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Physicochemical properties of nanostructured Pd/lanthanide-doped ceria spheres with high catalytic activity for CH_4 combustion.

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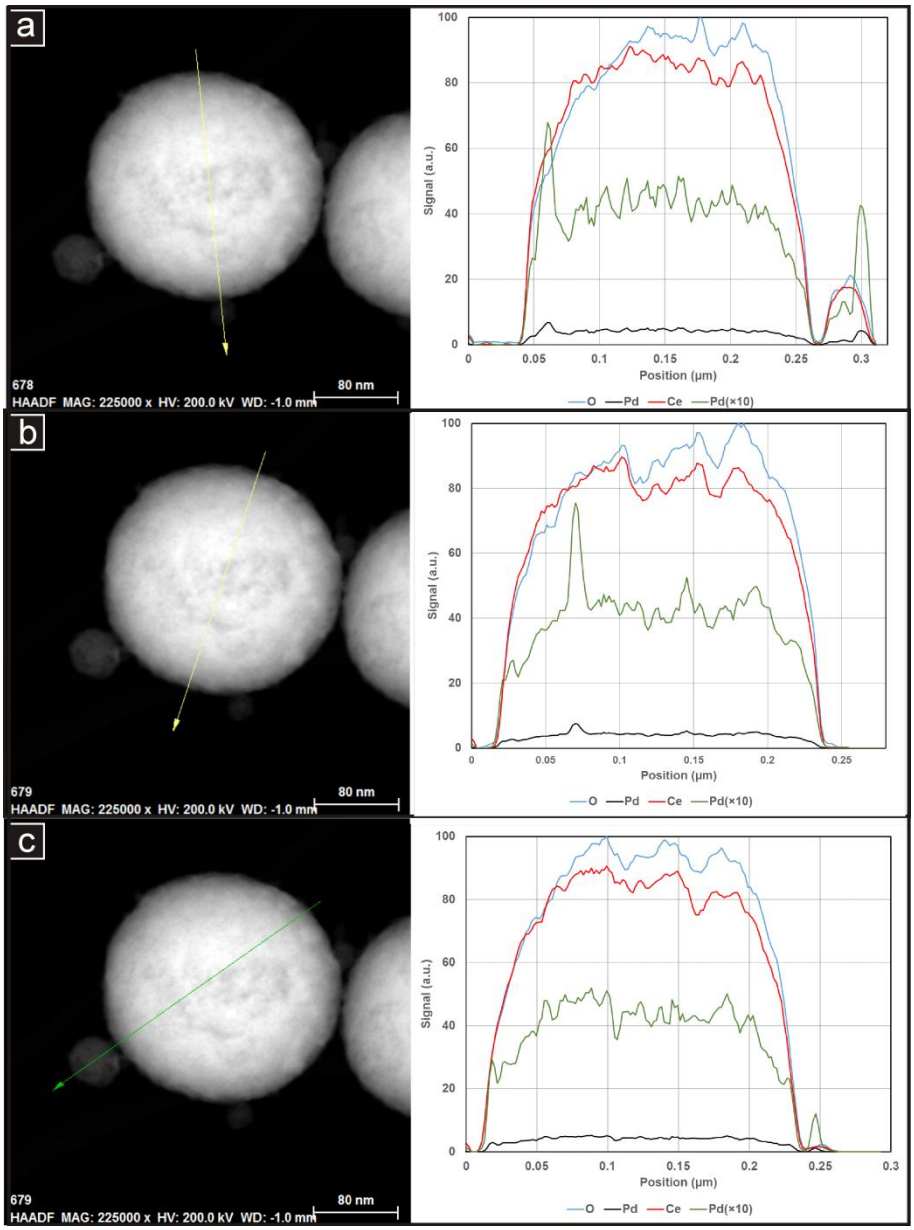

Figure S1. Elemental profiles along the lines indicated for three (a-c) diametrical sections through the same 1%wt Pd/PrDC sphere.

