

## Contributions of Support Effect to Impregnated Cobalt CeO<sub>2</sub> and SiO<sub>2</sub> Catalysts

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Supported transition metal oxides catalysts with high catalytic activity have gained great attention. Despite noble metal catalysts present superior low temperature activities, their manufacturing cost is also higher and they are easy to be deactivated. Among the various transition metal oxides, cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) has shown promising activity for CO oxidation, decomposition of N<sub>2</sub>O and methanol steam reforming [1]. For most heterogeneous catalysts, supporting material plays a critical role on the catalyst activity, however, the underlying mechanism seems only preliminary. It was found that the cobalt oxides supported on the reducible metal oxides, such as TiO<sub>2</sub> and CeO<sub>2</sub>, exhibited higher synergism and promoted catalytic activity compared with those supported on the irreducible metal oxides, like SiO<sub>2</sub>. In this study, a comparative investigation was conducted between Co<sub>3</sub>O<sub>4</sub> impregnated on ceria (CeO<sub>2</sub>) nanorods and silica (SiO<sub>2</sub>) nanospheres support to understand the effect of support reducibility and surface defects, and the metal oxide/support interactions during redox cycling.

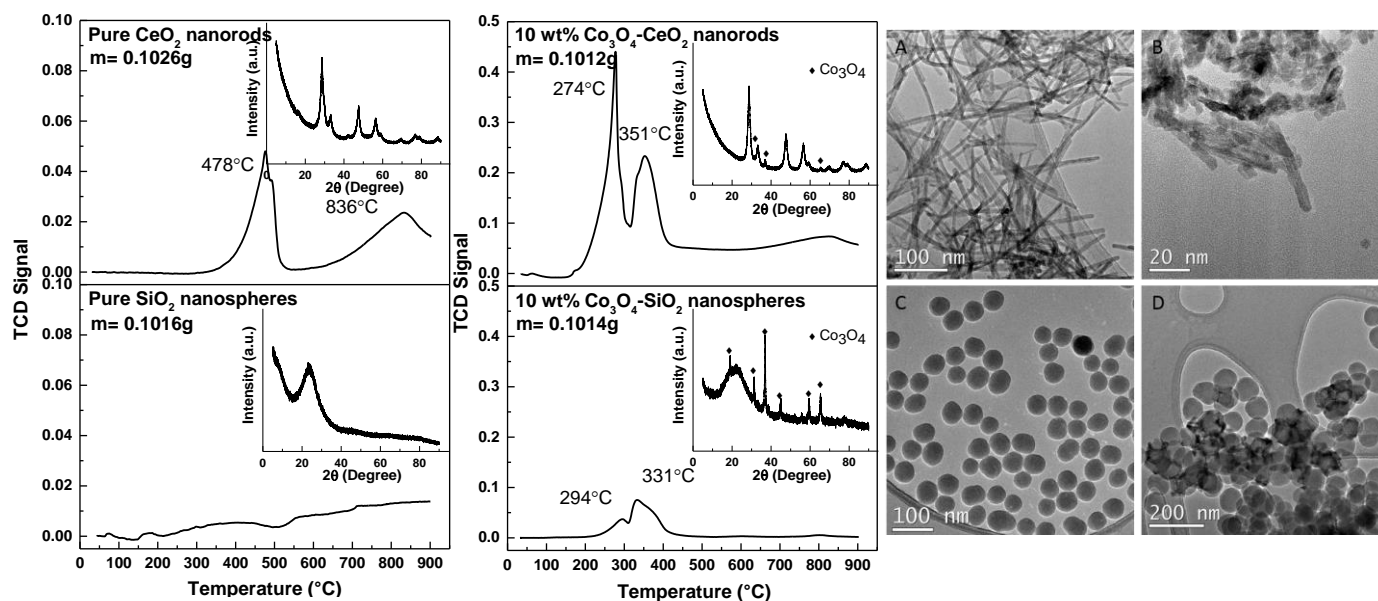
The ceria nanorods were prepared via a facile hydrothermal method [2]. Briefly, the aqueous NaOH (6 M, 8 mL) was added dropwise to Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (8.8 mmol) with quick stirring before the mixture was transferred into a sealed 200 mL Teflon-lined autoclave. The hydrothermal reaction procedure was carried out in a programmable box furnace at 90 °C for 48 hrs. After the autoclave was cooled down to room temperature, the precipitates were collected, and then washed with deionized water and ethanol. The CeO<sub>2</sub> nanorods were obtained by drying in air at 60 °C overnight. The SiO<sub>2</sub> nanospheres were prepared using the well-known Stöber method [3]. Cobalt was loaded onto the CeO<sub>2</sub> nanorods and SiO<sub>2</sub> nanospheres by impregnating CeO<sub>2</sub> and SiO<sub>2</sub> with an aqueous solution containing a required amount of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O for 2 hrs. Then the samples were heated at 100 °C on a hot plate to vaporize water and transferred into a drying oven kept overnight for further drying. After that, the as-prepared dry samples were calcined in air at 400 °C for 5 hrs. The structural characterization of different samples was carried out using an X-ray diffractometer (XRD, Philips X'Pert MPD) with Cu<sub>Kα</sub> radiation (λ: 1.5405 Å) and a Transmission Electron Microscope (TEM, FEI Tecnai F 20) operated at 200 kV. Hydrogen temperature programmed reduction (H<sub>2</sub>-TPR) was performed using a Micrometrics AutoChem<sup>TM</sup> II 2920 with the temperature rising from ambient temperature to 900 °C. Commercial cuprous oxide (Cu<sub>2</sub>O) was used for TPR calibration in order to calculate H<sub>2</sub> consumption.

