Supplementary Information

Nanostructured Pr-rich $Ce_xPr_{1-x}O_{2-\delta}$ mixed oxides for diesel soot combustion. Importance of oxygen lability.

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1. XPS analysis

Figure S1.a shows the Pr3d profiles of the catalysts studied, the Pr 3d spectrum contains 7 peaks organized in 3 spin-orbit coupling doublets, named a-b, a'-b' and a''-b'' and one Auger peak at high binding energy, belonging to the 3d3/2 sublevel [1]. The spectrum Pr3d for each catalyst indicates that Pr^{3+} and Pr^{4+} coexisted. Figure. S2.b exhibits the XPS spectra of Ce 3d of the catalysts. Ce 3d XPS spectra are well known to be complicated due to the hybridization of the Ce 4f orbitals with the ligand orbitals and the fractional occupation of the valence 4f orbitals and the O 2p states [2,3]. These spectra were decomposed into ten contributions. The peaks were labeled according to the standard nomenclature, in agreement with the literature[4,5]. Peaks associated with the Ce $3d_{5/2}$ state are labeled v, whereas those associated with the Ce $3d_{3/2}$ state are labeled u. However, the contributions v, v″, v‴, u, u″ and u‴ belong to Ce^{4+} 3d states indicating the main valence state of Ce in the sample as +4; while the v_0, v′, u_0 and u′ are attributed to the valence state of Ce^{3+} [4].

