Supporting Information

Understanding the role of oxygen vacancies in the water gas shift reaction on ceria-supported platinum catalysts

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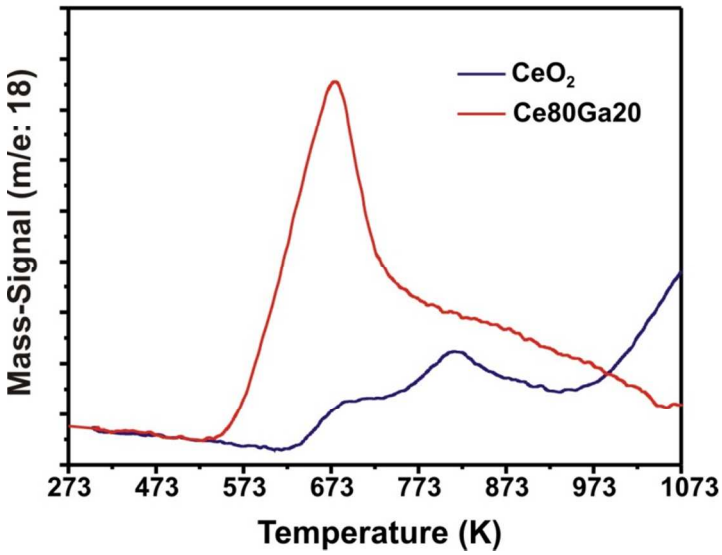

Figure S1. Temperature-programmed reduction under 5%H_2/Ar flow of the pure ceria and Ce80Ga20 supports.

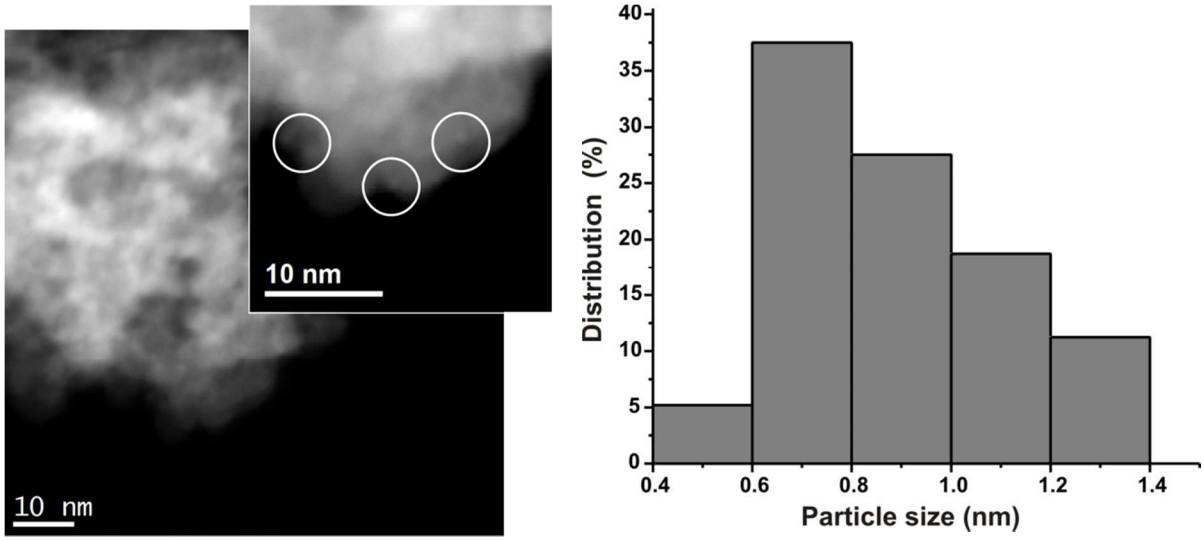

Figure S2. Representative STEM-HAADF Images and particle size distribution collected by STEM-HAADF for the reduced Pt/Ce80Ga20 catalyst before reaction (mean particle size = 0.81 ± 0.035 nm).