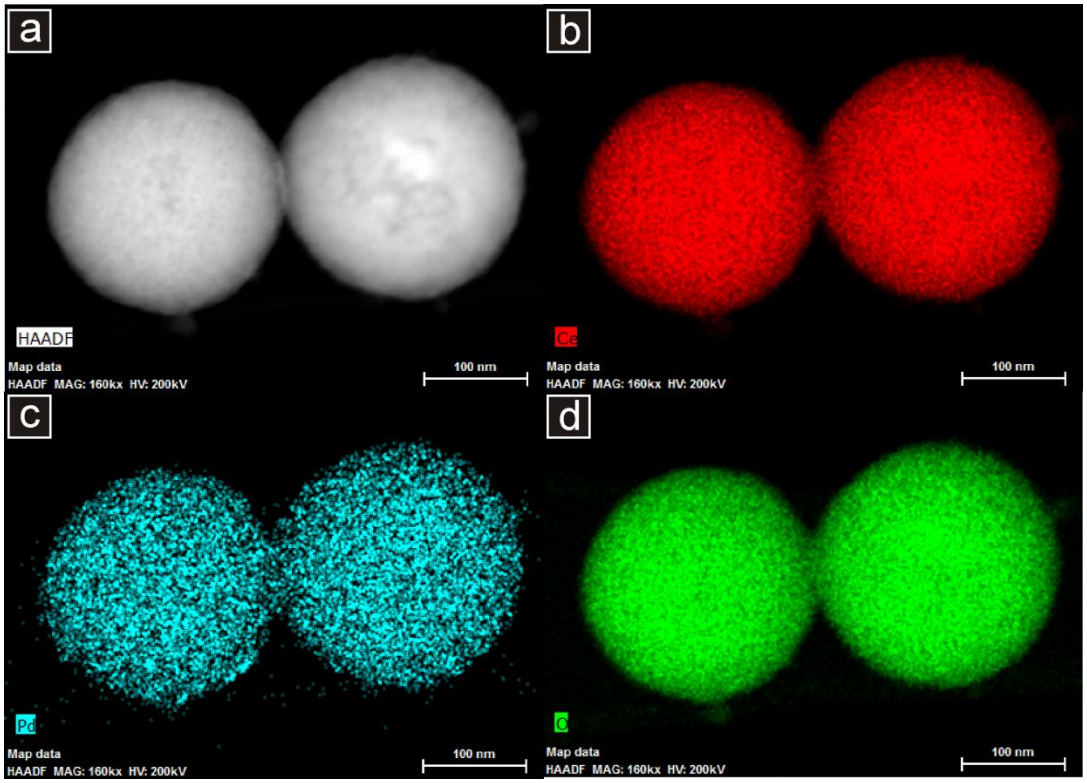

Figure S2. Electron (HAADF) image (a) and corresponding distribution maps for the elements Ce (b), Pd (c) and O (d) in two 1%wt Pd/PrDC spheres.

