

Understanding the RuO_x–Oxide Support Interactions: A TEM Study

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Supported ruthenium-based catalysts have been employed in many gas-solid reactions because of their excellent activities under low temperature and pressure conditions, including the catalytic oxidation of volatile organic compounds (VOCs), preferential oxidation of CO (PROX) and partial oxidation of CH₄ [1-3]. In supported metal catalysts, the primary function of the support is to enhance the dispersion and thermal stability of metal atom/nanocluster catalysts, however, the catalyst-support interactions are thought to be critical for some important reactions. For instance, reducible CeO₂ with various shapes has been widely reported to promote the catalyst activity and selectivity via a synergistic effect or catalyst-support interaction. This is mainly due to a reversible valence change ($2\text{Ce(IV)O}_2 \leftrightarrow \text{Ce}_2\text{(III)O}_3 + 1/2\text{O}_2$) of the cerium ions with formation or elimination of oxygen vacancies. In this work, non-reducible SiO₂ nanospheres and highly reducible CeO₂ nanorods were chosen to prepare supported ruthenium catalysts in order to understand the effect of support reducibility and thermal treatments (oxidation and reduction treatments) on the low temperature CO oxidation.

CeO₂ nanorods were prepared via a facile hydrothermal method. Briefly, aqueous NaOH (6.0 M, 8.0 mL) was added to Ce(NO₃)₃·6H₂O (8.8 mmol) with stirring before the mixture was transferred into a Teflon-lined autoclave. The hydrothermal reaction procedure was carried out in a box furnace at 90 °C for 48 hrs. After the autoclave was cooled down, the precipitates were collected, and then washed with deionized water and ethanol. CeO₂ nanorods were obtained by drying in air at 60 °C overnight. SiO₂ nanospheres were prepared using a modified Stöber method. 5.0 wt.% ruthenium was loaded onto CeO₂ nanorods and SiO₂ nanospheres by impregnating CeO₂ and SiO₂ with an aqueous solution containing a required amount of Ru(NO)(NO₃)₃ and tuning the PH value of the solution to ca. 9. Then the precipitates were heated at 80 °C under stirring for 4 hrs. In the end, the precipitates were heated to vaporize water and transferred to a drying oven kept overnight for further drying. After that, the as-prepared dry samples were calcined in air at 300 °C for 5 hrs. 5.0Ru/CeO₂-oxidation and 5.0Ru/SiO₂-oxidation catalysts were obtained. Finally, half of the samples was reduced by heating up in a 5% H₂/Ar flow (200 mL min⁻¹) to 300 °C and maintained for 5 hrs. After cooling down under the H₂ atmosphere, 5.0Ru/CeO₂-reduction and 5.0Ru/SiO₂-reduction catalysts were obtained. The structural characterization of those samples was carried out using an X-ray diffractometer (XRD, Philips X'Pert MPD) with CuK_α radiation (λ: 1.5405 Å) and a Transmission Electron Microscope (TEM, FEI Tecnai F20) operated at 200 kV. Hydrogen temperature programmed reduction (H₂-TPR) was performed using a Micrometrics AutoChemTM II 2920 with the temperature rising from 30 to 900 °C.

The X-ray diffraction patterns shown in Figure 1 confirm that ruthenium and ruthenium oxide were deposited on SiO₂, according to the diffraction peaks of RuO₂ (JCPDS 43-1027) and Ru (JCPDS 06-0663). However, for the 5.0Ru/CeO₂ samples after the oxidation and reduction treatments, apart from the characterized peaks of CeO₂ nanorods, the diffraction peaks of Ru or RuO₂ were not visible. The absence of peaks related to Ru species may be attributed to the diffusion of Ru species into the CeO₂ lattice, and/or high dispersion of Ru species with a small size by formation of strong Ru-O-Ce bond [4]. It can be observed clearly from the H₂-TPR profile in Figure 1 that the 5.0Ru/CeO₂-oxidation sample shows much improved reduction performance in terms of H₂ consumption and lower reduction