The X-ray diffraction patterns and TEM images shown in Figure 1 confirm that cobalt oxide has been impregnated on CeO<sub>2</sub> and SiO<sub>2</sub> well, corresponding to the spinel Co<sub>3</sub>O<sub>4</sub> crystal lattice (JCPDS 43-1003). Pure CeO<sub>2</sub> nanorods are characterized by a low-temperature reduction peak, at 478 °C attributed to the reduction of surface oxygen species and a high-temperature peak at 836 °C corresponding to the bulk reduction [4], which is also shown in Figure 1. Coincided with the irreducibility of silica, there is almost no reduction peak (or H<sub>2</sub> consumption) shown in the TPR profile of SiO<sub>2</sub> nanospheres. Reduction of Co<sub>3</sub>O<sub>4</sub> to Co can be described as a two-stage process: Co<sub>3</sub>O<sub>4</sub> → CoO → Co [5], which corresponds to those two peaks on TPR profile of ceria and silica with impregnation of cobalt. Nevertheless, it can be observed straightly from TPR profile in Figure 1 that 10 wt% Co<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub> shows much better reduction performance in terms of H<sub>2</sub> consumption and lower reduction temperature than 10 wt% Co<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>. The quantitative evaluation of the TPR curves according to H<sub>2</sub> consumption is further calculated.

Through the comparison of experimental H<sub>2</sub> consumption of 10 wt% Co<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub> (6.5531 mmol/g) and of 10 wt% Co<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub> (2.036 mmol/g), the presence of ceria in synergism with cobalt oxide shows great enhancement of reducibility. To further investigate this synergistic effect, we compared the data with TPR peak of pure Co<sub>3</sub>O<sub>4</sub>, which possesses two main peaks at 310 °C and 396 °C respectively. Obviously, the presence of CeO<sub>2</sub> lowered the reduction temperature about 40 °C, and improved the first reduction peak (Co<sub>3</sub>O<sub>4</sub> → CoO) significantly in terms of H<sub>2</sub> consumption. The H<sub>2</sub>-TPR result reveals that ceria support, which own highly mobile surface oxygen species can release lattice oxygen through a strong metal-support interaction with cobalt oxide. Meanwhile, we believe that surface oxygen vacancies of ceria support and other interfacial defects are also involved in the interactions. Figure 1 also represents the low magnification TEM images of the as-prepared CeO<sub>2</sub> nanorods with the length of 150-200 nm and 5-10 in diameter (A), as well as SiO<sub>2</sub> nanospheres with particle size of near 50 nm (C). It can also be observed from TEM images that the shape and size for these two different catalyst supports (B and D) changed a little bit after cobalt loading and thermal treatment. We will present a detailed atomic level structure and composition analysis at the interfaces in these samples using HRTEM, EDX and EELS [6], and correlate the interfacial structure with their catalytic activity [6].

#### References:

- [1] Mahammadunnisa, S.K. *et al*, J. Chem. Sci. **128** (2016) p.1795.
- [2] Wang, R. *et al*, RSC Adv. **4** (2014) p.3615.
- [3] Stöber, W. *et al*, J. Colloid Interface Sci. **26** (1968) p.62.
- [4] Mock, S.A. *et al*, J. Colloid Interface Sci. **466** (2016) p.261.
- [5] Voß, M. *et al*, J. Catal. **212** (2002) p.10.
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**Figure 1.** XRD patterns and H<sub>2</sub>-TPR profiles of CeO<sub>2</sub> nanorods, SiO<sub>2</sub> nanospheres, 10 wt% Co<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub> nanorods and 10 wt% Co<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub> nanospheres and corresponding TEM images.