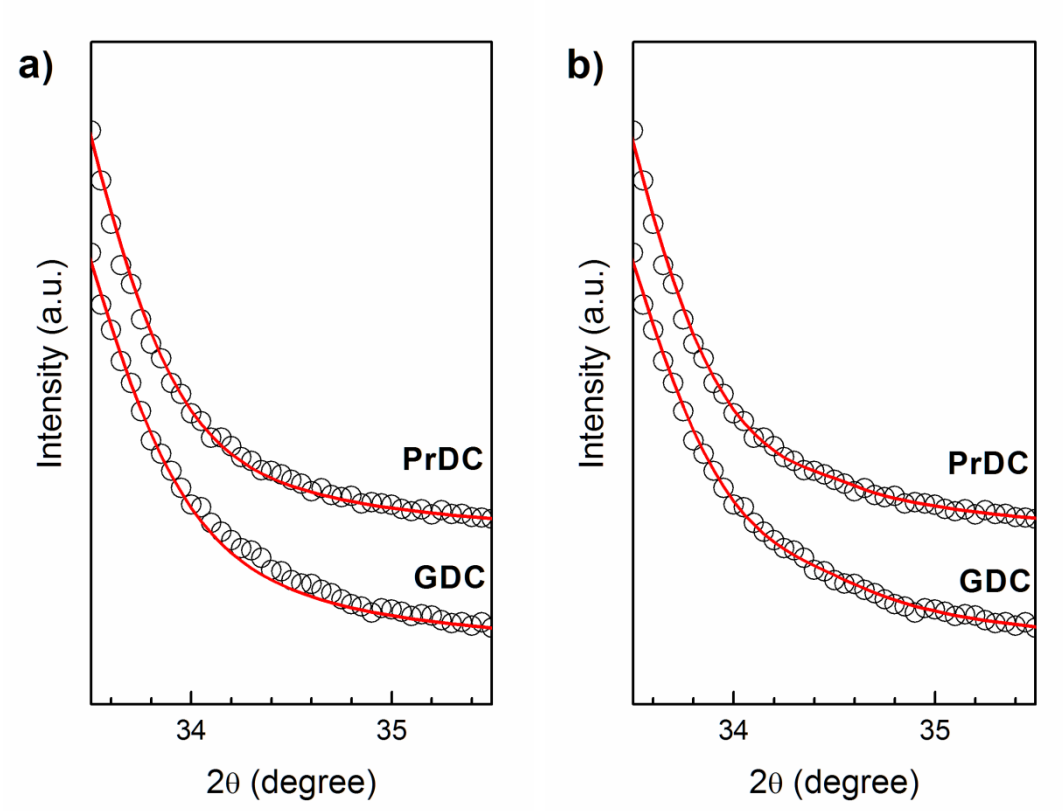

Figure S3. Expanded area of the SR-XRD patterns of 1 wt% Pd/LnDC samples in the vicinity of PdO (100) at room temperature (circles) with the Rietveld-fitted pattern (red line), a) not including and b) including a second phase of PdO.

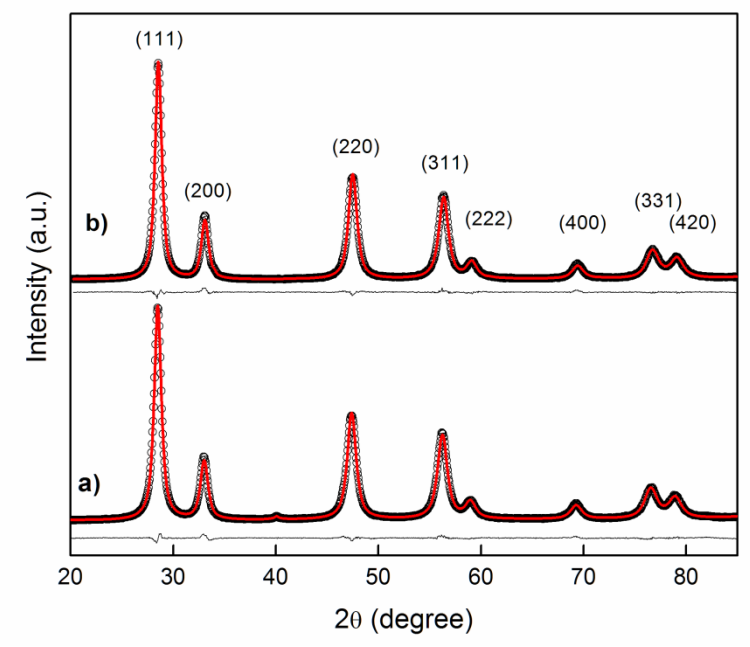

Figure S4. Synchrotron XRD patterns recorded at 500 ºC (empty circles) with the Rietveld-fitted pattern (red line) and the difference plot for 1 wt% Pd/GDC spheres under (a) reducing and oxidizing (b) conditions.

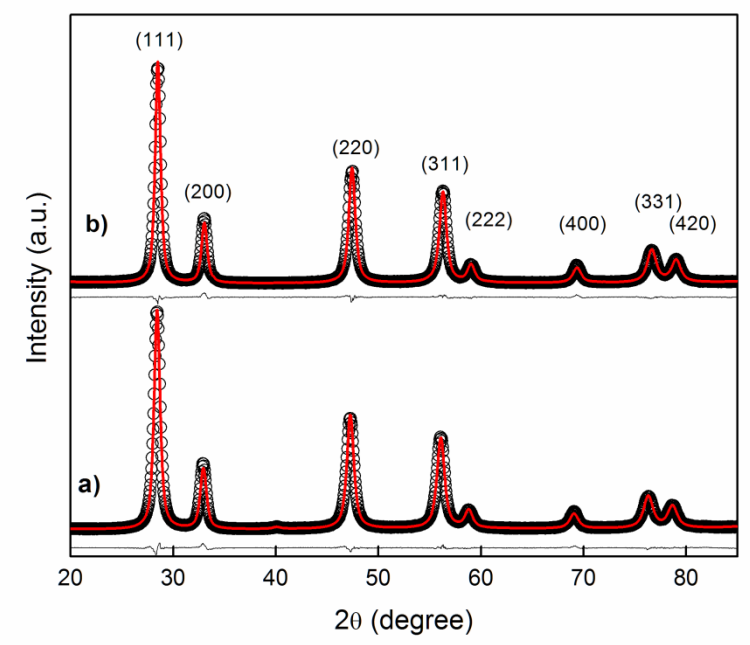

Figure S5. Synchrotron XRD patterns recorded at 500 ºC (empty circles) with the Rietveld-fitted pattern (red line) and the difference plot for 1 wt% Pd/PrDC spheres under (a) reducing and (b) oxidizing conditions.

