Electronic Supplementary Information

In-situ investigation of the mechanochemically promoted Pd-Ce interaction under stoichiometric methane oxidation conditions

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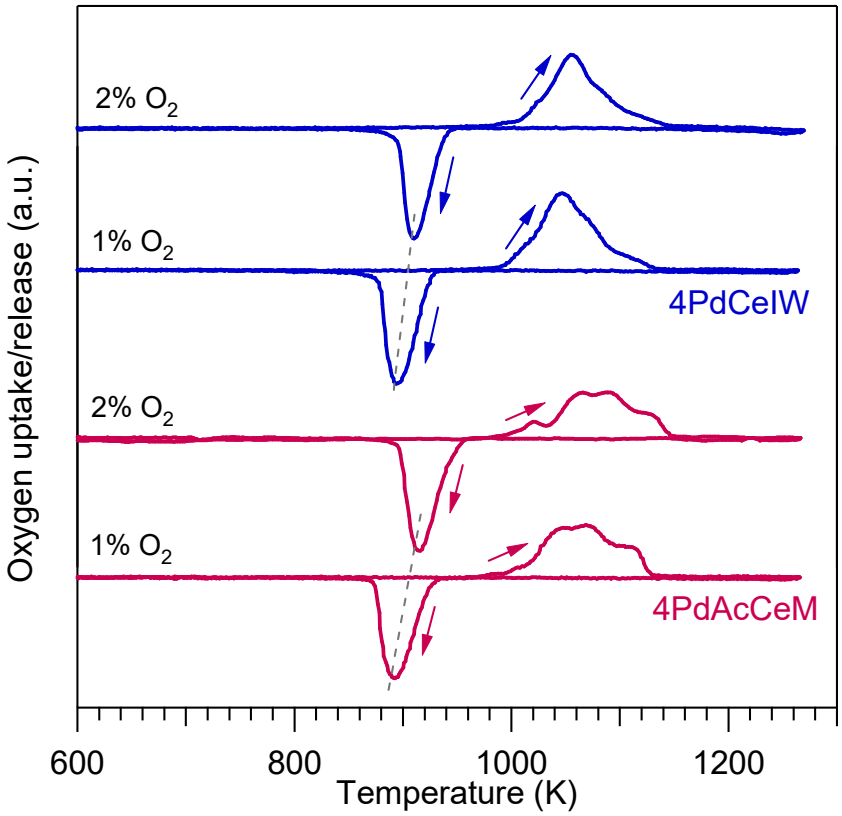

Fig. S1. Oxygen uptake profiles recorded on 4PdAcCeM and 4PdCeIW during Temperature Programmed Oxidation (TPO) tests carried out under different O_2 concentration; third heating/cooling TPO cycle.

Table S1. Quantitative analysis of the O_2 exchanged in the 3rd heating/cooling TPO cycle on M and IW catalysts (Figure S1). In parentheses the corresponding amount of reacting Pd (%)* is reported.

Sample	O_2 content (vol%)	Heating: O_2 release (µmoles O_2/g)	Cooling: O_2 uptake (µmoles O_2/g)
4PdCeIW	2%	147.6 (80)	123.2 (67)
	1%	163.2 (89)	148.8 (81)
4PdAcCeM	2%	140.3 (76)	133.9 (73)
	1%	145.9 (79)	144.0 (78)

*Ratio between the moles of Pd atoms reacting with the calculated amount of O_2 consumed/released, following the stoichiometry Pd+1/2O_2 →PdO, and the amount of Pd loaded on the catalyst as measured by ICP analysis:

$$reacting\ Pd\ (\%) = \frac{2\left[moles\ of\ O_2\ consumed/released\right]}{amount\ of\ Pd\ (moles)} \cdot 100$$

$$= \frac{2\left[moles\ of\ O_2\ consumed/released\right]}{\frac{cat.\,wt\ (g) \cdot Pd\ loading}{MW_{Pd}(\frac{g}{mol})}} \cdot 100$$

