Supplementary Information

Engineering Pt-CeO_2 interfaces for Reverse Water-Gas Shift (RWGS) reaction

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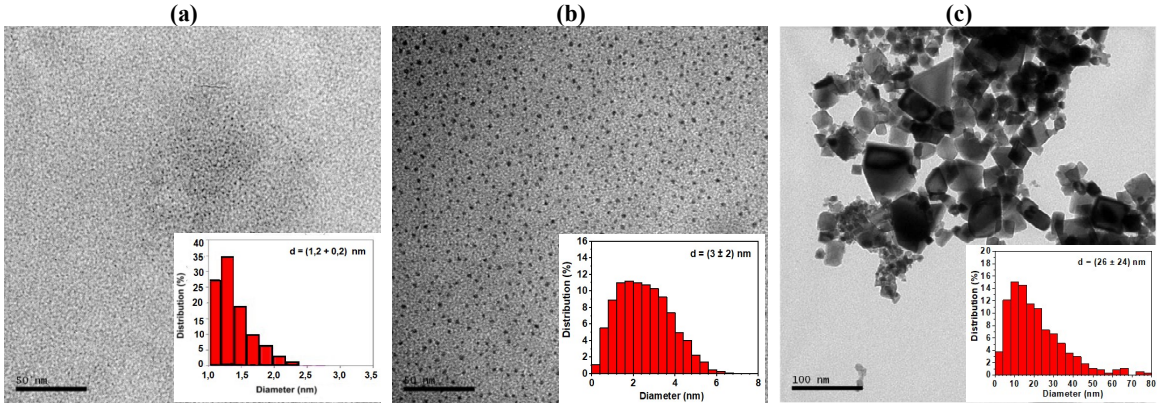

Figure 1 – Typical TEM images of (a) CeO_2 Hyd, (b) CeO_2 High S, and (c) CeO_2 Std nanoparticles.

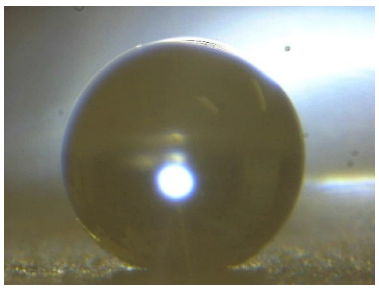

Figure 2 – Typical image of the water drop during the contact angle measurement.

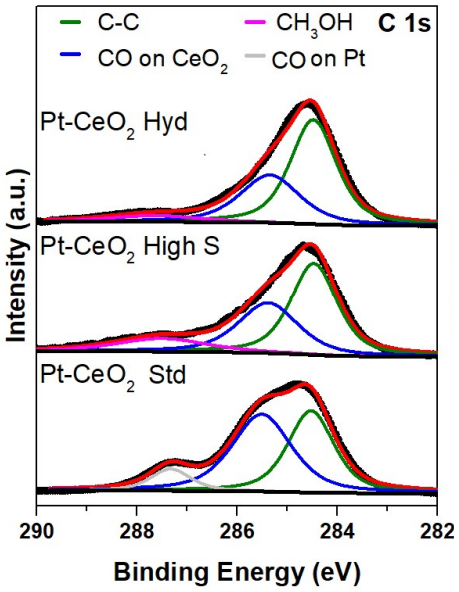

Figure 3 – C 1s XPS spectra of the as prepared Pt-CeO_2 nanoparticles.

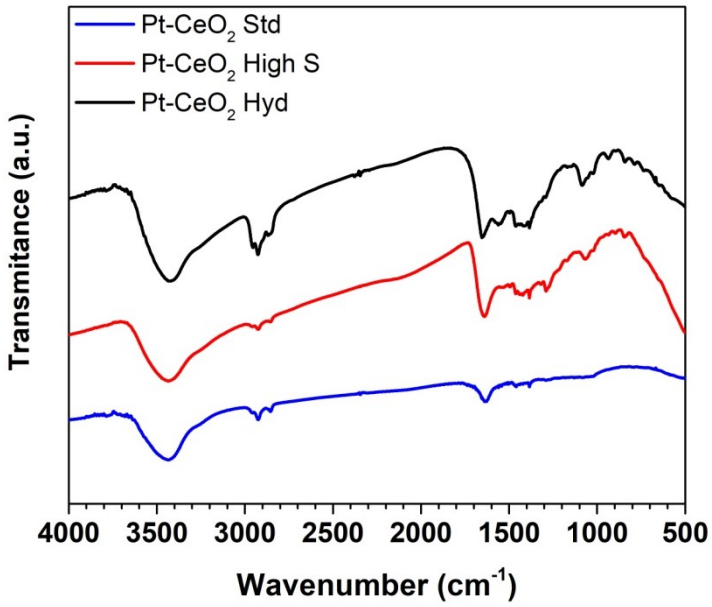

Figure 4 – FTIR spectra of the Pt-CeO_2 nanoparticles.