Table S1. Structural parameters and standard Rietveld agreement factors for nanostructured 1wt%Pd/GDC spheres.

Atmosphere	Air*	5%H_2/He	Air*
T (ºC)	25	500	500
a (Å)	5.4192(6)	5.4514(8)	5.4416(8)
R_p	3.36	3.18	3.03
R_{wp}	4.18	3.88	3.68
R_e	2.53	2.44	2.49
χ^2	2.73	2.53	2.19

*Air corresponds to synthetic air (21% O_2/N_2).

Table S2. Structural parameters and standard Rietveld agreement factors for nanostructured 1wt%Pd/PrDC spheres.

Atmosphere	Air*	5%H_2/He	Air*
T (ºC)	25	500	500
a (Å)	5.4197(6)	5.4667(6)	5.4457(5)
R_p	2.77	3.27	3.32
R_{wp}	3.59	4.09	4.13
R_e	2.40	2.34	2.40
χ^2	2.22	3.05	2.95

*Air corresponds to synthetic air (21% O_2/N_2).

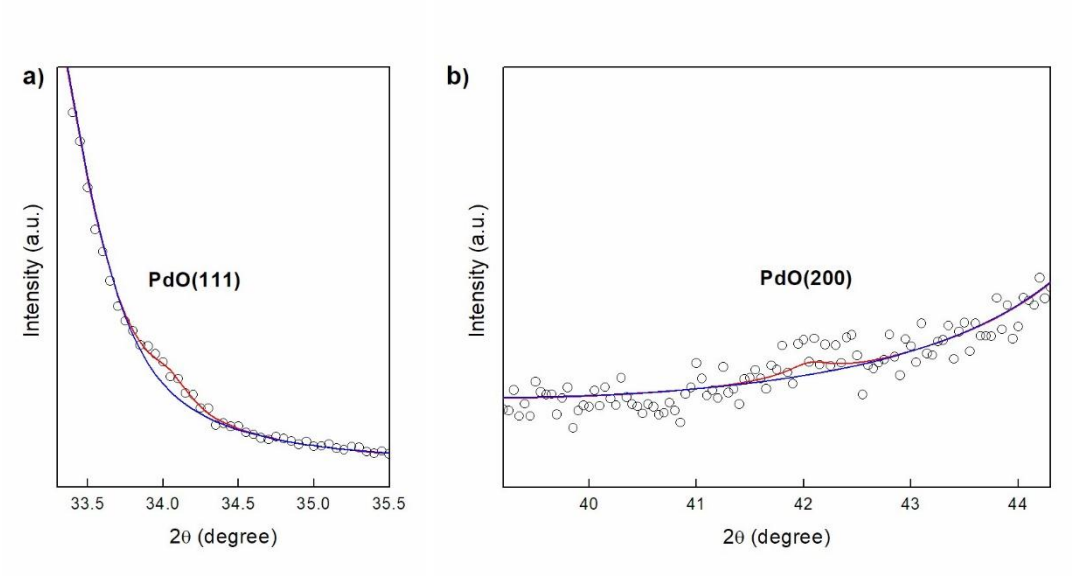

Figure S6. Synchrotron XRD patterns recorded at 500 ºC in synthetic air (21% O_2/N_2) - empty circles- with the Rietveld-fitted pattern considering PdO as a second phase (red line) and without PdO as a second phase (blue line) for1 wt% Pd/GDC spheres in the region close to (a)PdO (111) and (b) PdO (200).

