WP} = \frac{-r'_A(obs)\rho_c R^2}{D_e C_{As}} = \begin{cases} \ll 1 & no\ mass\ transfer\ limitations \\ \gg 1 & severe\ mass\ transfer\ limitations \end{cases} \tag{3}$$

where R is the pellet radius ($D_p/2$), ρ_c is the bulk density of the catalytic material, D_e is the effective diffusivity and C_{As} is the methane concentration at the pellet surface (assumed equal to $C_{A,b}$ due to the previous calculations). Substituting the values of Table S2, the CWP results equal to $3.59{\cdot}10^{-3}$, which is indeed << 1. Consequently, no internal mass transfer limitations are present.

To investigate the heat transfer limitations the Anderson criterion was used (4). If satisfied, it implies that the reaction rate does not differ more than 5% of the rate at constant temperature, i.e. that the heat transfer limitations are negligible.

$$\frac{|\Delta H_{Rx}|(-r'_A)\rho_c R^2}{\lambda^e T_s} < 0.75\frac{R_g T_s}{E} \tag{4}$$

In the equation above, ΔH_{Rx} is the heat of reaction, λ_e is the effective thermal conductivity, T_s is the particle surface temperature, R_g is the gas constant and E is the activation energy. Using reasonable values for the parameters, reported in Table S2, results in a left term equal to $6.5{\cdot}10^{-9}$ and a right term equal to 0.02. The criterion is thus satisfied.

Table S2: Input data.

$-r'_A$**(obs)**	$1.66 \cdot 10^{-6}$	mol/(g·s)
ρ_b	2300	kg/m^3
ρ_c	7220	kg/m^3
D_p	$7 \cdot 10^{-6}$ [b]	m
Sh	1.5 [a]	
$C_{A,b}$ **(≈**$C_{A,s}$**)**	0.0108	mol/m^3
D_{AB}	$6.1 \cdot 10^{-5}$ [a]	m^2/s
D_e	$3.8 \cdot 10^{-7}$ [a]	m^2/s
ΔH_{Rx}	830	kJ/mol
E	$1.8 \cdot 10^5$	kJ/kmol
R_g	8.314	J/(mol·K)
λ_e	30 [a]	J/(m·s·K)
T_s	623	K

[a] values are assumed based on reference 2. [b] as the tests were carried out in powder form, the pellet size was measured by laser scattering of the catalytic powders in a Horiba LA950 laser scattering particle size analyzer.

References

1 S. Colussi, A. Gayen, J. Llorca, C. de Leitenburg, G. Dolcetti and A. Trovarelli, *Industrial & Engineering Chemistry Research*, 2012, **51**, 7510–7517.

2 J. Nilsson, P.-A. Carlsson, N. M. Martin, E. C. Adams, G. Agostini, H. Grönbeck and M. Skoglundh, *Journal of Catalysis*, 2017, **356**, 237–245.