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Low-Temperature CO Conversion on 1wt%Pt/CeO_2 Nanocubes

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CO conversion via a catalytic oxidation has wide applications in the vehicle emission control, water-gas shift reaction, and CO preferential oxidation for proton exchange membrane fuel cells [1-3]. Noble metal nanoparticle catalysts (Pt/Pd) for CO oxidation can be promoted by cerium oxide (CeO_2) support. Cerium oxide based supports are shown to have superior oxygen mobility via an easy redox reaction ($4CeO_2 \leftrightarrow 2Ce_2O_3 + O_2$), which enhances catalyst activity. The role of cerium oxide is believed to involve the adsorption and interaction of CO at the noble metal/CeO_2 interface. Several theoretical studies [4-6] have investigated the structure and relative stability of the surfaces of CeO_2 crystals, and the results have indicated that the compact {111} surfaces are the most stable (and are therefore the least reactive), followed by {110}, {100}, and {211}. In this paper, we report a shape-controlled synthesis of CeO_2 nanocubes by a hydrothermal reaction, and preparation and catalytic activity characterization of 1wt% Pt/CeO_2 nanocubes with {100} surfaces, aiming to identify potential shape effects for the low temperature CO oxidation.

Shape/size-controlled CeO_2 nanopowder samples were synthesized using a hydrothermal method. Typically 0.1M $Ce(NO_3)_3{\cdot}6H_2O$ and 6M NaOH mixtures were heated to 50~220 °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. 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 300^{o}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)-(f) shows representative TEM images of CeO_2 nanocrystals (NCs) with controlled shapes prepared by a hydrothermal method. The monodisperse cerium oxide NCs with different shapes including nanorods, nanosheets, nanocubes, and nanocuboids can be achieved by the control of reaction temperature, dwell time, and Ce^{3+}/OH^- ratio. In general, the cerium oxide nanocrystals seem to prefer the shapes of nanorods and nanosheets at low-temperature (<100^{o}C) hydrothermal condition, while at higher temperature the nanocube-like or irregular shapes are observed. Figure 1 (g)-(h) presents the high resolution TEM images of CeO_2 nanocubes before and after 1wt%Pt loading using a impregnation method, indicating a good dispersion of Pt nanoparticles on CeO_2 nanocubes. Figure 1 (i) displays the light-off temperature results for the CO oxidation ($2CO + O_2 \rightarrow 2CO_2$) in a 1vol%CO/20vol%$O_2$/79vol%He atmosphere on the 1wt%Pt/CeO_2 nanocubes catalysts.

The corresponding light-off temperatures for 50% (*T*50) and 100% (T100) CO conversion are 156 ^{o}C and 229^{o}C, respectively, indicating a superior low temperature catalytic activity of CO oxidation over Pt/(100)CeO_2 nanocubes, compared to Pt/(111)CeO_2 nanooctahedra [7]. We will present the correlation study between the nanoparticle size/shape and reactivity as determine by TEM, hydrogen temperature programmed reduction (H_2-TPR), and flow reactor test on the catalyst activity.

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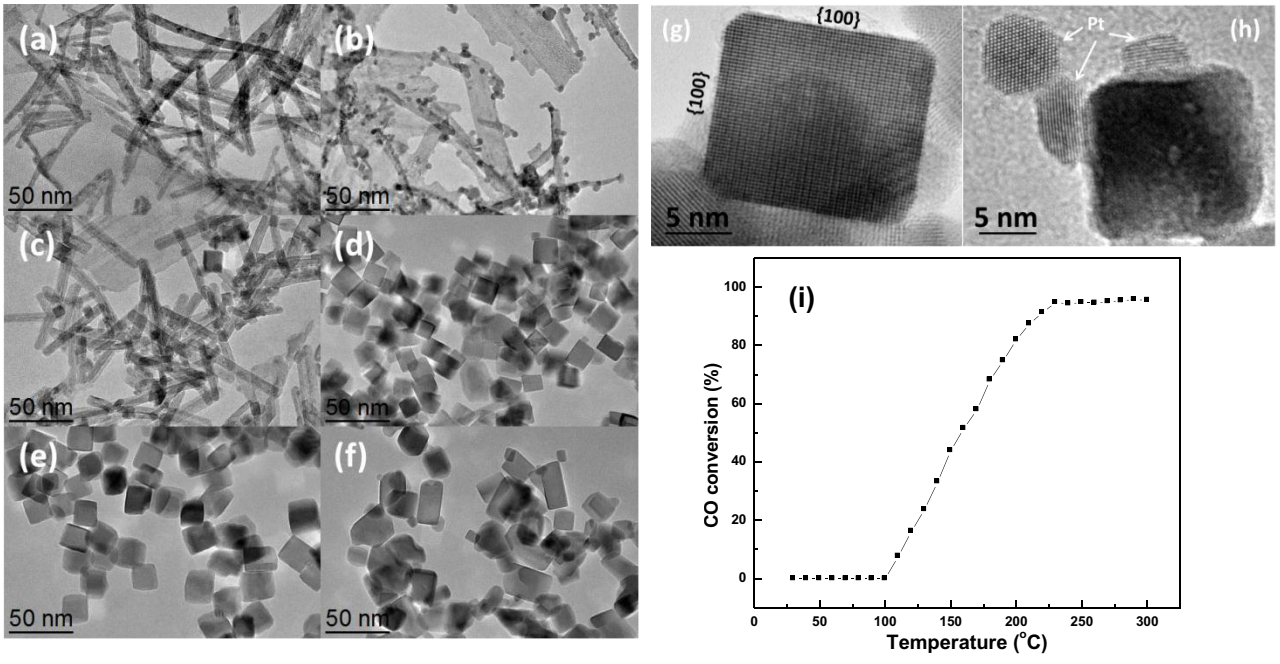

Figure 1 Some typical shapes of CeO_2 nanoparticles prepared by a facile hydrothermal method at different temperatures with a constant dwell time 48 hrs: (a): 50°C; (b): 70°C; (c): 90°C; (d): 110°C; (e): 130°C; (f): 170°C. High resolution TEM images of CeO_2 nanocubes before and after Pt loading are shown in (g) and (h), respectively. (i): CO oxidation over 1wt%Pt/CeO_2 nanocubes.

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