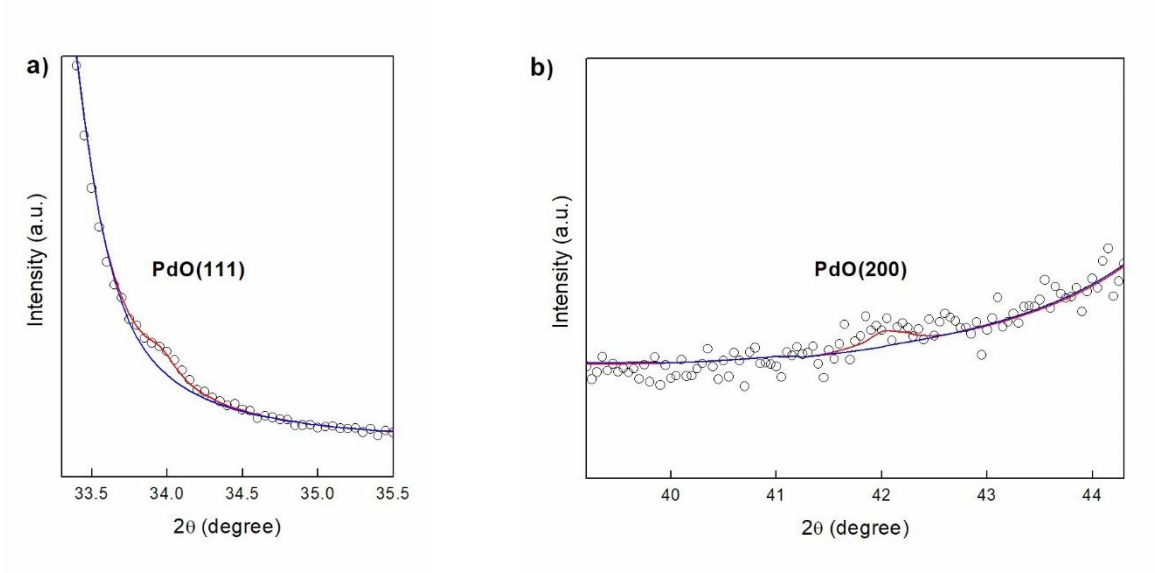

Figure S7. Synchrotron XRD patterns recorded at 500 ºCin synthetic air (21% O_2/N_2) - empty circles-with the Rietveld-fitted pattern considering PdO as second phase (red line) and without PdO as a second phase (blue line) for 1 wt% Pd/PrDC spheres in the region close to (a)PdO (111) and (b) PdO (200).

Table S3. Catalytic performance over the catalysts for CH_4 oxidation reported in the literature.

Sample	CH_4 oxidation at 300ºC		F_{CH4} (mmols.min^{-1})	Ref.
	Reaction rate* (mmols.g_{Pd}^{-1}.min^{-1})	X_{CH4}(%)		
1 wt% Pd/GDC-CC	7.1	5.9	0.0625	19
5 wt% Pd/GDC-CC	4.3	15.4	0.0625	19
1 wt% Pd/GDC	29	23.2	0.0937	This work
1 wt% Pd/PrDC	28.4	22.7	0.0937	This work

(*) The reaction rates were calculated using the methane signal and the following equation (1):

$$rate = \frac{F_{CH_4} * X_{CH_4}}{100 * W_{Pd}} \quad (1)$$

F_{CH_4} is the molar flow of methane in mmols.min^{-1}
W_{Pd} is the mass of Pd in grams
X_{CH_4} is the CH_4 conversion in percent.