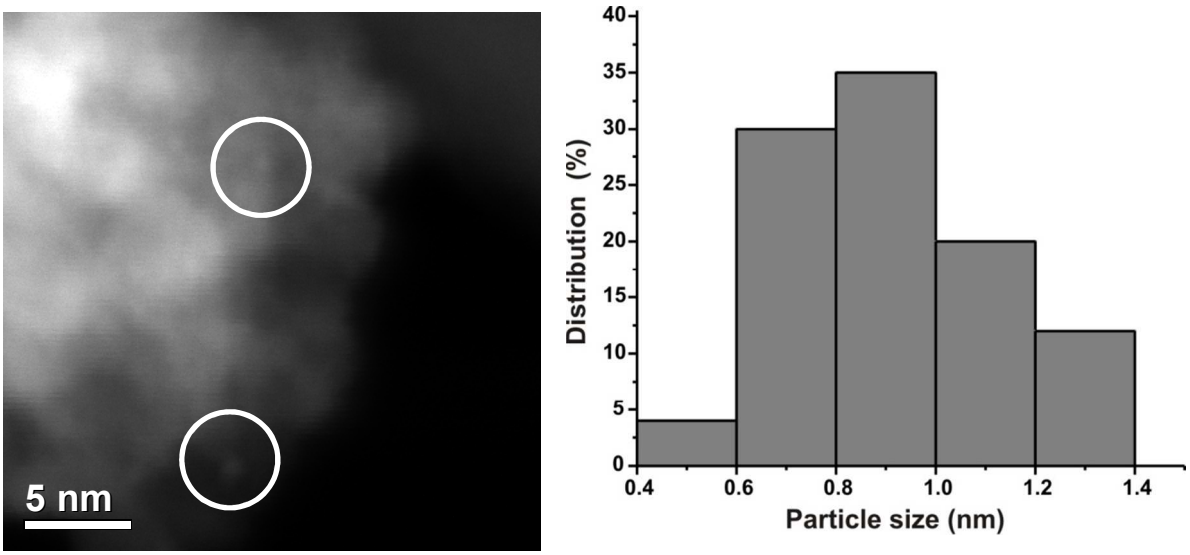

Figure S3. Representative STEM-HAADF Images and particle size distribution collected by STEM-HAADF for Pt/Ce80Ga20 catalyst after WGS reaction (mean particle size = 0.88 ± 0.038 nm).

Table S1. Lattice parameter values (a) and their differences (Δa), obtained during the pretreatments and the WGS reaction over Pt/CeO_2 and Pt/Ce80Ga20.

Catalyst	a (Å)		Δa_{Rxn} [(a)]	Δa_{rt} [(b)]	T_{50} [(c)] (K)
	298 K	523 K	(Å)	(Å)	
Pt/CeO_2	5.414	5.436	0.022	0.022[(d)]	556
Pt/Ce80Ga20	5.416	5.448	0.033	0.040[(d)]	580

(a) Difference between the lattice parameter values during WGS reaction at 523 and 298 K [Δa_{Rxn} = a (523 K) - a (298 K)].
(b) Difference between the lattice parameter values for under the reducing treatment at 523 and 298 K [Δa_{rt} = a (523 K) - a (298 K)].
(c) Temperature for 50% of CO conversion.
(d) It only contains the contribution of the lattice parameter expansion due to the reduction of the catalyst, since the thermal expansion of the reduced support was subtracted (0.01).

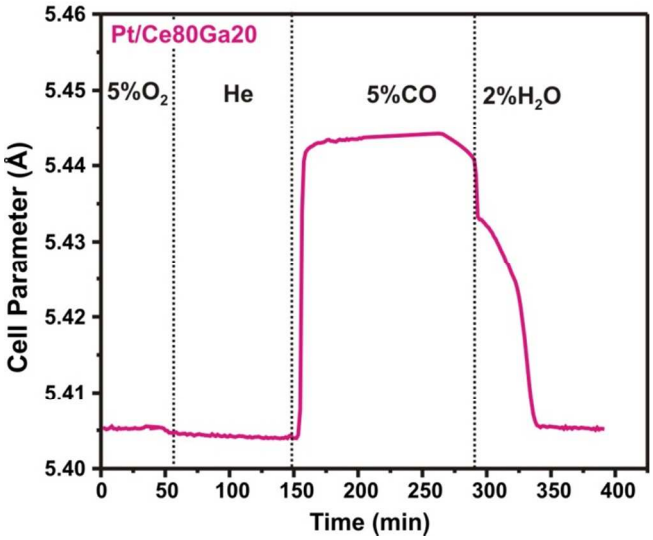

Figure S4. Evolution of the cell parameter during the reduction and oxidation with CO and water, respectively, at 523 K for Pt/Ce80Ga20.