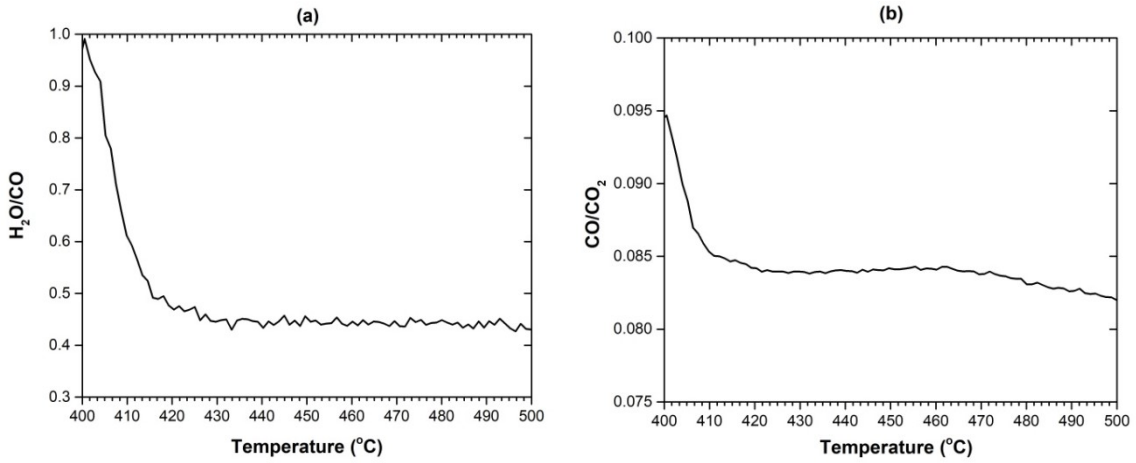

Figure 5 - (a) H_2O/CO and (b) CO/CO_2 ratio from mass spectrometry measurements during RWGS reaction from 400 °C to 500 °C.

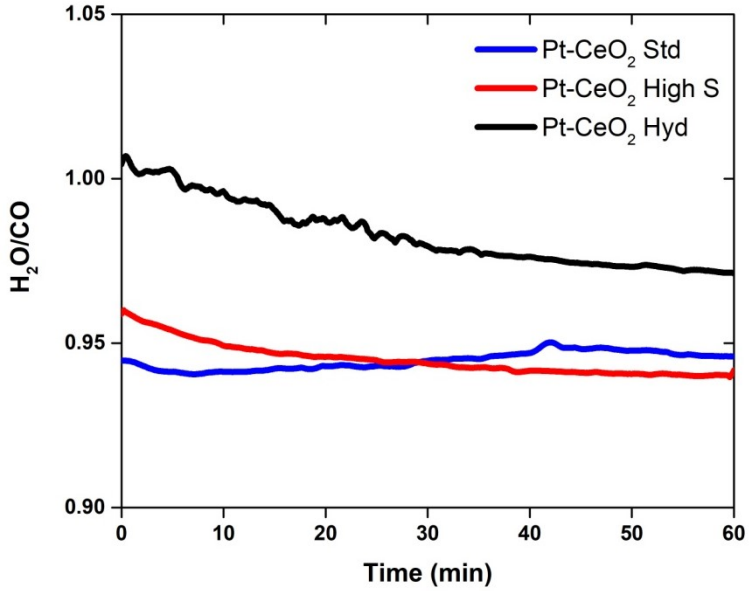

Figure 6 – H_2O/CO ratio from mass spectrometry measurements during RWGS reaction at 400 °C.