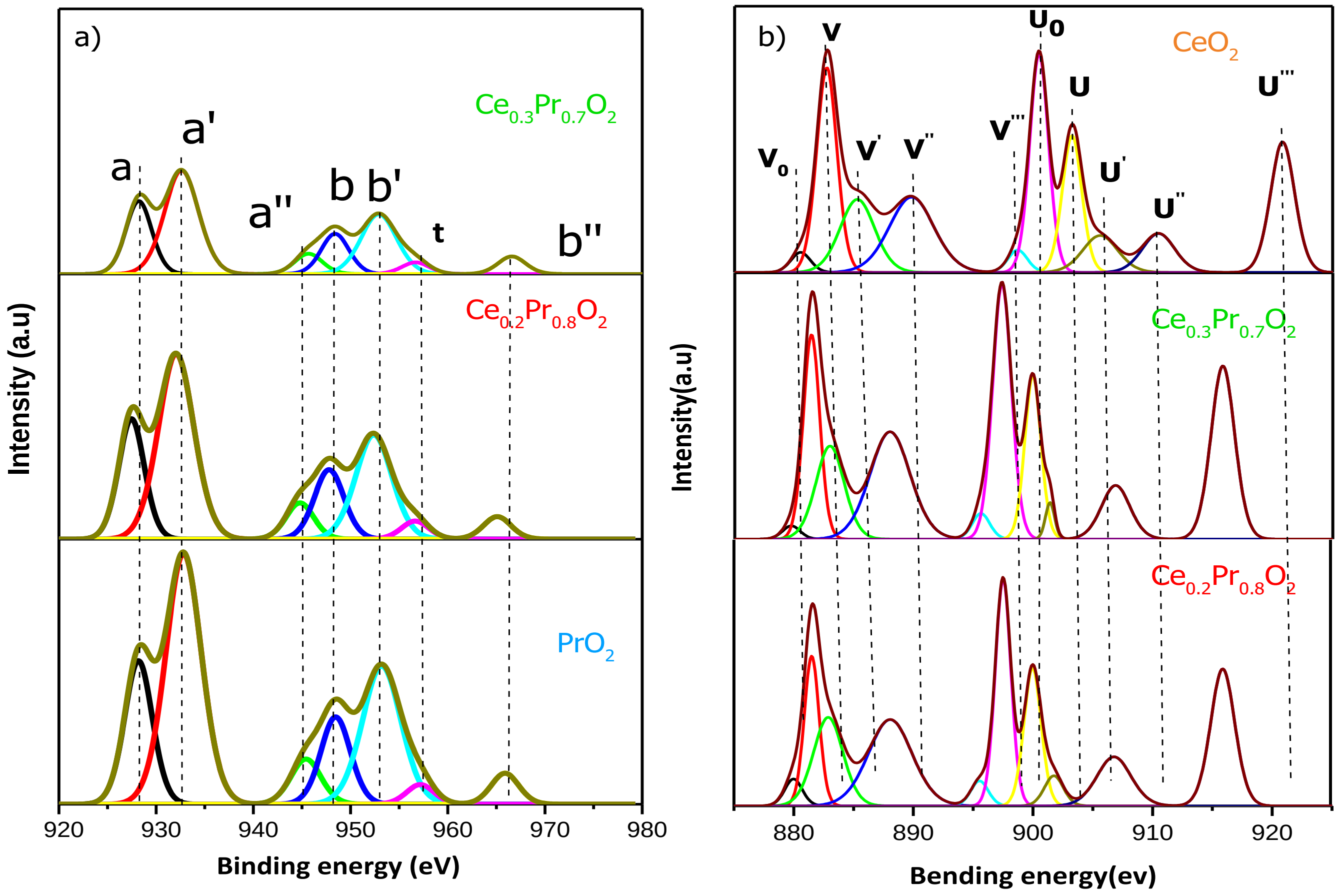

Figure S1. XPS spectra of a) Pr 3d and b) Ce3d

2. Details on the procedure and estimation of the number of oxygen vacancies.

The number of oxygen vacancies created in the surface/subsurface/bulk of the solids under the different treatments was estimated by assuming that the amount of oxygen released after the different treatments (either as H_2O from H_2-TPR or as O_2 from O_2-TPD under He) proceeds from the surface/lattice oxygen corresponding (eventually) to the creation of the oxygen vacancies by assuming the following global stoichiometries (Reaction 1 and 3).

Therefore, the H_2 consumption (μmol/g_{cat}) estimation is the same as the H_2O emitted during the experiment and agrees with the μmoles O/g_{cat}, corresponding to the oxygen vacancies generated during the experiment (according to the stoichiometry of reaction 1).

By means of H_2-TPR:

$$H_2 + 2MO_2 \rightarrow H_2O + M_2O_3 \qquad \text{R.1.}$$

(by using the calibration of CuO as a standard and assuming that one mole of H_2 is consumed for each mole of CuO to reduce the total Cu^{2+} to Cu^0 according to the following reaction):

$$CuO + H_2 \rightarrow Cu + H_2O\ ) \qquad \text{R.2}$$

By means of O_2-TPD:

$$MO_2 \rightarrow MO_{2-\delta} + 1/2\delta O_2 \qquad \text{R.3}$$

the O_2 emission (μmol/g_{cat}) would be double the amount of the estimation of μmoles O/g_{cat}, corresponding to the oxygen vacancies generated during the experiment (according to the stoichiometry of Reaction 3).

(by using the calibration of CuO, where the stoichiometric reduction/decomposition of CuO to Cu_2O emitting O_2 occurs under an inert atmosphere, according to the reaction 4)

$$2\ CuO \rightarrow Cu_2O + 1/2O_2) \qquad \text{R.4}$$

Oxygen delivery capacity is, the capacity of the catalysts to emit oxygen, and in turn, to create oxygen vacancies in their structures.

3. Theoretical non-stoichiometric phase of the Bevan's cluster

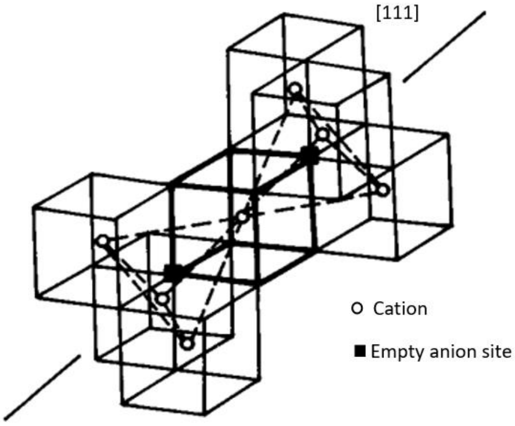

Figure S2. Bevan cluster in MO_{2-x} oxides of fluorite structure. Adapted from reference [1]

4. References

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