Novel Synthesis of Nanoscale Ceria and Gold-doped Ceria

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Introduction

Nanostructured ceria has been reported to promote the CO oxidation activity of metals, such as Pt, Au, and Cu and to keep them in highly dispersed state [1-4]. How exactly this promotion takes place and how the composite system of M-O-Ce activates redox reactions, such as the water-gas shift reaction is currently being debated in the literature. One of the key issues for the wide application of ceria-based nanomaterials is to correlate the complex catalytic phenomena with the nanoscale structure and texture of catalysts. To date, different solution-based methods, such as solvothermal, reverse micellar, and sonochemical routes, have been used to achieve ultra-small (2 − 3 nm) ceria nanocrystals [5]. In this paper, we will present novel synthesis of ultra-small, surfactant-free, and air-stable ceria particles and gold-doped ceria nanocatalysts. We also present H_2-TPR and Raman characterization of the prepared nanocrystalline samples.

Materials and Methods

2.6 nm ceria was prepared by a modified thermolysis method [6]: Cerium 2,4-pentanedionate was heated in oleylamine at 250 °C in air. Ethanol was used as both a precipitating reagent and a washing solvent. The as-washed gel was dried and then calcined at 300 °C to remove adsorbed surfactants. 3.0 nm ceria was prepared by a modified hydrolysis method at room temperature [7]. Cetyltrimethylammonium bromide (CTAB) was used as a surfactant and similarly removed by calcination. Morphology and particle size of the as-calcined powders were determined on a JEOL-200CX TEM at 200 kV. Their surface oxygen reducibility was investigated by H_2-TPR conducted on a Micromeritics Pulse ChemiSorb 2705 instrument equipped with a thermal conductivity detector. Raman spectra were obtained using the 514.5 nm line of a tunable Ar-ion laser. The spectra were acquired in back-scattering configuration and the power was kept at less than 2 mW to avoid sample heating.

Results and Discussion

The as-obtained CeO_2 powders were pure yellow in color, indicating the complete elimination of organic surfactants after air calcination at 300 °C. The samples synthesized via thermolysis and hydrolysis methods were composed by highly crystallized nanoparticles in sizes of 2.6±0.2 and 3.0±0.3 nm, respectively (see Figure 1). Thus, ultra-small, surfactant-free, and air-stable ceria nanocrystals have been obtained. The H_2-TPR data displayed a surface reduction peak at 475 °C with a shoulder at 363 °C for the 2.6 nm sample; and two reduction peaks located at 416 and 534 °C for the 3.0 nm one. Thus, the reducibility of these nanocrystalline ceria materials is higher than that of CeO_2 prepared via conventional hydrolysis (562 °C) [8]. Applying hydrolysis-based co-precipitation method under optimized conditions (precipitating reagent, pH value, aging temperature and time, etc.), we can produce nanoscale, homogenous gold-doped ceria solid solutions. We also use the CO-TPR and CO oxidation reaction to probe the surface reducibility and reactivity of these nanomaterials.

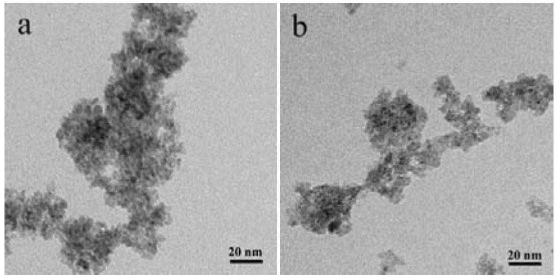

Figure 1. TEM images of 2.6 nm CeO_2 nanoparticles via thermolysis method (a) and 3.0 nm CeO_2 nanoparticles via hydrolysis method (b).

A Raman peak between 540 – 620 cm^{-1} has been seen to increase with decreasing particle size and the incorporation of other ions in the CeO_2 lattice. This peak is thought to represent defect sites in the nanocrystalline lattice, and its intensity increases relative to the first-order T_{2g} peak near 464 cm^{-1}. Furthermore, for the nanocrystalline samples, the triply-degenerate first-order Raman peak exhibits asymmetric broadening on the low-energy side due to phonon confinement effects. We are currently employing in situ Raman spectroscopy to investigate the catalytic activity of nanoscale ceria and gold-doped ceria as a function of the various oxygen species and defect sites present.

Significance

Novel synthesis methods, surfactant-assisted thermolysis and hydrolysis, have been developed towards 2.6 and 3.0 nm ceria nanocrystals, respectively. The as-calcined particles have narrow size-distribution and low reduction temperature. Further, the hydrolysis-based co-precipitating route can also be used to synthesize stable gold-doped ceria nanocatalysts.

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