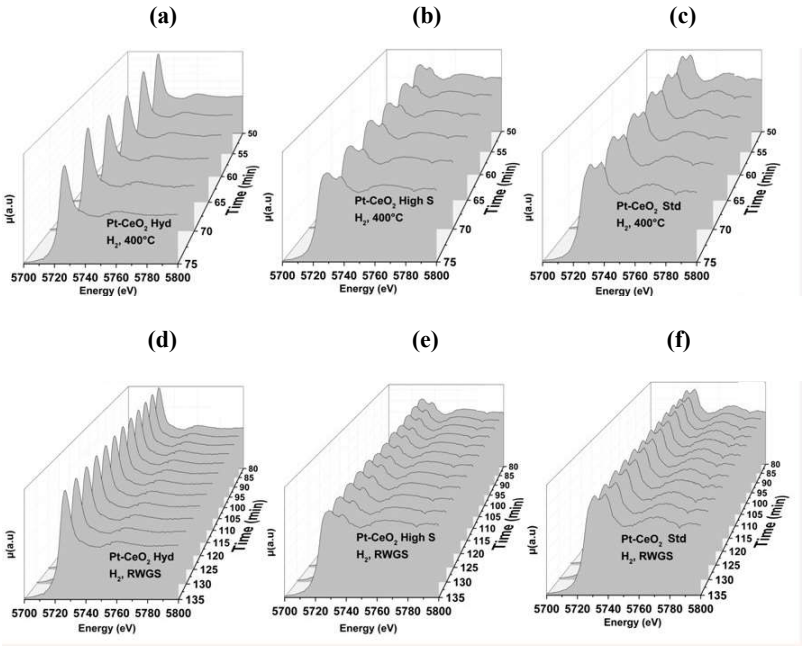

Figure 7 – In situ time-resolved XANES spectra at the Ce L_3 edge of the Pt-CeO_2 samples during (a-c) reduction treatment at 400 °C under H_2 atmosphere and (d-f) RWGS reaction at 400 °C.

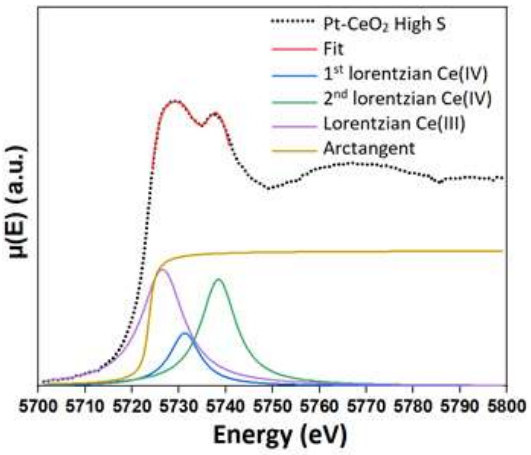

Figure 8 - Typical fit of the in situ XANES spectrum at the Ce L_3 edge for the Pt-CeO_2 High S sample at the end of the heating process at 400 °C.

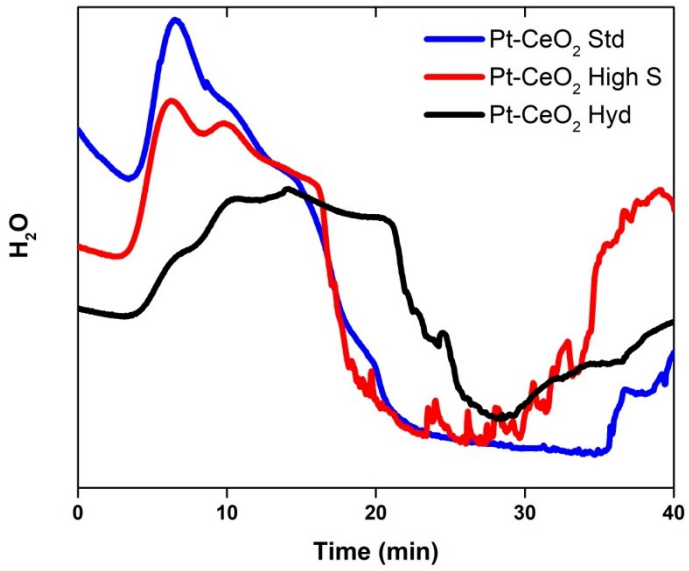

Figure 9 – H_2-TPR measurement showing the detection of H_2O as a function of temperature during heating to 400 ^oC.

