

Investigation of reversible influence of nonstoichiometry on the profile of the Raman band, XRD pattern and activity catalytic of CeO₂

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Introduction

Cerium(IV) oxide (CeO₂) has a variety of applications, including catalytic converters and fuel additives¹. One remarking property extremely related to these applications is CeO₂ capacity to form nonstoichiometric oxygen vacancies (OV)¹. Once CeO₂ presents a Raman band of T_{2g} symmetry at 464 cm⁻¹ sensitive to lattice changes, including OV², it was applied a cyclic in situ reduction and oxidation strategy in order to investigate changes in CeO₂ Raman band profile under conditions able to control the concentration of OV. Different gases took part as reducing and oxidizing agents, and the compound was synthesized in a variety of morphologies, with specific exposure of facets, via hydrothermal and metalloorganic decomposition methods. Likewise, the same strategy of Raman spectroscopy was applied to X-ray diffractometry, performed using synchrotron radiation, and thermogravimetry measurements of oxygen storage capacity. Finally, the different morphology samples were compared as catalysts for carbon monoxide oxidation.

Results and Discussion

Some spectra exhibited asymmetric bands, and it was attributed to a overlapping band at around 400 cm⁻¹, associated with surface modes. After exposure to a hydrogen-containing atmosphere, at the temperature of 400 °C, it was observed a red-shift in CeO₂ Raman band frequency and its blue-shift to the original frequency after exposure to oxygen-containing atmosphere. Comparing to the other techniques, it was observed a lattice expansion and a loss of mass after hydrogen exposure (Figure 1). These observations demonstrate that OV induce CeO₂ Raman band red-shift, and the generation and suppression of OV is reversible at the temperature of 400 °C. The greatest red-shift was observed for comminuted CeO₂ nanorods, while no red-shift was observed for CeO₂ nanorods. This morphology also presents the best performance as a catalyst (Figure 2), in terms of starting conversion and reaching total conversion at a lower temperature in comparison to the other morphologies. Since the catalytic mechanism is dependent on OV, comminuted CeO₂ nanorods facilitates OV generation, possible because the comminuting process promotes the exposure of {110} facets, favorable for OV generation.

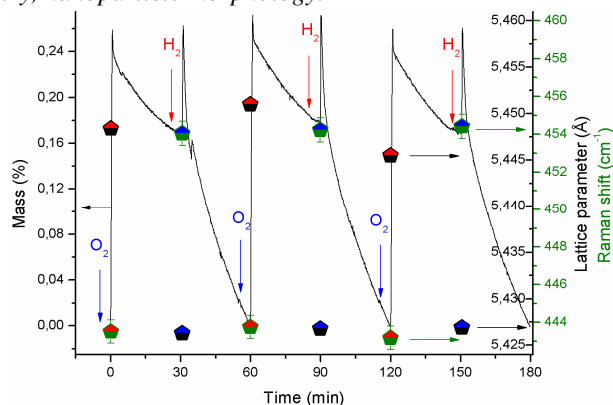


Figure 1. Comparison of results to comminuted CeO₂ nanorods.

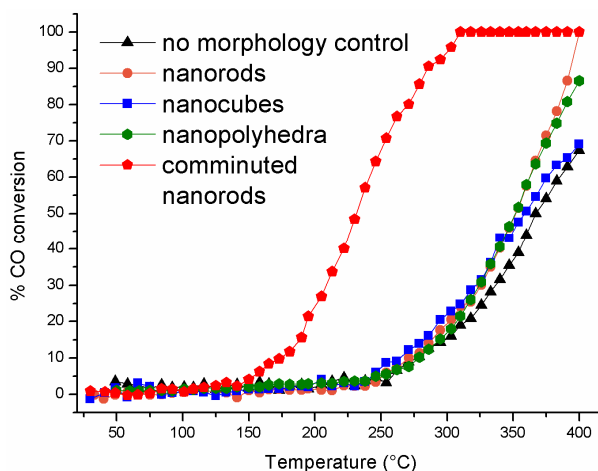


Figure 2. Comparison between different CeO₂ morphologies for carbon monoxide oxidation.

Conclusions

It was demonstrated that OV induces a red-shift in CeO₂ Raman band frequency. The morphology of the crystals play a crucial role, and {110} facet dominated morphology facilitates OV generation, and consequently enhances its activity as a carbon monoxide oxidation catalyst.

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