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Preparation of 3D micro/nanostructured CeO_2: Influence of organic/inorganic acids

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ABSTRACT

CeO_2 is an important porous material with a wide range of applications in the abatement of volatile organic compounds (VOCs). In this paper, we prepared a series of novel three-dimensional (3D) micro/nanostructured CeO_2 materials via a solvothermal method. Organic acid-assisted synthesis and inorganic acid post-treatment were used to adjust the CeO_2 microstructures. The size of the 3D micro/nanostructures could be controlled in the range from 180 nm to 1.5 μm and the surface morphology changed from rough to smooth with the use of different organic acids. The CeO_2 synthesized with acetic acid featured a hierarchical porosity and showed good performance for toluene catalytic combustion: a T_{50} of 187 °C and a T_{90} of 195 °C. Moreover, the crystallite size, textural properties, and surface chemical states could be tuned by inorganic acid modification. After treatment with HNO_3, the modified CeO_2 materials exhibited improved catalytic activity, with a T_{50} of ~175 °C and a T_{90} of ~187 °C. We concluded that the toluene combustion activity is related to the porosity and the amount of surface active oxygen of the CeO_2. Both these features can be tuned by the co-work of organic and inorganic acids.

Introduction

In recent decades, inorganic oxides, such as transition metal oxides and rare earth oxides, have drawn attention for their excellent performance as heterogeneous catalysts. Among these materials, cerium is one of the most abundant rare earth elements (Sun, Li, & Chen, 2012). Hence, CeO_2 and Ce-based materials have traditionally been used as catalysts and catalytic supports for three-way catalysis, VOC abatement, the water gas shift reaction, and steam reforming of alkanes (Delimaris & Ioannides, 2008; López et al., 2015), owing to their large surface area, rapid oxygen mobility, reversible redox chemistry, and cost effectiveness.

The catalytic activity of CeO_2 is strongly dependent on its microstructure, including the dimensions of its nanocrystallites, morphology, textural properties, and surface environment (Wu, Wang, & Li, 2014). In terms of dimensions and morphology, CeO_2 with fine nanocrystallites generally exhibits higher catalytic performance than that of bulk materials (Guo et al., 2010; Yin, Wang, Pang, Koltypin, & Gedanken, 2002). The exposed crystal planes of CeO_2 also influence catalytic performance, because the surface energy of the different crystal planes decreases in the order: (100) > (110) > (111) (Li, Wu, & Overbury, 2013; Tana et al., 2009; Wang, Jiang, Zheng, