Supporting Information

Structure of reduced cerium oxide ultrathin films on Pt(111): local atomic environment and long-range order

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1. LEED patterns

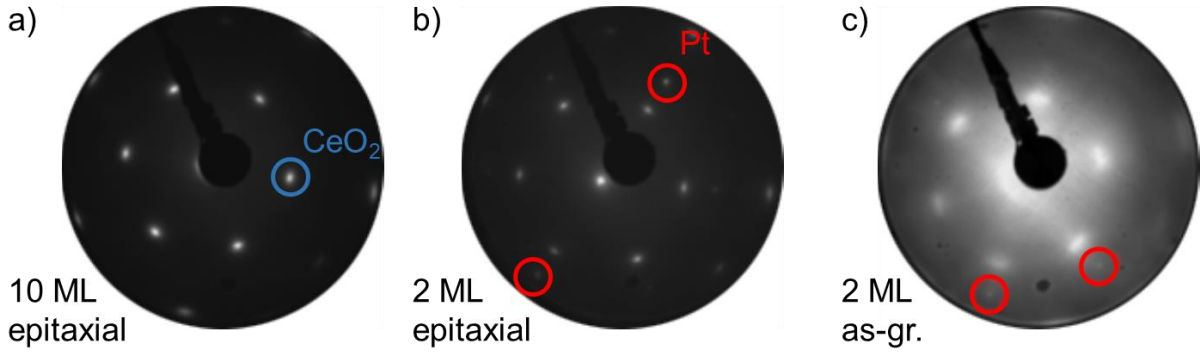

Figure S1: Low energy electron diffraction (LEED) patterns (primary beam energy of 60 eV) acquired on the a) 10 ML and b) 2 ML samples treated at 1040 K in an O_2 partial pressure P_{O2}= 1×10^{-7} mbar and c) on the 2 ML as grown samples. The blue circle in a) evidences one of the CeO_2-related spots, while the red circles in b) and c) evidence the Pt substrate-related spots. The narrow and intense diffraction spots in the patterns in a) and b) indicate a good crystal quality, while the diffuse background in c) is a consequence of a worse structural order. The CeO_2(111) // Pt(111) and CeO_2[110] // Pt[110] epitaxial relation is evident from the alignment of the CeO_2 and Pt related LEED patterns.

2. Procedure used for the fitting of the XANES spectra

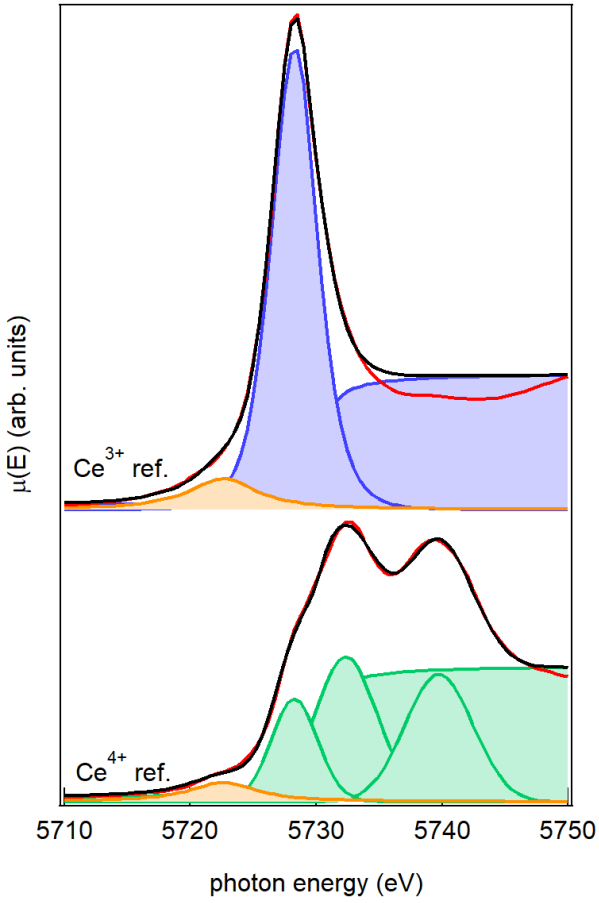

Figure S2: XANES spectra of the Ce^{3+} and Ce^{4+} reference samples (red lines) and the corresponding fitting curves (black lines). The figure also shows the components used for the fitting of each spectrum. The step edge is simulated by an arctangent function with the maximum of the first derivative fixed to the value of the first derivative of the experimental spectrum. In addition, two and four Gaussian curves are used to fit the near edge structures of the Ce^{3+} and Ce^{4+} spectra, respectively. The XANES spectra of the samples, shown Figure 1 of the main manuscript, were fit using an arctan function and five Gaussian curves, one related to Ce^{3+}, three related to Ce^{4+} and one for the pre-edge peak. The relative area and distance of the three Ce^{4+}-related components were fixed for all samples to the values obtained from the fit of the Ce^{4+} reference sample. The Ce^{3+} concentration was evaluated as

the ratio of the area of the Ce^{3+}-related peak and the total area of the XANES, neglecting the pre-edge peak intensity. The error on the Ce^{3+} concentration given by the fit is estimated to be of the order of 10%.

