

Engineering Oxygen Vacancy Defects in CeO₂ Nanocrystal Catalysts

An important application of CeO₂ converts toxic carbon monoxide produced in combustion processes into environmental friendly carbon dioxide. We have developed a new approach to enhance the catalytic activity of these CeO₂ nanostructure. High density of oxygen vacancy defects can be introduced into cerium oxide. The local atomic structure and the Ce-O bond length were investigated by extended X-ray absorption fine structure. Our results explain the activity enhancement effect in these ceria nanostructured catalysts.

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Recently, cerium oxide has attracted considerable interest due to its promising catalytic applications in a variety of chemical processes. One important application is to convert toxic carbon monoxide produced in combustion processes into carbon dioxide. To increase the catalytic activity, many nanostructures of cerium oxides with different shapes, sizes, and elemental compositions have been developed. In contrast to these conventional methods, enhancing catalytic activity by defect engineering is a potentially simpler and effective

approach that deserves extensive and in-depth investigation.

In the present work, we demonstrate using a low pressure thermal activation process to introduce high density of oxygen vacancy defects (OVDs) into cerium oxide nanostructures.¹ The oxidative catalytic activity of the activated nanostructures was found to drastically increase as evaluated by the bench mark test of carbon monoxide (CO) oxidation reaction in a fixed bed reactor. The reaction $\text{CO} + 1/2\text{O}_2 \rightarrow \text{CO}_2$ was monitored by quantifying the production of carbon dioxide (CO₂) with a gas chromatography (GC) instrument equipped with a thermal conductivity detector.

To probe the oxygen vacancy defects in the activated ceria nanostructures, extended X-ray absorption fine structure (EXAFS) measurements^{2,3} were carried out on the samples at beamline 07A of National Synchrotron Radiation Research Center (NSRRC). The local structural parameters were determined by curve-fitting of the EXAFS χ -functions extracted from the raw experimental data. The experimental EXAFS χ -functions and their Fourier transforms for the low pressure thermally activated samples are plotted with their respective curve-fitted model curves in Fig. 2. The average Ce-O bond length of low pressure thermally activated nanoceria is on average 2% shorter than the theoretical bond length of bulk ceria. The coordination numbers for both the cerium and oxygen neighboring atoms from the cerium central atoms in nanoceria are reduced from the theoretical values, clearly indicating fewer interatomic bonds than those of an ideal CeO₂ structure. The shorter Ce-O bond length and the reduced coordination numbers in nanoceria suggest an increased OVD density in the low-pressure thermally activated nanoceria.

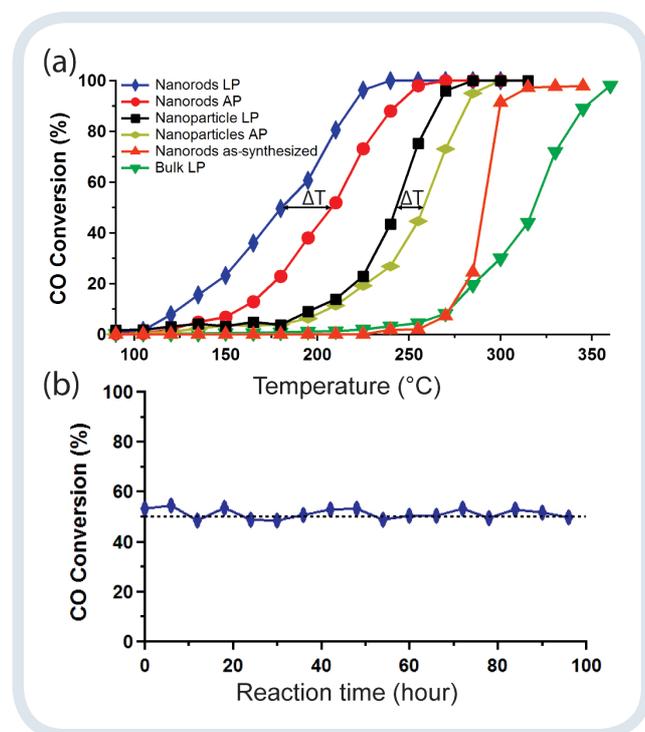


Fig. 1: (a) Comparison of the catalytic activity of ceria samples. (b) Time dependence of CO conversion for the ceria nanorod samples.