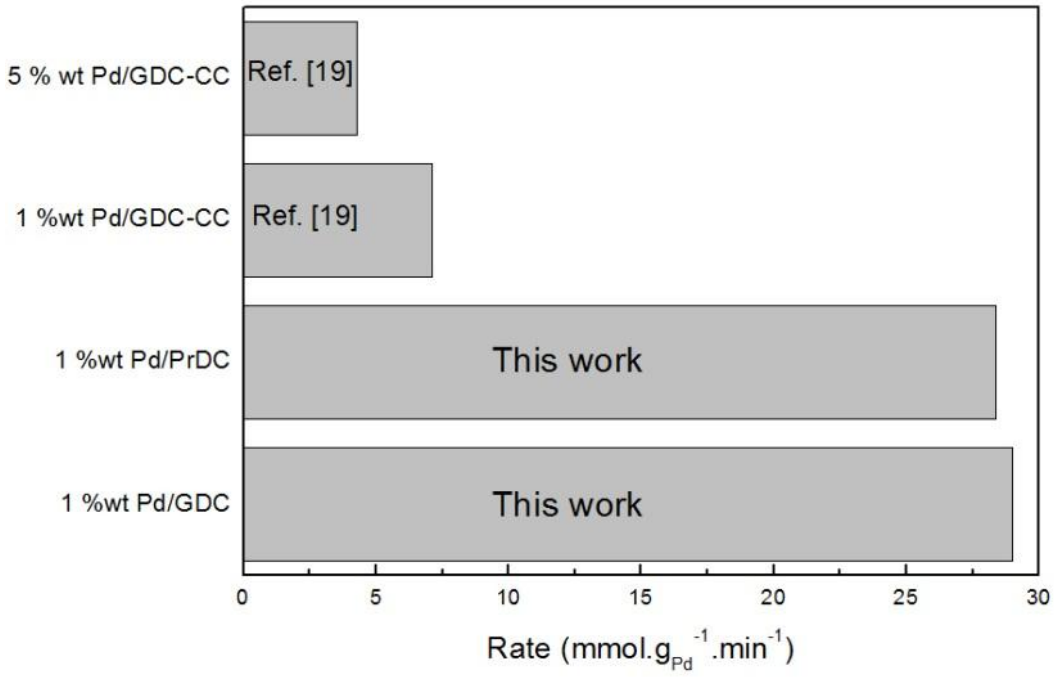

Figure S8. Methane oxidation rates at 300 ^{o}C of the studied Pd catalysts in comparison with previous values reported in the literature for 1%wt and 5%wt Pd/GDC-CC. [19]

References (same numeration of main text)

[19] F.F. Muñoz, R.T. Baker, A.G. Leyva, R.O. Fuentes, Appl. Catal. B: Environmental, 2013, 136-137, 122-132.

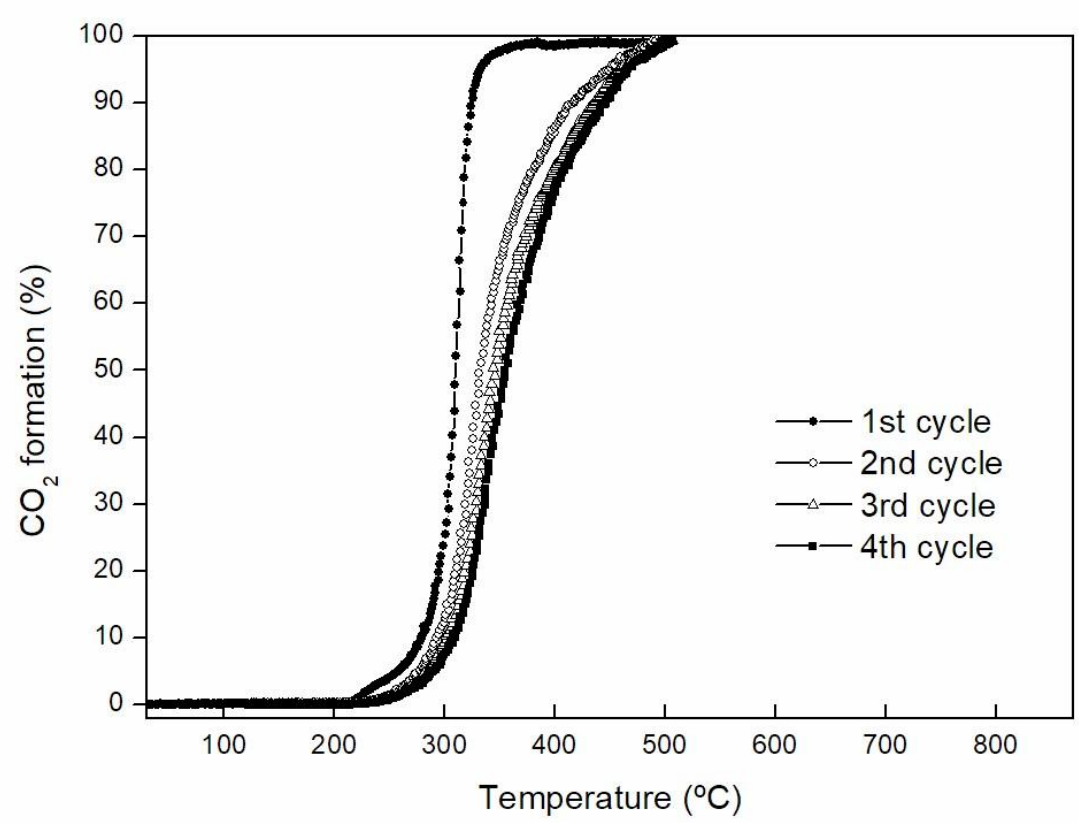

Figure S9. Catalytic activities for CO_2 formation of 1 wt% Pd/GDC after 4 cycles at 500 ºC for 2 h in the reaction mixture (2.1 mL.min^{-1} of CH_4, 11.6 mL.min^{-1} of O_2 and 61.3 mL.min^{-1} of Ar).