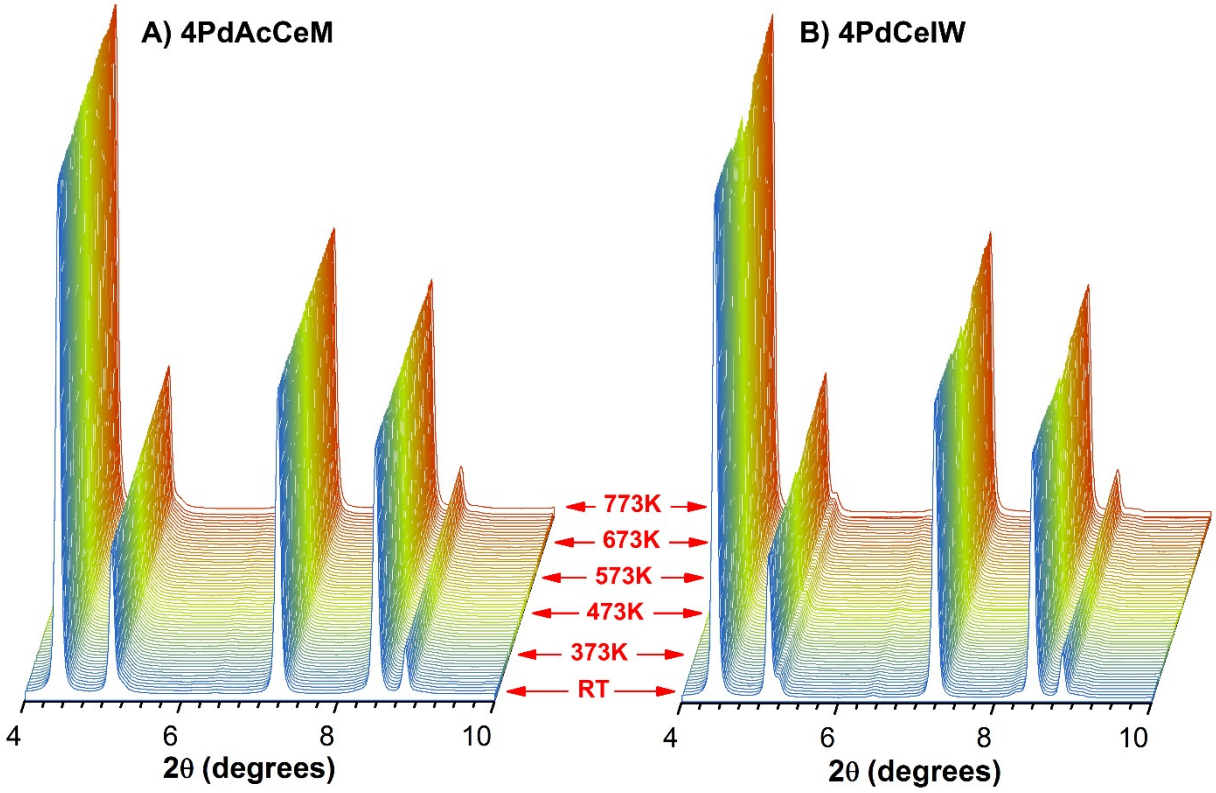

Fig. S2. In-situ XRD diffraction patterns collected under stoichiometric methane oxidation conditions (0.3%CH_4, 0.6%O_2 in He) on (A) 4PdAcCeM and (B) 4PdCeIW; samples were heated from RT to 773K at a 10°C/min heating rate, scans were collected every 60s.