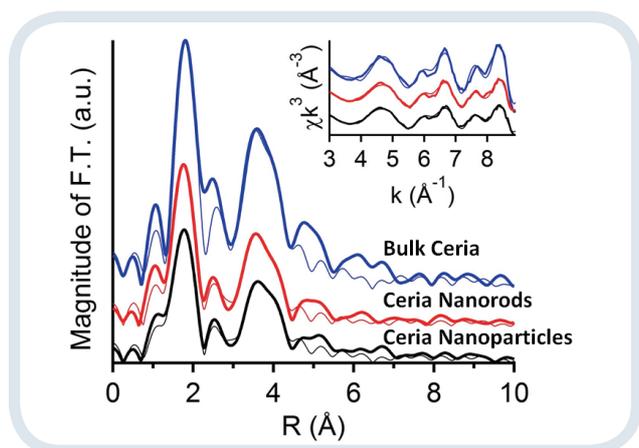


Fig. 2: Fourier transforms of Ce L_1 -edge EXAFS data of ceria samples.

To elucidate the observed lowered coordination numbers, shortened Ce-O bond length and their effects on catalytic activity enhancement in the defective nanoceria, a theoretical model based on a chemical formula rich in OVDs, $\text{CeO}_{1.5}$, was constructed and the density of states (DOS) were calculated by using density functional theory. The low energy (111) surface structure of this optimized $\text{CeO}_{1.5}$ slab model was found to contain both surface and subsurface OVDs. Significantly, the model demonstrates comparable shortening of the average Ce-O bond length and atomic coordination number reduction agreed well with our EXAFS analysis. The surface partial electronic density of states (PEDOS) was calculated from the optimized (111) $\text{CeO}_{1.5}$ slab and compared to that of an optimized non-defective (111) CeO_2 slab (Figs. 3(b) and 3(c)). We found the Ce $4f$ states are partially filled in the $\text{CeO}_{1.5}$ (111) surface, which is possibly

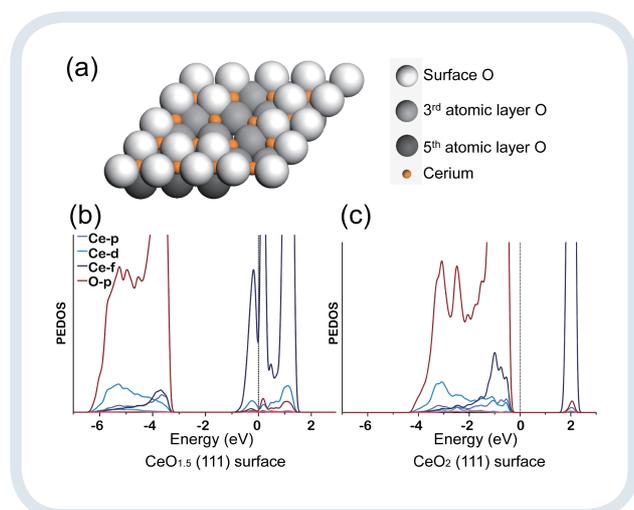


Fig. 3: (a) Optimized model of (111) ceria slab corresponding to the chemical formula $\text{CeO}_{1.5}$. Partial electronic density of states for (b) an optimized (111) $\text{CeO}_{1.5}$ slab and (c) an optimized (111) CeO_2 slab.

caused by the Ce atoms adjacent to the OVDs becoming more non-bonded. Thus we expect the defective surface to be more reactive particularly near the OVD sites due to the proximity of the Fermi level and Ce $4f$ states as shown in Fig. 3.

In summary, we have demonstrated successful enhancement of catalytic activity in nanoceria using defect engineering strategies. The low-pressure activated ceria nanostructures exhibit largely increased carbon monoxide to dioxide conversion efficiency. EXAFS measurements performed at the high-intensity X-ray beamline 07A of NSRRC revealed the structural origins of such enhancements. Energetically optimized structural model based on the presence of oxygen vacancy defects in nanoceria samples has theoretically reproduced the coordination number reduction and bond length shortening effects observed in EXAFS experiments. Density of states calculated from such model provides insightful theoretical explanation to the activity enhancement effects in these ceria nanostructures. The X-ray results obtained at NSRRC are of pivotal importance for understanding the mechanism of catalytic activity enhancement in these uniquely engineered nanostructures.

Beamline 07A1 EXAFS end station

References

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