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Crystal Plane Effect of CeO_2 in Metal-CeO_2 Nanocatalysts for CO Oxidation

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In oxide-supported metal heterogeneous catalysts, it has been recognized that metal catalysts supported on different oxides have different catalytic properties, depending on the reducibility of the oxide [1], the surface acidity and basicity of the oxide [2], and the metal-oxide interaction/reaction [3]. Charge transfer or redox reactions are essential steps for the catalytic reaction at elevated temperature, therefore the reducible oxide support presents a potential advantage compared to conventional non-reducible oxide support, e.g. silica and alumina. Reducible metal oxides are solid state compounds exhibiting variable valence or oxidation states of the metal, such as CeO_2, TiO_2, VO_x, FeO_x, CoO_x, MnO_x, HfO_x, PrO_x, TbO_x, SmO_x. Many transition and lanthanide metals possess variable oxidation states because of the occupancy of 3d and 4f orbitals, respectively. In this paper, we report a facile hydrothermal synthesis of CeO_2 nanorods and nanocubes, and catalytic activity characterization of 10wt% Ni/CeO_2 nanorods and nanocubes, aiming to understand the support crystal plane effect of CeO_2 in metal-CeO_2 nanocatalysts for low temperature CO oxidation.

CeO_2 nanorods and nanocubes were prepared using a hydrothermal method [4-5]. Typically 0.1M $Ce(NO_3)_3{\cdot}6H_2O$ and 6M NaOH mixtures were heated to 90~210 °C and held for 48 hrs in a sealed 200 mL Teflon-lined autoclave (∼50 % fill). Then the autoclave was cooled to room temperature before the solid products were recovered by suction filtration. The materials were washed thoroughly with distilled water to remove any co-precipitated salts, then washed with ethanol to avoid hard agglomeration in the nanoparticles, and dried in air at 50 °C for 12 hrs. Transmission electron microscopy (TEM) characterization was performed using a JEOL2100 operated at 200 kV and equipped with an EDAX detector and annular dark-field detector. Hydrogen temperature programmed reduction (H_2-TPR) study was examined using hydrogen chemisorption on the Quantachrome iQ and Micrometrics 2920 to explore how much hydrogen adsorbs as a function of temperature. The catalytic oxidation of CO was conducted by using a fixed bed plug flow reactor system. 1vol%CO/20vol%O_2/79vol%He with a 70 mL/min flow rate was supplied through mass flow controller and passed through the catalyst bed. The catalyst (~100 mg) was mixed with quartz wool (coarse, 9 μm) and filled in the quartz tube reactor. The reaction temperature was programmed between room temperature and 350°C and monitored by thermocouple. The reactant CO and product CO_2 were analyzed by using an on-line gas chromatograph (SRI multiple gas analyzer GC, 8610C chassis) system.

Figure 1 (a) and (b) shows typical TEM images of CeO_2 nanorods and nanocubes prepared by a hydrothermal method, respectively. Figure 1 (c) compares the Raman spectra of CeO_2 nanorods and nanocubes, showing a higher concentration of oxygen vacancy in rods sample. Figure 1 (d) compares the shape (crystal plane) effect of CeO_2 support on hydrogen consumption of 10wt%Ni-CeO_2 nanorods and nanocubes. All metal-loaded samples show improved low-temperature activity, compared to pure CeO_2 nanorods and nanocubes. When comparing the low temperature hydrogen consumption over the temperature range from room temperature to 350°C, Ni-CeO_2 nanorods show higher hydrogen consumption compared to Ni-CeO_2 nanocubes. This could be attributed to the interfacial anchoring effect of metals on different crystal planes on CeO_2 with different shapes. We will present the atomic level interfacial structure and chemical composition of Ni-CeO_2 nanorods and nanocubes using HRTEM, EDX and EELS in details.

