

Ruthenium Diffusion on Different CeO₂ Surfaces: Support Shape Effect

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Ceria (CeO₂) is often used to support transition or noble metal catalysts providing enhanced catalytic properties. The main reason is that CeO₂ possesses high oxygen storage capacity and oxygen mobility, arising from the easy switch between the Ce⁺⁴ and Ce⁺³ 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 CeO₂ nanoparticles. It has been found that tailoring CeO₂ 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 CeO₂ particles [1]. Recently, CeO₂ supported ruthenium-based catalysts have attracted much attention in the catalytic combustion of chlorobenzene, low-temperature CO₂ methanation and ammonia synthesis. In this work, CeO₂ 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 CeO₂ support and their low-temperature CO oxidation activity, which can deepen our understanding of the interactions between Ru and CeO₂ at the interfaces.

CeO₂ NR and NC were prepared via a facile hydrothermal method [2]. CeO₂ NO powder was prepared by a precipitation method and then calcined in air at 700 °C. 5 wt.%Ru/CeO₂-r (r refers to reduction treatment) catalysts with different shaped CeO₂ 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 (H₂-TPR) was performed using a Micrometrics AutoChemTM 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/CeO₂NR-r sample displays the highest low-temperature CO oxidation among the three different shaped 5Ru/CeO₂ catalysts after reduction treatment. The 5Ru/CeO₂NR-r sample surprisingly shows ~ 9% CO conversion at room temperature and achieves 50% CO conversion at around 50 °C. The H₂ consumption below 100 °C of the 5Ru/CeO₂NR-r sample was much larger than those of the other two samples (Fig. 1c). The enhanced hydrogen consumption indicates a strong Ru-CeO₂ interaction (i.e. the existence of Ru-O-Ce bond) in CeO₂ NR-supported RuO_x 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_x particles on the surface of CeO₂ nanorods (Fig. 1e3 and e4) confirm the existence of highly dispersed RuO_x due to RuO_x diffusion into the lattice of CeO₂. Possible interaction mechanisms between ruthenium species and different shaped CeO₂ supports after reduction treatment is illustrated as shown in Fig. 1d. Owing to the large surface area and

enriched surface defects of CeO₂ NR, Ru species are homogeneously dispersed by forming Ru-O-Ce structure and concurrently partial Ruⁿ⁺ ions diffusing into the lattices of CeO₂ NR support. However, due to the weak interaction between Ru species and CeO₂ NC or NO, large metallic Ru⁰ clusters and small RuO₂ clusters were observed on the surface of these CeO₂ supports. In this study, we will also present that the distribution and valence states of RuO_x on CeO₂ supports play a vital role for the low-temperature CO oxidation of RuO_x/CeO₂ 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.
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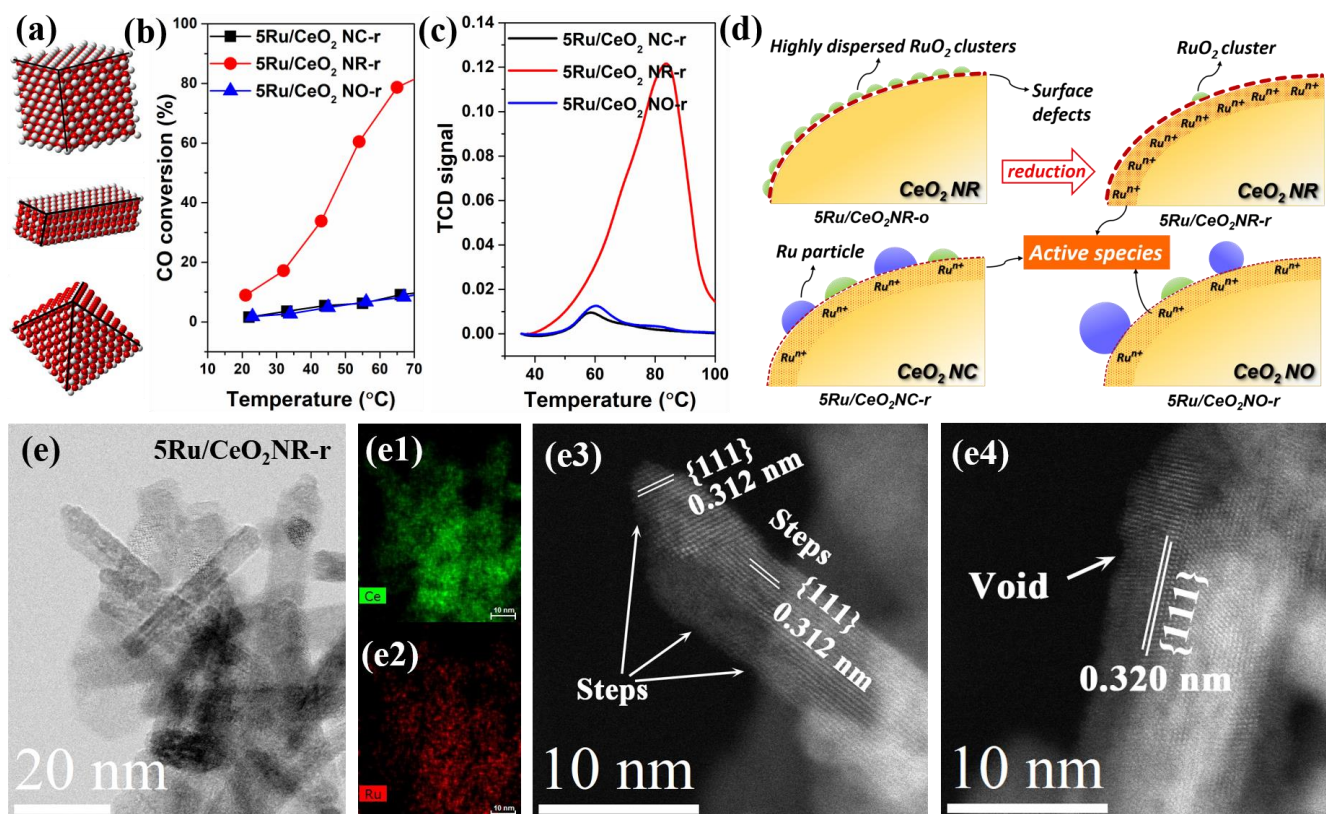


Figure 1. (a) Crystal structure models of CeO₂ nanocubes, nanorods and nanoctahedra; (b) and (c) low-temperature CO oxidation and H₂-TPR performance of different shaped 5 wt.%Ru/CeO₂ catalysts after reduction treatment; (d) schematic diagram showing the interaction between ruthenium species and different shaped CeO₂ supports; (e) TEM image of 5 wt.%Ru/CeO₂NR catalysts after reduction treatment; (e1) and (e2) elemental maps for Ce and Ru, respectively, (e3) and (e4) HAADF-STEM images of 5 wt.%Ru/CeO₂NR catalysts after reduction treatment showing a significant amount of surface defects of CeO₂ nanorods.