

## Ruthenium Diffusion on Different CeO<sub>2</sub> Surfaces: Support Shape Effect

Junhao Li<sup>1</sup>, Zhongqi Liu<sup>1</sup>, David A. Cullen<sup>2</sup> and Ruigang Wang<sup>1\*</sup>

<sup>1</sup> Department of Metallurgical and Materials Engineering, The University of Alabama, Tuscaloosa, AL 35487, United States

<sup>2</sup> Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States

\* Corresponding author: [rwang@eng.ua.edu](mailto:rwang@eng.ua.edu)

Ceria (CeO<sub>2</sub>) is often used to support transition or noble metal catalysts providing enhanced catalytic properties. The main reason is that CeO<sub>2</sub> possesses high oxygen storage capacity and oxygen mobility, arising from the easy switch between the Ce<sup>+4</sup> and Ce<sup>+3</sup> oxidation states with formation and elimination of oxygen vacancies from different surfaces. In the last decade, substantial efforts have been devoted to understanding the facet-dependent chemical reactivity of CeO<sub>2</sub> nanoparticles. It has been found that tailoring CeO<sub>2</sub> into different morphologies such as rods or cubes and exposing distinct facets ({100}, {110}, or {111}) can lead to considerable improvement in many redox related catalytic performances, compared to thermally stable octahedral CeO<sub>2</sub> particles [1]. Recently, CeO<sub>2</sub> supported ruthenium-based catalysts have attracted much attention in the catalytic combustion of chlorobenzene, low-temperature CO<sub>2</sub> methanation and ammonia synthesis. In this work, CeO<sub>2</sub> nanorods (NR), nanocubes (NC) and nanooctahedra (NO) were selected to prepare supported ruthenium catalysts in order to investigate the correlation between the morphology and exposed crystal plane of nanoscale CeO<sub>2</sub> support and their low-temperature CO oxidation activity, which can deepen our understanding of the interactions between Ru and CeO<sub>2</sub> at the interfaces.

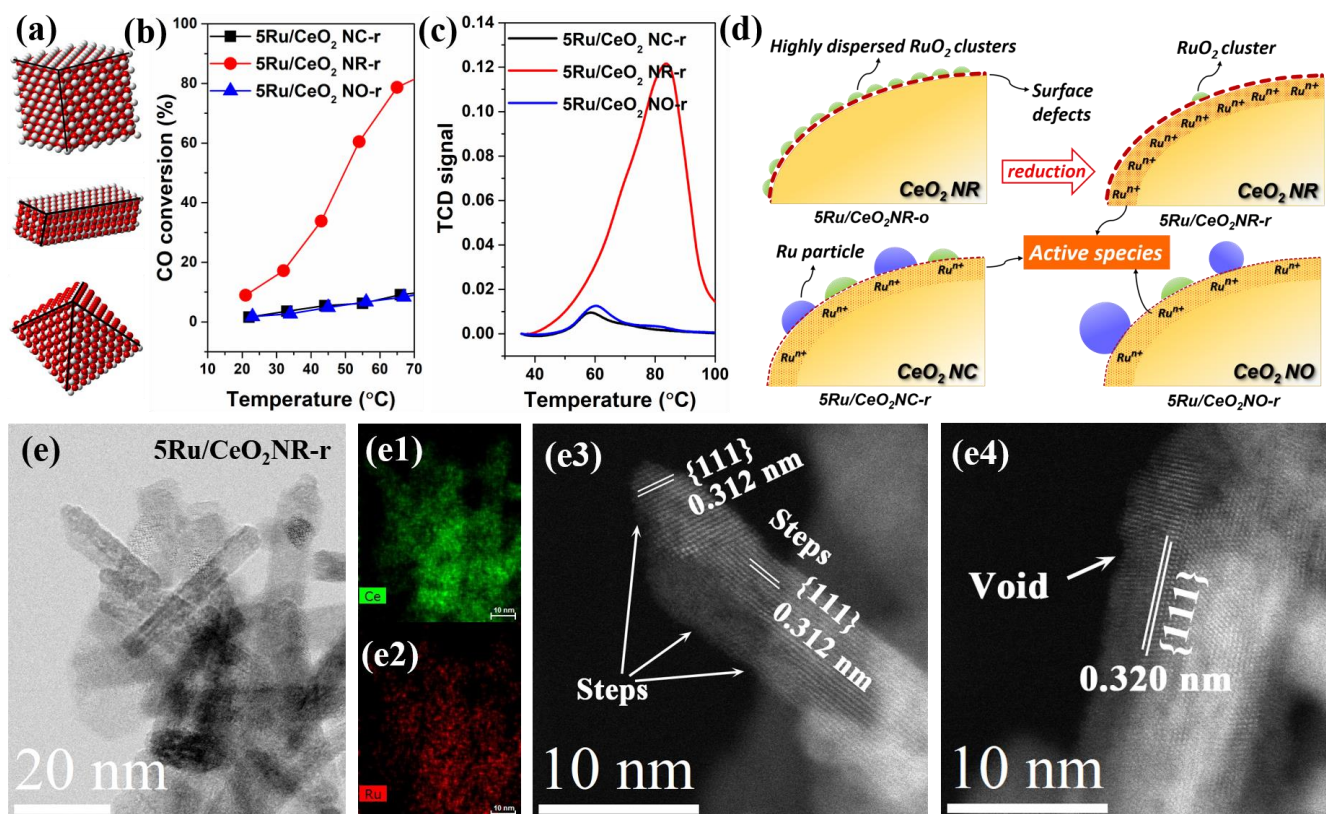
CeO<sub>2</sub> NR and NC were prepared via a facile hydrothermal method [2]. CeO<sub>2</sub> NO powder was prepared by a precipitation method and then calcined in air at 700 °C. 5 wt.%Ru/CeO<sub>2</sub>-r (r refers to reduction treatment) catalysts with different shaped CeO<sub>2</sub> supports were prepared by the impregnation method and further treated in reducing atmosphere with hydrogen. The atomic-level structural characterization was performed on JEOL JEM2200FS operated at 200 kV and equipped with a third-order CEOS aberration corrector and Bruker XFlash silicon drift detector. Hydrogen temperature programmed reduction (H<sub>2</sub>-TPR) was performed using a Micrometrics AutoChem<sup>TM</sup> II 2920 chemisorption analyzer. The catalytic oxidation of CO was conducted using a fixed bed plug flow reactor system and simultaneously analyzed using an online gas chromatograph (SRI multiple gas analyzer GC, 8610C chassis) system.