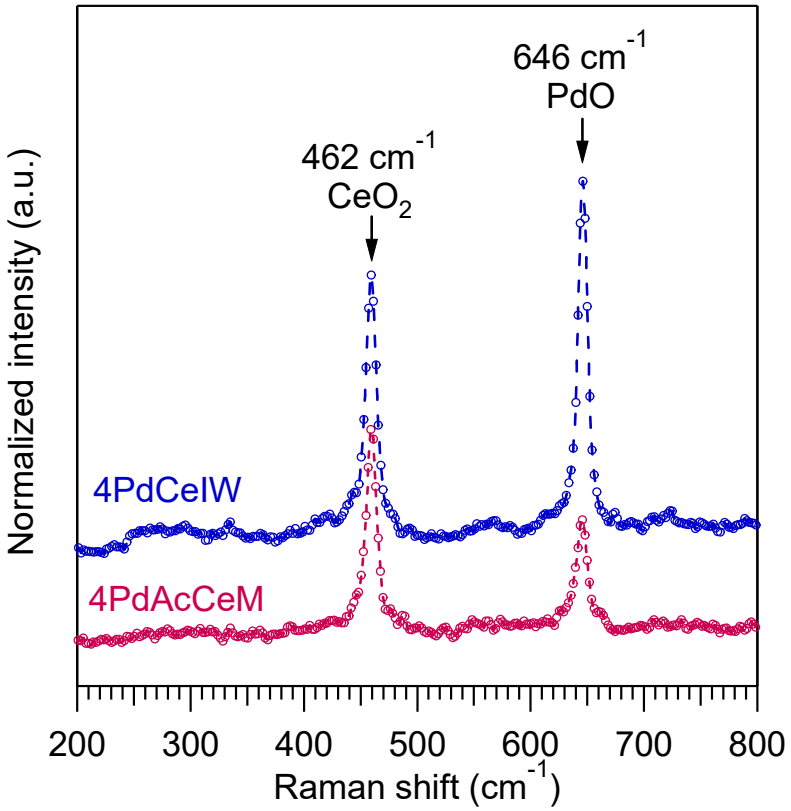

Fig. S3. Ex-situ Raman characterization of 4PdAcCeM and 4PdCeIW samples after reaction at 1173K. Collected spectra were normalized using the intensity of the CeO_2 F_{2g} peak (at 462 cm^{-1}); the low Signal-to-Noise Ratio (SNR) is due to the dark color of the 4wt%Pd loaded samples.

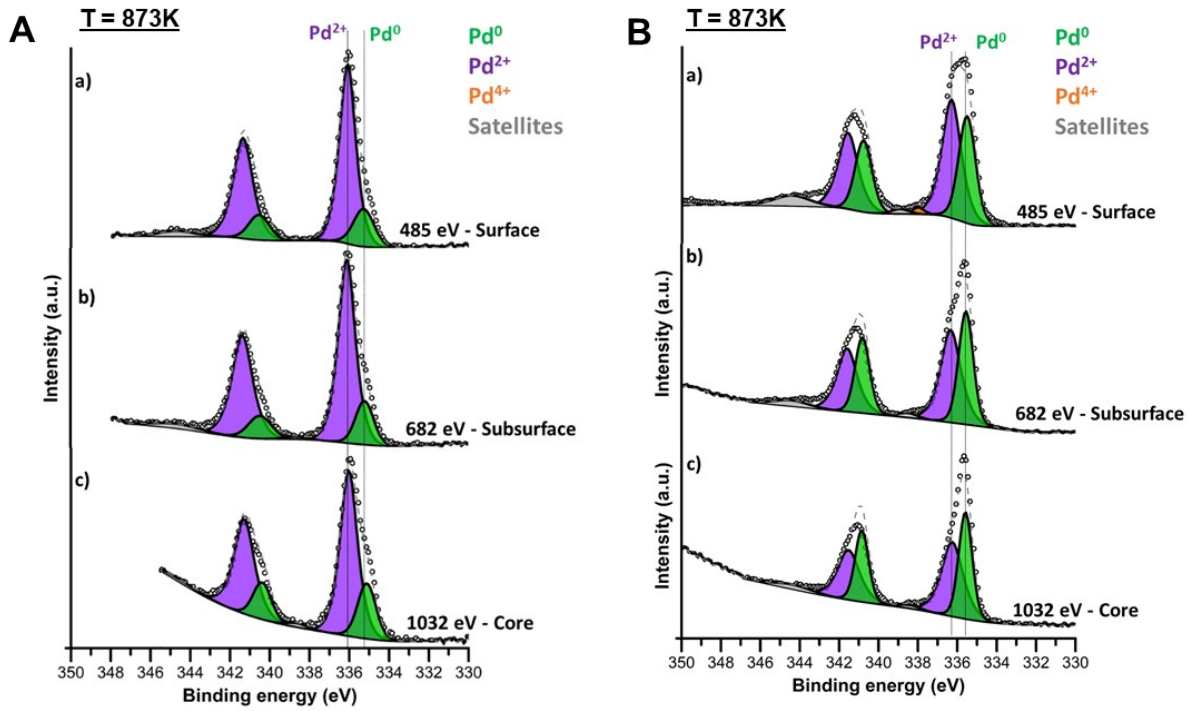

Fig. S4. Comparison of the NAP-XPS spectra collected in the Pd 3d region at different penetration depths on (A) 4PdCeIW and (B) 4PdAcCeM under 0.6 mbar CH_4, 1.4 mbar O_2 at 873K.