DFT calculations

The unit cell for the surface calculations is based on a 3x4 (111)-terminated CeO2 slab (dimensions 15.45×11.58×31 Å3, vacuum ~17 Å). It contains 4 CeO2 layers-thick with 12 CeO2 per layer. The doped system is modeled by substitution of two Ce sites by two Ga sites; one oxygen is removed to keep stoichiometry. A Pt_8 cluster is deposited on top of the slab as in reference[1]. The final composition of the system is: $Pt_8Ce_{48}O_{96}$ (denoted as Pt/CeO2) and $Pt_8Ce_{46}Ga_2O_{95}$ (4.16% total molar content in Ga, 16.6% surface content in Ga, denoted as Pt/CeGa). The two uppermost layers are fully relaxed in the optimization calculations, performed with the conjugate gradient algorithm.

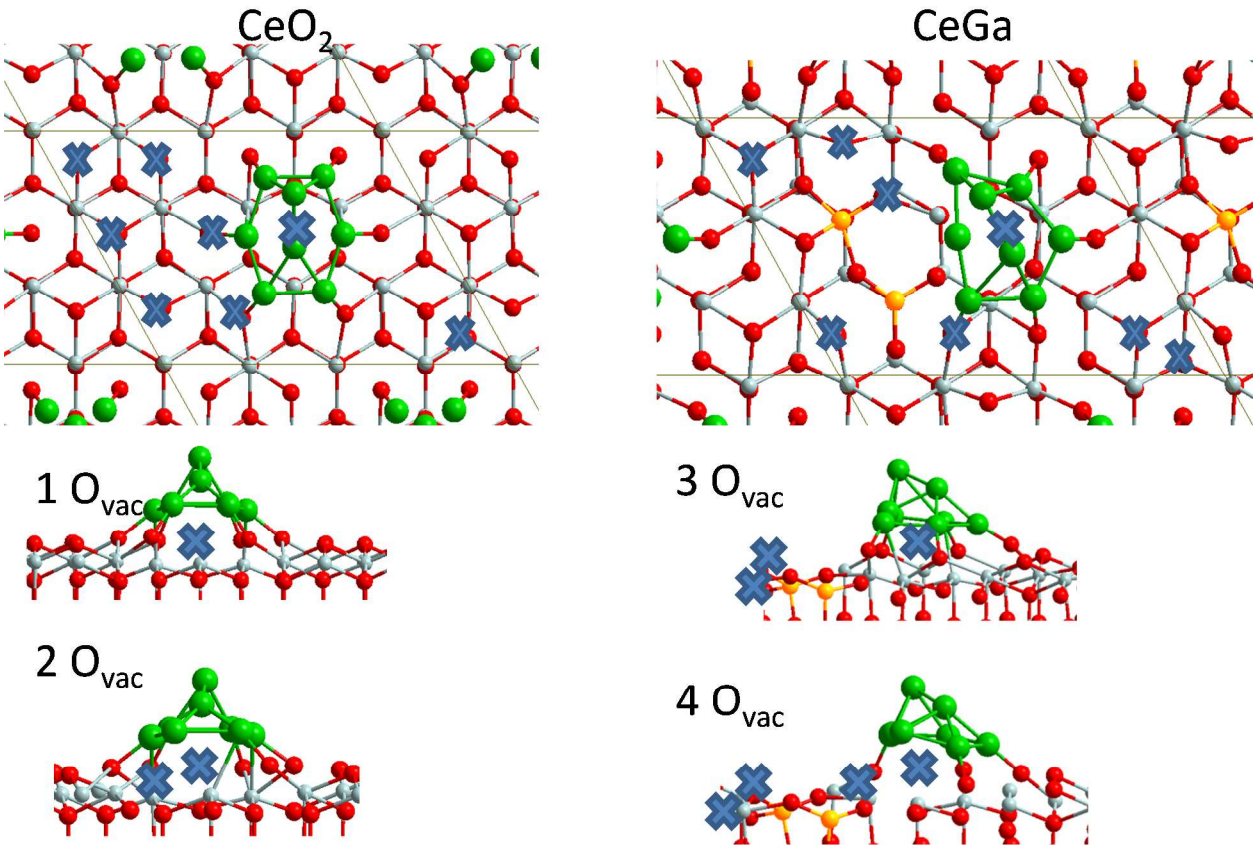

Figure S5. Top and side views of the model surfaces used for CeO_2 and CeGa supported Pt_8 slabs (top view), with 1 and 2 oxygen vacancies (Pt/CeO_2) and 3 and 4 vacancies (Pt/CeGa), side view. Green (Pt), yellow (Ga), gray (Ce), red (O). Crosses indicate the positions of the oxygen atoms removed to create vacancies.