From Fig. 1b, the 5Ru/CeO<sub>2</sub>NR-r sample displays the highest low-temperature CO oxidation among the three different shaped 5Ru/CeO<sub>2</sub> catalysts after reduction treatment. The 5Ru/CeO<sub>2</sub>NR-r sample surprisingly shows ~ 9% CO conversion at room temperature and achieves 50% CO conversion at around 50 °C. The H<sub>2</sub> consumption below 100 °C of the 5Ru/CeO<sub>2</sub>NR-r sample was much larger than those of the other two samples (Fig. 1c). The enhanced hydrogen consumption indicates a strong Ru-CeO<sub>2</sub> interaction (i.e. the existence of Ru-O-Ce bond) in CeO<sub>2</sub> NR-supported RuO<sub>x</sub> catalyst which promotes the low-temperature reducibility and CO oxidation. Uniform distribution of Ru species shown in EDS mapping (Fig. 1e2) and the absence of apparent RuO<sub>x</sub> particles on the surface of CeO<sub>2</sub> nanorods (Fig. 1e3 and e4) confirm the existence of highly dispersed RuO<sub>x</sub> due to RuO<sub>x</sub> diffusion into the lattice of CeO<sub>2</sub>. Possible interaction mechanisms between ruthenium species and different shaped CeO<sub>2</sub> supports after reduction treatment is illustrated as shown in Fig. 1d. Owing to the large surface area and

enriched surface defects of CeO<sub>2</sub> NR, Ru species are homogeneously dispersed by forming Ru-O-Ce structure and concurrently partial Ru<sup>n+</sup> ions diffusing into the lattices of CeO<sub>2</sub> NR support. However, due to the weak interaction between Ru species and CeO<sub>2</sub> NC or NO, large metallic Ru<sup>0</sup> clusters and small RuO<sub>2</sub> clusters were observed on the surface of these CeO<sub>2</sub> supports. In this study, we will also present that the distribution and valence states of RuO<sub>x</sub> on CeO<sub>2</sub> supports play a vital role for the low-temperature CO oxidation of RuO<sub>x</sub>/CeO<sub>2</sub> catalysts [3].

#### References:

- [1] Trovarelli, A. *et al.*, ACS Catal. **7** (2017), p. 4716.  
 [2] Li, J. *et al.*, J. Colloid Interface Sci. **531** (2018), p. 204.  
 [3] The authors acknowledge funding from National Science Foundation (CHE-1657943) and American Chemical Society Petroleum Research Fund (#52323). Electron microscopy performed at ORNL's Center for Nanophase Materials Sciences (CNMS), which is a U.S. DOE Office of Science User Facility.



**Figure 1.** (a) Crystal structure models of CeO<sub>2</sub> nanocubes, nanorods and nanoctahedra; (b) and (c) low-temperature CO oxidation and H<sub>2</sub>-TPR performance of different shaped 5 wt.%Ru/CeO<sub>2</sub> catalysts after reduction treatment; (d) schematic diagram showing the interaction between ruthenium species and different shaped CeO<sub>2</sub> supports; (e) TEM image of 5 wt.%Ru/CeO<sub>2</sub>NR catalysts after reduction treatment; (e1) and (e2) elemental maps for Ce and Ru, respectively, (e3) and (e4) HAADF-STEM images of 5 wt.%Ru/CeO<sub>2</sub>NR catalysts after reduction treatment showing a significant amount of surface defects of CeO<sub>2</sub> nanorods.