Table S4. Temperature at which 10, 50 and 90% of CO_2 formation was reached (T_{10}, T_{50} and T_{90}, respectively), estimated from the experimental curves (**Figure S8**).

Cycle	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)
1st	282	310	324
2nd	292	332	418
3rd	301	344	436
4th	310	355	446

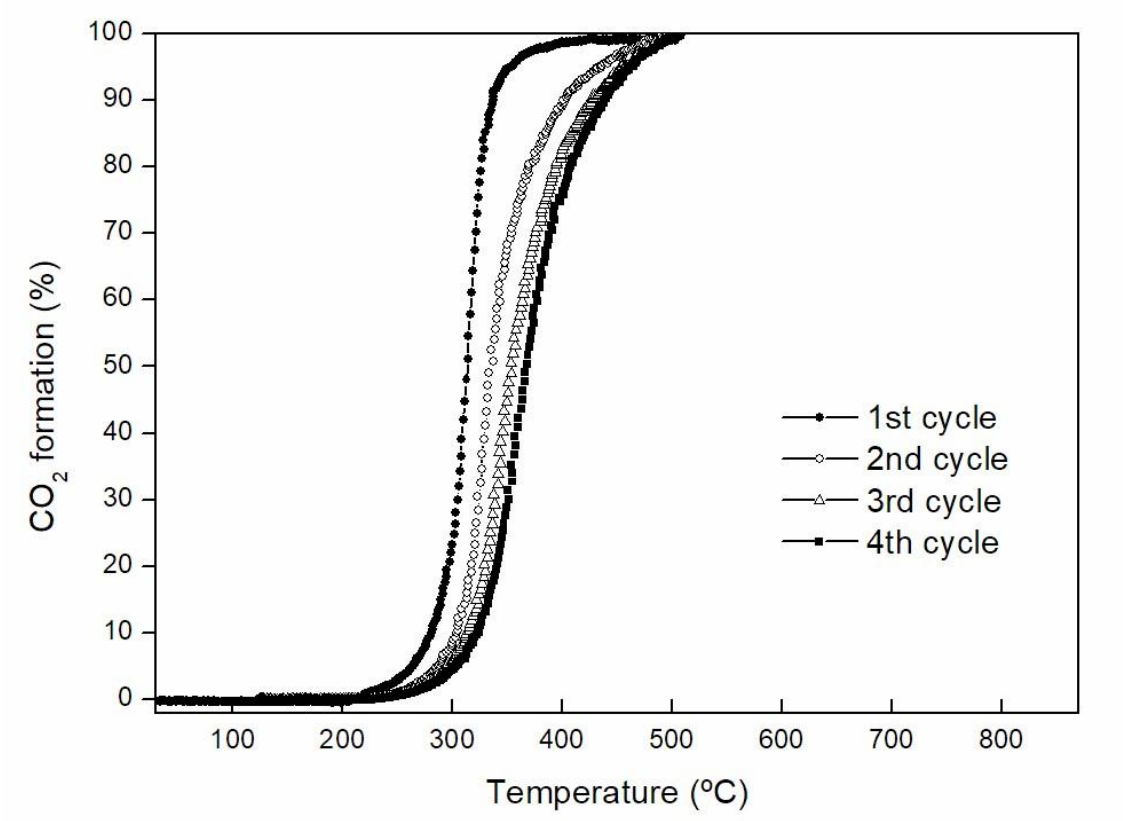

Figure S10. Catalytic activities forCO_2 formation of 1 wt% Pd/PrDC after 4 cycles at 500 ºC for 2 h in the reaction mixture (2.1 mL.min^{-1} of CH_4, 11.6 mL.min^{-1} of O_2 and 61.3 mL.min^{-1} of Ar).

Table S5. Temperature at which 10, 50 and 90% of CO_2 formation was reached (T_{10}, T_{50} and T_{90}, respectively), estimated from the experimental curves (**Figure S9**).

Cycle	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)
1st	282	310	336
2nd	303	337	401
3rd	315	353	427
4th	320	367	437