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Short communication

Accurate hierarchical control of hollow nanocube Pd/CeO_2 catalysts for the low-temperature oxidation of CO

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ABSTRACT

An effective approach of simultaneous coordinating etching and Pd nano coating technology is employed to prepare hollow Pd/CeO_2 nanocubes as catalysts for the low-temperature oxidation of CO. The activities of Pd/CeO_2 catalysts are higher than that of Pd supported on Al_2O_3, and the activity of 1 wt.% Pd/CeO_2 can be enhanced obviously and its T_{90} (which denotes the temperatures at which a 90% conversion of the initial reactants is attained) is as low as −5.6 °C. The intrinsic hollow nature as well as high porosity of the unique nanostructures of CeO_2 support contributes greatly to the formation of large numbers of surface oxygen vacancies on the as-prepared Pd/CeO_2 catalysts, and therefore it exhibits outstanding catalytic activity. This strategy method is simple, of low cost, which may shed light on a new avenue for fast synthesis of hollow cube-like nano functional materials for catalyst, drug delivery, energy storage and other new applications.

1. Introduction

Accurate designing molecular architectures of nano/micro-materials is one of central tasks of modern science and technology due to the fascinating properties that are most dependent on its structure, such as size, morphology and component [1–4]. Most recently, hollow-structured mesoporous materials, which integrate hollow interior or voids with mesoporous shells of various dimensions into one nanostructure, have attracted even more attention owing to their outstanding features of well-defined interior voids, high specific surface area, low density, and the extensive presence of mesoporous channels on the shell [5–9].

Such materials have been proved great potential in a diverse range of applications such as catalysis, environmental remediation, energy storage and various new applications [7–19]. For example, Teng and co-workers obtained Mn_3O_4–Co_3O_4 hollow spheres with a high catalytic activity for CO oxidation [20]. Lou and co-workers synthesized hollow $CoSnO_3$@C microcubes and hollow $CoMn_2O_4$ nanoboxes with highly reversible lithium storage [21,22]. Our previously prepared hollow porous Ag@TiO_2 materials exhibit enhanced photocatalytic activity [23].

Herein, we propose a fast strategy to prepare hollow Pd/CeO_2 nanocubes with high purity, high surface area, and excellent catalytic activity for the low-temperature oxidation of CO (LTO CO) as illustrated in Scheme 1. Compared with conventional methods of CeO_2 production, the hollow porous Pd/CeO_2 materials prepared as such have relatively lower density, higher surface area and more stable hollow configuration without the destructive effect of template removal on product morphology. Hence, a higher degree of metal utilization as enhanced catalytic activity for LTO CO can be expected. Additionally, this route is environmentally friendly, capable of being scaled up for mass-production and low cost.

2. Experimental

2.1. Materials and synthesis

2.1.1. Preparation of Cu_2O nanocubes

All the reagents are analytical grade and used without further purification. In a typical synthesis process, with the conditions of constant stirring and heated in a water bath at 55 °C, 0.11 g polyvinylpyrrolidone (PVP, MW30000) and 0.17 g $CuCl_2 \cdot 2H_2O$ were dissolved in 100 mL distilled water to form a homogeneous solution. Subsequently, NaOH (10.0 mL, 2.0 M) aqueous solution was added into the above transparent light green solution dropwise and stirred for 0.5 h to form a dark brown solution. Then, an ascorbic acid solution (10.0 mL, 0.6 M) was added dropwise and a turbid red liquid gradually formed. The mixture was aged for 3 h. The resulting precipitate was harvested by several rinse-centrifugation cycles with deionized water and absolute ethanol. Then, all precursors were dried at 70 °C for 8 h and stored for further usage in the etching stage.

2.1.2. Preparation of hollow CeO_2 nanocubes

To synthesize the CeO_2 hollow nanocubes, Cu_2O nanocube (50 mg) and PVP (0.725 g, MW30000) were dispersed in a mixture solution of deionized water and absolute ethanol (V_{H2O}:V_{EtOH} = 1:1) under a

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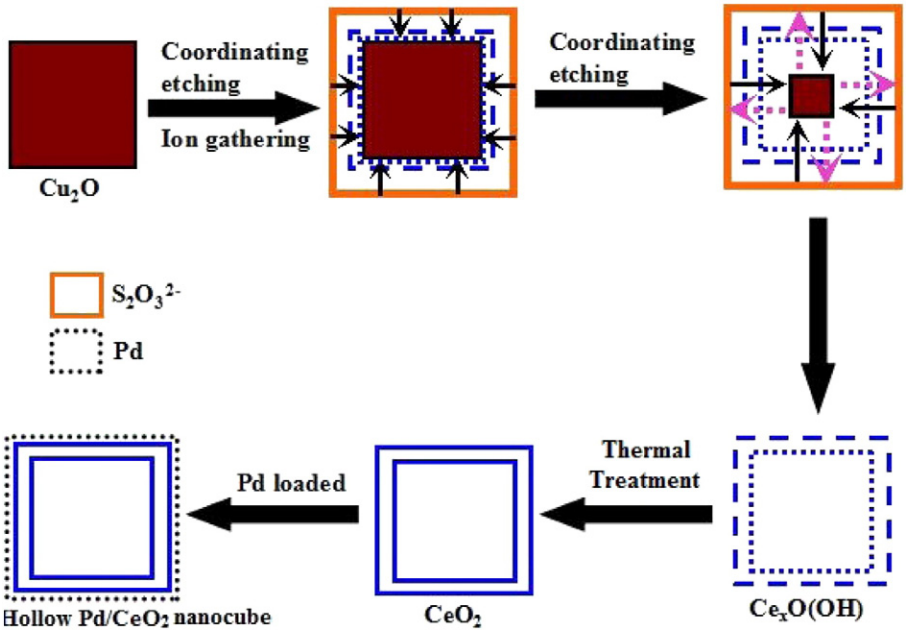