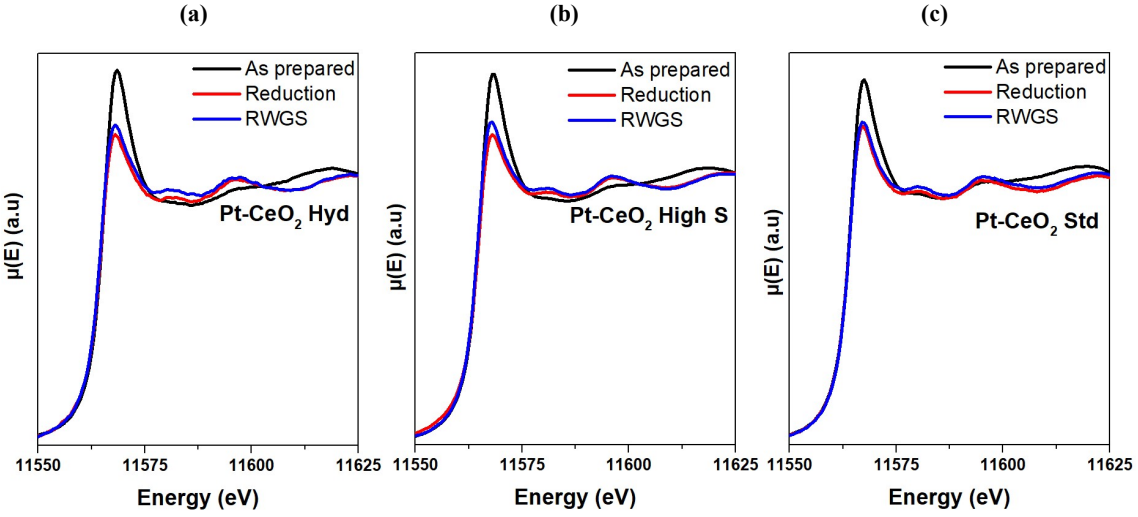

Figure 10 - In situ XAS spectra at the Pt L_3 edge of the (a) Pt-CeO_2 Hyd, (b) Pt-CeO_2 High S, and (c) Pt-CeO_2 Std. samples as prepared, during reduction treatment and RWGS reaction.

Table 1 – Parameters obtained from the fit result of the in situ EXAFS measurements at Pt L_3 edge. In the table, N, ΔR, σ^2, c_3 and c_4 stand for the coordination number, variation of the interatomic distance between the absorbing and scattering atom, Debye-Waller factor, and third and fourth order EXAFS cumulant, respectively. The parameters associated to Pt-Pt, Pt-O and Pt-$(OH)_x$ scattering paths are associated to metallic Pt, PtO_2, $H_2Pt(OH)_6$ clusters, respectively.

Sample	Parameters	As Prepared	Reduction	RWGS reaction
Pt-CeO_2 Hyd	N_{Pt-Pt}	8.0 ± 1.0	9.7 ± 0.7	10.0 ± 0.8
	N_{Pt-O}	-	0.2 ± 0.2	0.8 ± 0.2
	$N_{Pt-(OH)x}$	2.8 ± 0.3	-	-
	ΔR_{Pt-Pt}	0.03 ± 0.01	0.014 ± 0.004	0.014 ± 0.004
	ΔR_{Pt-O}	-	-0.11 ± 0.02	-0.11 ± 0.03
	$\Delta R_{Pt-(OH)x}$	-0.12 ± 0.01	-	-
	σ^2_{Pt-Pt}	0.004 ± 0.003	0.0084 ± 0.0009	0.0084 ± 0.0009
	σ^2_{Pt-O}	-	0.014 ± 0.006	0.014 ± 0.006
	$\sigma^2_{Pt-(OH)x}$	0.008 ± 0.002	-	-
	c_3	-	0.0008 ± 0.0002	-0.0007 ± 0.0003
	c_4	-	0.0004 ± 0.0001	0.0004 ± 0.0001
Pt-CeO_2 High S	N_{Pt-Pt}	7.2 ± 0.6	9.6 ± 0.4	9.8 ± 0.04
	N_{Pt-O}	-	0.62 ± 0.08	0.9 ± 0.1
	$N_{Pt-(OH)x}$	2.1 ± 0.1	-	-
	ΔR_{Pt-Pt}	0.010 ± 0.007	0.026 ± 0.003	0.026 ± 0.003
	ΔR_{Pt-O}	-	-0.077 ± 0.009	-0.077 ± 0.009
	$\Delta R_{Pt-(OH)x}$	-0.114 ± 0.006	-	-
	σ^2_{Pt-Pt}	0.005 ± 0.001	0.0109 ± 0.0005	0.0108 ± 0.0005
	σ^2_{Pt-O}	-	0.011 ± 0.002	0.011 ± 0.002
	$\sigma^2_{Pt-(OH)x}$	0.004 ± 0.001	-	-
	c_3	-	0.00006 ± 0.00002	-0.0001 ± 0.0002
	c_4	-	0.00048 ± 0.00007	0.00049 ± 0.00007
Pt-CeO_2 Std	N_{Pt-Pt}	8.6 ± 0.7	9.3 ± 0.7	9.8 ± 0.7
	N_{Pt-O}	-	0.5 ± 0.1	0.7 ± 0.1
	$N_{Pt-(OH)x}$	2.0 ± 0.2	-	-
	ΔR_{Pt-Pt}	0.017 ± 0.007	0.015 ± 0.004	0.015 ± 0.004
	ΔR_{Pt-O}	-	-0.06 ± 0.02	-0.06 ± 0.02
	$\Delta R_{Pt-(OH)x}$	-0.109 ± 0.08	-	-
	σ^2_{Pt-Pt}	0.005 ± 0.001	0.0103 ± 0.0008	0.0103 ± 0.0008
	σ^2_{Pt-O}	-	0.007 ± 0.003	0.007 ± 0.003
	$\sigma^2_{Pt-(OH)x}$	0.006 ± 0.002	-	-
	c_3	-	-0.0005 ± 0.0003	-0.0005 ± 0.0003
	c_4	-	0.0005 ± 0.0001	0.0006 ± 0.0001