temperature compared to the 5.0Ru/SiO₂-oxidation sample. The quantitative evaluation of H₂ consumption is further calculated according to the TPR curves. Through the comparison of the experimental H₂ consumption of the 5.0Ru/CeO₂-oxidation sample (5147.0 μmol/g) and of the 5.0Ru/SiO₂-oxidation sample (1262.2 μmol/g), the presence of CeO₂ in synergism with ruthenium oxide promoted significantly the H₂ consumption of the catalyst material. The shifted reduction peak to a lower temperature for the Ru/CeO₂ sample after the reduction treatment compared with the sample after the oxidation treatment can be explained by the weakening of the Ce-O bond by the strongly bound Ru species [5]. After the reduction treatment, the total H₂ consumption of the 5.0Ru/CeO₂ sample (1554.7 μmol/g) was much higher than the 5.0Ru/SiO₂ sample. The enhanced hydrogen consumption confirms the existence of Ru-O-Ce bond which promotes the low-temperature reducibility of the CeO₂-supported RuO_x catalyst. The H₂-TPR result reveals that CeO₂ nanorods support, which owns highly mobile surface oxygen species can release lattice oxygen through a strong catalyst-support interaction. Meanwhile, our hypothesis is that the surface oxygen vacancies on CeO₂ nanorods and other interfacial defects also promote the interactions between RuO_x and CeO₂. We will present a detailed atomic-level structure and composition analysis at the interfaces in these samples using HRTEM, EDX, and EELS, and correlate the interfacial structure with their catalytic activity [6].

References:

- [1] Hosokawa, S. *et al*, Appl. Catal., B **45** (2003) p.181.
- [2] Echigo, M. *et al*, Catal. Today. **90** (2004) p.269.
- [3] Lanza, R. *et al*, Appl. Catal., A **325** (2007) p.57.
- [4] Satsuma, A. *et al*, Catal. Today. **201** (2013) p.62.
- [5] Tan, H. *et al*, Environ. Sci. Technol. **49** (2015) p.8675.
- [6] This work is supported by National Science Foundation (CHE-1657943) and American Chemical Society Petroleum Research Fund (#52323).

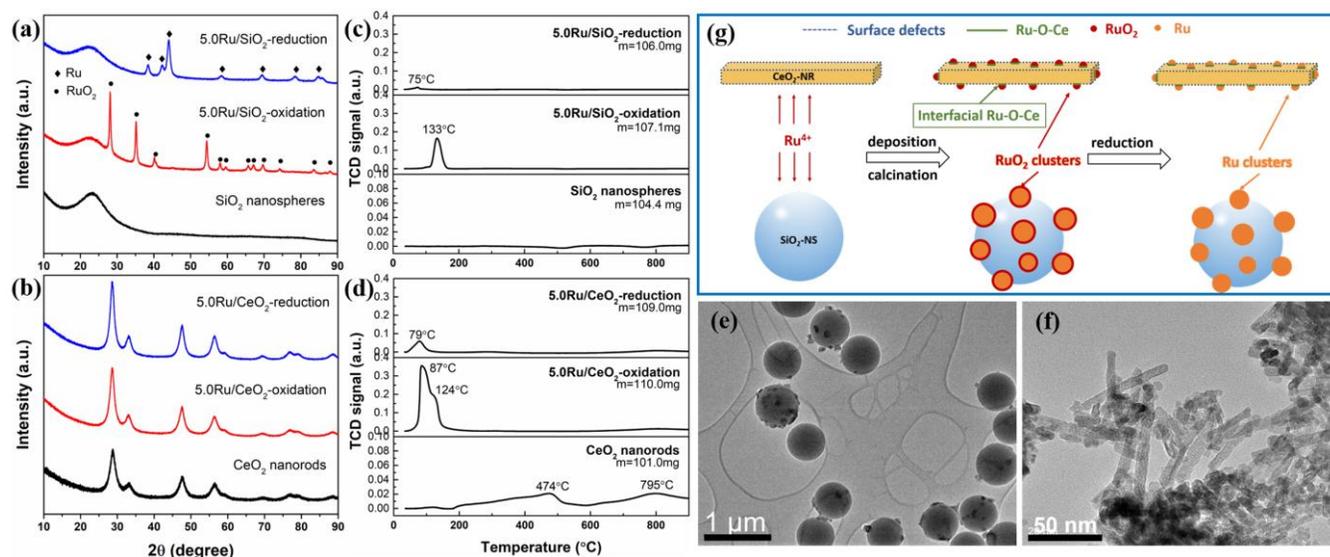


Figure 1. (a) and (b) XRD patterns and (c) and (d) H₂-TPR profiles of SiO₂ nanospheres, CeO₂ nanorods, 5.0 wt.% Ru/SiO₂ nanospheres and 5.0 wt.% Ru/CeO₂ nanorods samples after the oxidation and reduction treatments; (e) and (f) TEM images of the 5.0 wt.% Ru/SiO₂ nanospheres and 5.0 wt.% Ru/CeO₂ nanorods samples after the oxidation treatment; (g) schematic illustration of the interaction between ruthenium species and two supports.