References

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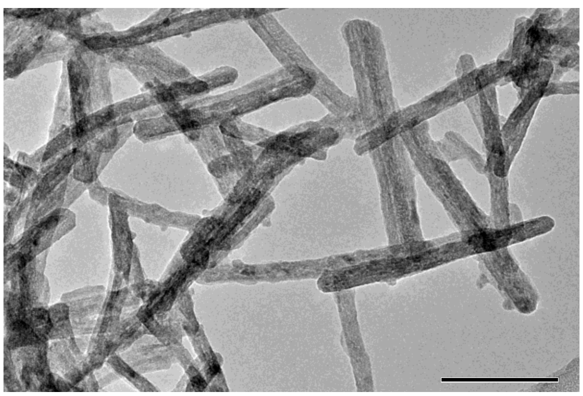
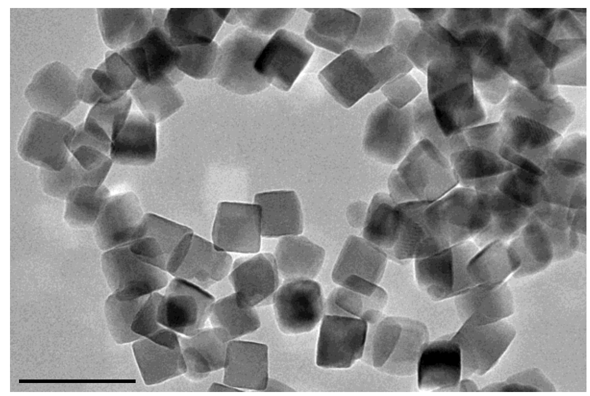
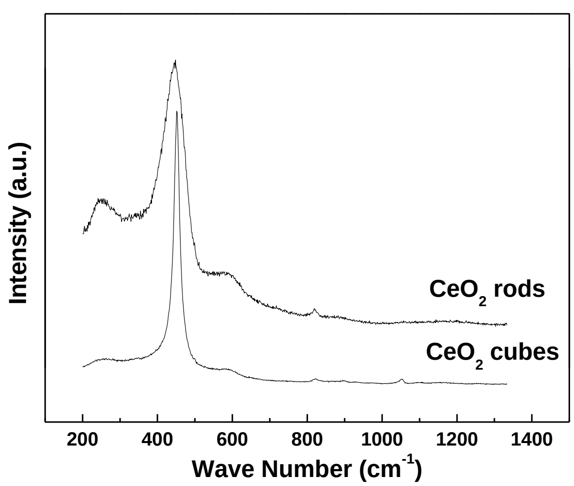


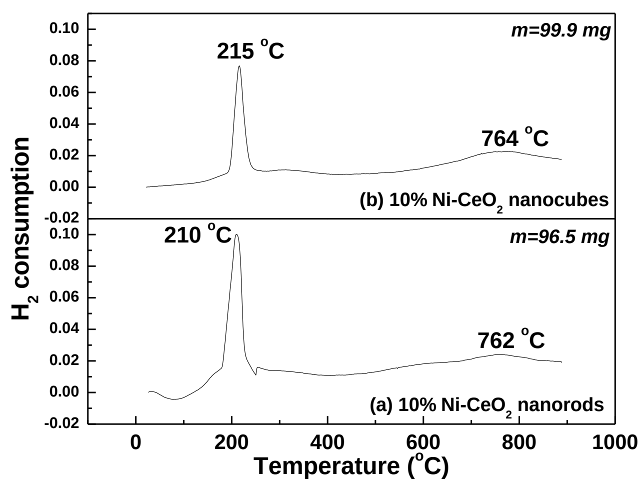
(a) CeO_2 nanorods



(b) CeO_2 nanocubes



(c) Raman spectra



(d) H_2-TPR

Figure 1 TEM images (a)/(b) (scale bar: 50 nm) and Raman spectra (c) of CeO_2 nanorods and nanocubes, and H_2-TPR profiles (d) of 10wt% Ni/CeO_2 nanorods and nanocubes under a 5%H_2/95%Ar gas atmosphere.