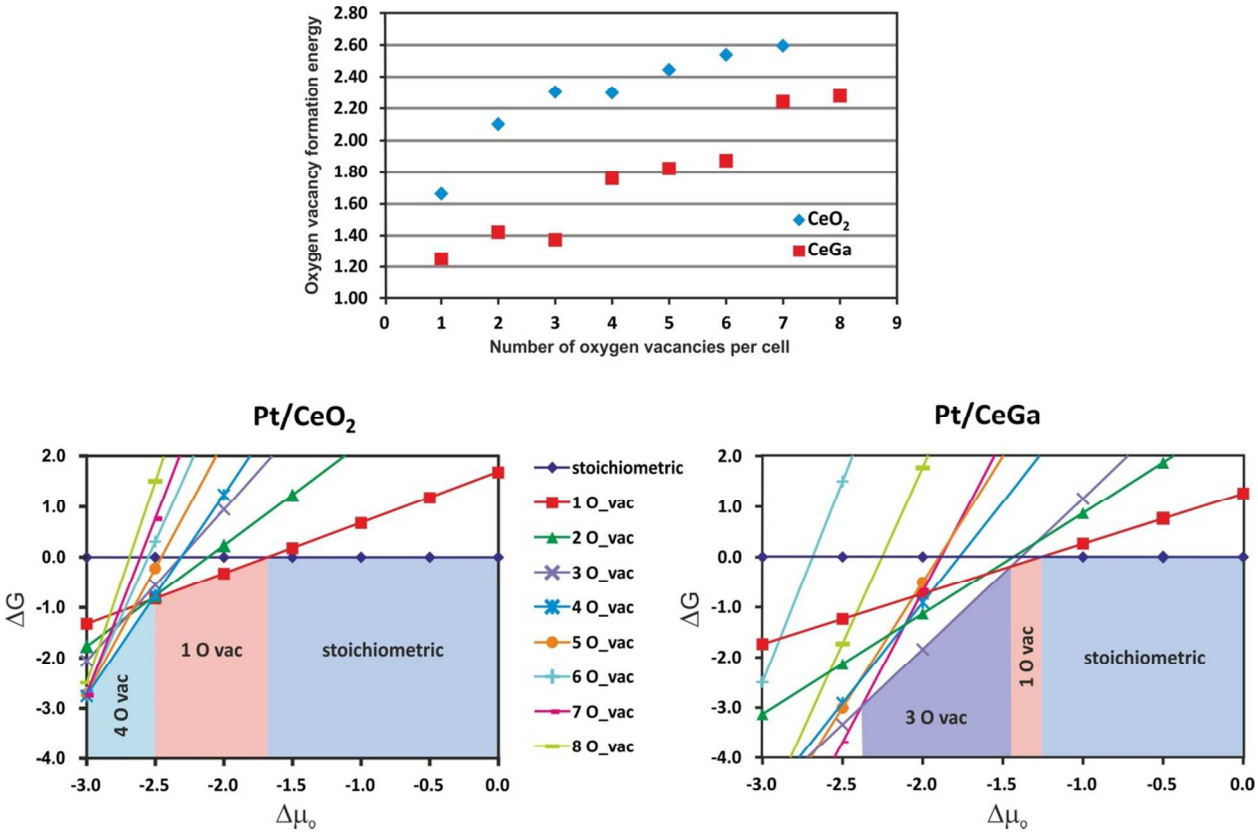

Figure S6. Top: oxygen vacancy formation energy for the CeO_2 and CeGa Pt_8 slabs (in eV, per vacancy). Bottom: ΔG vs $\Delta\mu_O$ diagrams for the two systems Pt/CeO_2 and Pt/CeGa. The dash arrow indicates the oxygen chemical potential -2.2 eV for which the most stable slabs are the 1Ovac-Pt/CeO_2 and 3Ovac-Pt/CeGa.

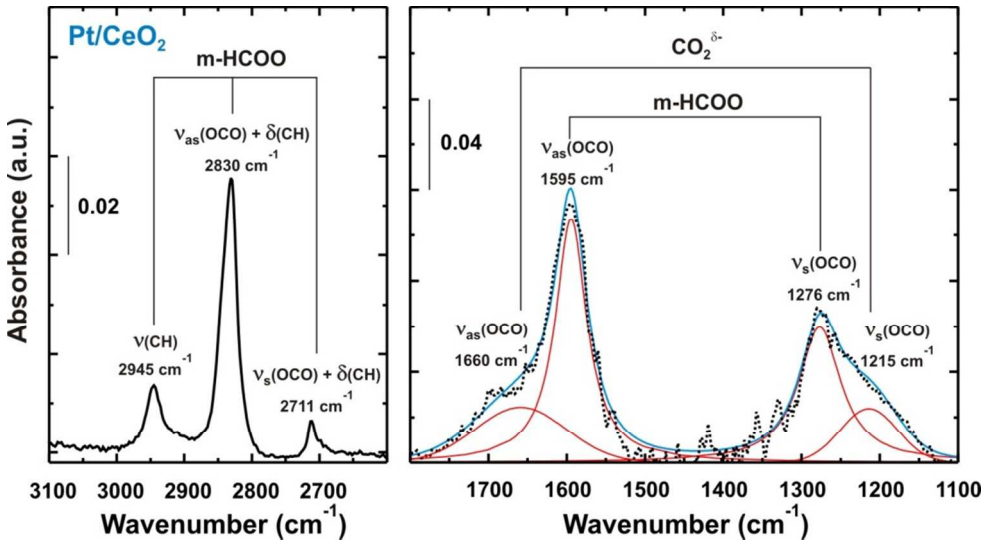

Figure S7. Resolution of the infrared bands in the phase-domain DRIFT spectrum after PSD demodulation (φ = 320°). Spectra acquired during a c-MES cycle (CO+H2O)-He (100cm^3/min, 523 K, ω=4.2 mHz), over Pt/CeO_2.

Table S2. Assignation of the infrared modes of surface and gas phase species and phase lag in degree.

	IR mode	m-HCOO		$CO_2^{\delta-}$		CO		CO_2	
		υ/cm^{-1}	ϕ	υ/cm^{-1}	ϕ	υ/cm^{-1}	ϕ	υ/cm^{-1}	ϕ
Pt/CeO_2	υ_{as}(COO)	1595	320°	1660	329°				
	υ_{a}(COO)	1276	320°	1215	330°				
	υ(CH)	2945	318°						
	υ_{as}(COO)+ δ(CH)	2830	318°						
	υ_{a}(COO)+ δ(CH)	2711	320°						
	υ(CO)					2180	360°	2360	332°
Pt/Ce80Ga20	υ_{as}(COO)	1585	318°	n.d.	-				
	υ_{a}(COO)	1280	320°	n.d.	-				
	υ(CH)	2949	317°						
	υ_{as}(COO)+ δ(CH)	2848	320°						
	υ_{a}(COO)+ δ(CH)	2705	320°						
	υ(CO)					2180	360°	2360	336°

References

(1) Aranifard, S.; Cheettu Ammal, S.; Heyden, A. *J. Phys. Chem. C* **2012,** *116*, 9029–9042.