Scheme 1. Representative illustration of the formation of hollow Pd/CeO_2 nanocubes by simultaneous coordinating etching of Cu_2O nanocubes and Pd nano coating technology.

constant stirring at room temperature. Then $Ce(NO_3)_3\ 6H_2O$ (30.4 mg) was added to the above solution and stirred for 20 min. Finally, $Na_2S_2O_3 \cdot 6H_2O$ (40.0 mL, 1.0 M) was added dropwise into the mixture solution with a continual stirring for 60 min. Eventually, the resulting product $Ce_xO(OH)$ was harvested by several rinse-centrifugation cycles with deionized water and ethanol then dried at room temperature for further characterization. Finally, certain amount of $Ce_xO(OH)$ nanoboxes was successively annealed in Ar flowing at 450 °C for 4 h with a slow ramp rate of 1 °C min^{-1} to make the hollow CeO_2 nanoboxes.

2.1.3. Synthesis of Pd catalysts supported by hollow CeO_2 nanocubes

The Pd/CeO_2 catalysts were prepared through the following method. For a typical procedure: 5 g of CeO_2 was added to mixed solution of ethylene glycol (EG) and polyvinylpyrrolidone (PVP) under stirring. The solution was heated and kept at 120 °C, and followed by addition of some 0.5 gL^{-1} Pd^{2+} solution, drop-by-drop. The mixture was stirred for 6 h. The precipitate was harvested by centrifugation and washed with deionized water and glycerol three times. The obtained product was dried in air at 60 °C for 12 h and calcined at 500 °C for 4 h to form final products. According to different contents of Pd loading determined by Inductively Coupled Plasma (ICP), 0.2, 0.5 and 1 wt.% Pd/CeO_2 support catalysts are synthesized. Before the catalytic activity test, supported Pd catalysts are further pretreated by 10% H_2/N_2 (50 mL min^{-1}) at 50 °C for 0.5 h.

2.2. Characterization

X-ray diffraction (XRD) was carried out to identify the phase composition of synthesized samples over the 2θ range from 10° to 90° using a Rigaku D/max-A diffractometer with Co Kα radiation. A Fourier transform infrared spectroscope (FTIR, Themo Nicolet 670FT-IR) was used for recording the FTIR spectra of the sample ranged from 400 to 4000 cm^{-1}. Morphologies of the synthesized samples were observed with a AMRAY 1000B scanning electron microscope (SEM), and the microstructural characteristics of hollow nanocube Pd/CeO_2 nanoparticle aggregates were observed by high-resolution transmission electron microscope (HR-TEM, JEOL JEM-2100) working at 200 kV accelerating voltage and the lattice structure was identified by selected area electron diffraction (SAED) technique. Nitrogen adsorption–desorption measurements were conducted at 77 K on a Micromeritics Tristar apparatus. Specific surface areas were determined following the Brunauer–Emmet–Teller analysis.

2.3. Catalytic properties study

The catalytic properties of the samples were studied with the CO oxidation reaction using temperature-programmed mode. 0.2 g catalyst samples were placed in a stainless-steel reactor. The reaction mixtures in helium (Vol.%) 0.2 CO, 1.0 O_2, 0.5 Ne were fed to the initial catalyst that was cooled to −30 °C. The feed flow rate was 50 ml min^{-1} and space velocity was 15,000 ml h^{-1}. The catalyst was heated in the reaction mixture from −30 to 150 °C at a heating rate of 10 °C min^{-1}. The reactants and products were analyzed online by gas chromatograph (GC) equipped with a column packed with carbon molecular sieve, a methanator and a FID.

3. Results and discussion

XRD patterns of the synthesized 1 wt.% Pd/CeO_2 (Fig. S1) and N_2 adsorption/desorption isotherms with the pore size distribution inset of the obtained hollow 1 wt.% Pd/CeO_2 nanocubes (Fig. S2) are listed in supporting information.

SEM images of the hollow 1 wt.% Pd/CeO_2 nanocubes are shown as Fig. 1a and b. It is obvious that the synthesized 1 wt.% Pd/CeO_2 nanocubes maintain the cube morphology of prepared Cu_2O except for a little shrinkage in size, which are nanocube ca. 400 nm uniformly. Observation on part particles with partially broken shell, as shown in Fig. 1b indicates that the thickness of shell is estimated to be 30–50 nm and the surface of the samples is made up by nano-sized small particles. The EDX analysis (inset in Fig. 1a) detects some Pd on the surface of CeO_2. It can be clearly noticed that the obtained Pd/CeO_2 powder is not a solid but a hollow microstructure characteristic according to Fig. 1b. The cleft of these nanoboxes might be caused by rapid mass-transport across the shells during fast dissolution of the Cu_2O. The unique hollow morphology of 1 wt.% Pd/CeO_2 nanocubes is also characterized by TEM and HR-TEM, as illustrated in Fig. 1c–f. Fig. 1c–e shows that the resulting Pd/CeO_2 samples are typical hollow nanoboxes with well-defined interior and very thin shell and the thickness of the shell wall is estimated to be ca. 30 nm, which is consistent with the