Table S2. Quantification of AP-XPS spectra for samples 4PdCeIW and 4PdAcCeM.

4PdCeIW	at.%Pd	Ce^{4+}/Ce	Pd^0/Pd	ΔEB (Pd^{2+}-Pd^0)*	O-Ce/O	O-H_2O gas/O lattice
673K	10.2	95.8	14.5	0.69	33.7	2.9
773K	19.4	93.9	18.0	0.81	31.5	3.6
873K - 485 eV	19.6	93.7	19.5	0.81	32.4	3.1
873K - 682 eV (Subsurface)			18.6			
873K - 1032 eV (Core)			24.4			

4PdAcCeM	at.%Pd	Ce^{4+}/Ce	Pd^0/Pd	ΔEB (Pd^{2+}-Pd^0)*	O-Ce/O	O-H_2O gas/O lattice
673K	24.3	96.8	22.3	0.89	87.0	1.6
773K	21.7	95.4	39.4	0.83	77.4	2.7
873K - 485 eV	21.9	93.3	40.0	0.79	90.0	1.1
873K - 682 eV (Subsurface)			43.3			
873K - 1032 eV (Core)			43.6			

*ΔEB: binding energy difference.

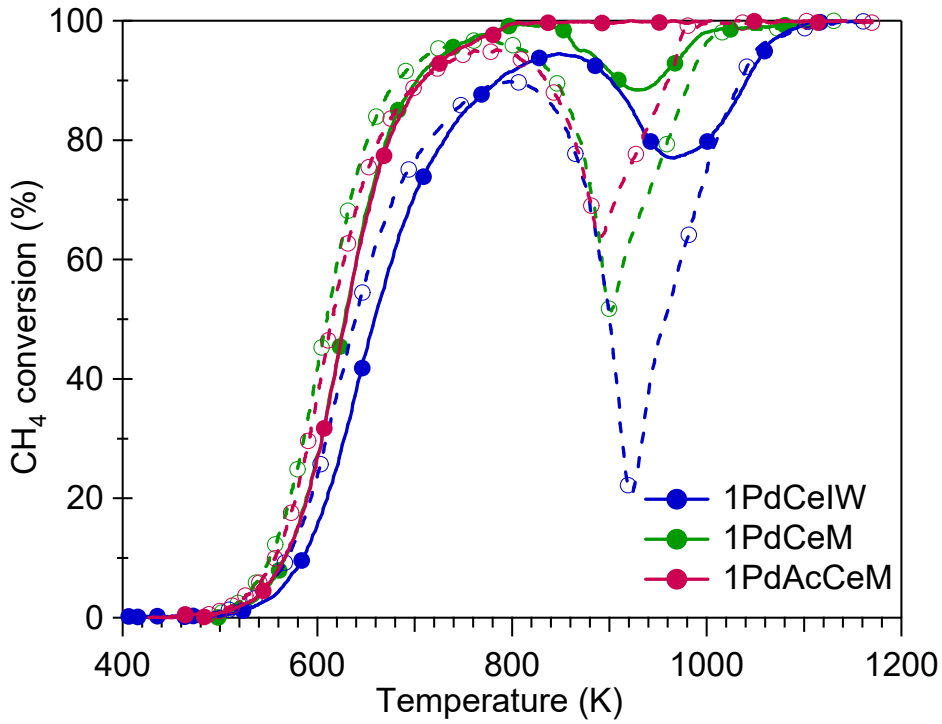

Fig. S5. Methane oxidation activity of 1wt%Pd/CeO_2 samples under stoichiometric methane oxidation conditions (0.5% CH_4, 1% O_2, He to balance); GHSV = 180,000 h^{-1}.