3. Fitting of the EXAFS spectrum of the CeO_2 reference in the extended k-range

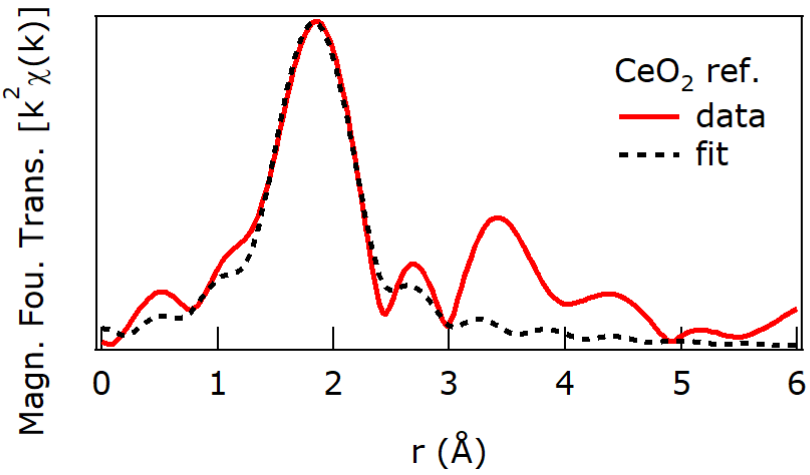

Figure S3: Magnitude of the Fourier transform of the k^2-weighted EXAFS function $\chi(k)$ and corresponding fit in the k range 3 - 10 Å of the CeO_2 reference sample.

	R factor	**S_0^2**	**R** (Å)	**σ^2** (Å^2)
Bulk CeO_2	0.029	0.86 (12)	2.34 (1)	0.003 (3)

Table S1: R-factor and parameters obtained from the fitting of the EXAFS data of the CeO_2 reference sample. It has to be noted that the Ce-O distance is well consistent with the value of the Ce-O distance for bulk CeO_2, i.e. 2.34 Å.

4. Structure of Ce-Pt alloys

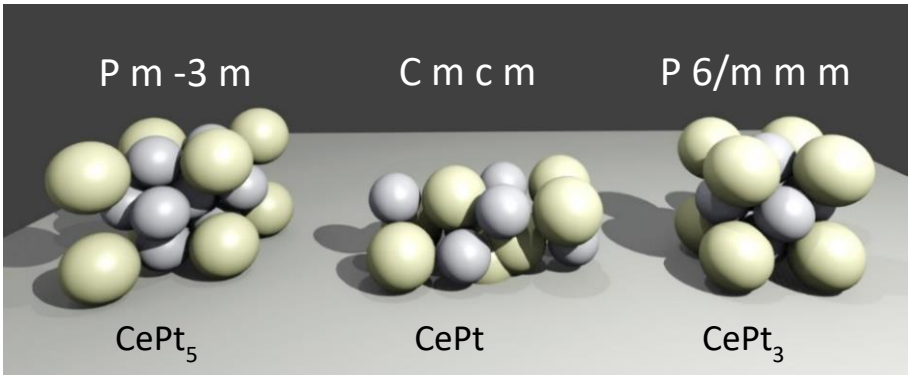

Figure S4: Representation of the unit cells of the considered Ce-Pt alloys with Pt atoms in grey and Ce atoms in yellow.

Alloy	Paths	Dist. (Å)	N
$CePt_5$	Ce-Pt	3.097	6
	Ce-Pt	3.463	12
	Ce-Ce	4.379	2
$CePt_3$	Ce-Pt	2.943	12
	Ce-Ce	4.162	6
CePt	Ce-Pt	3.020	5
	Ce-Pt	3.105	2
	Ce - Ce	3.719	2
	Ce - Ce	3.874	6

Table S2: Interatomic distances and coordination numbers for the different coordination shells in the Ce-Pt alloys shown in Figure S3.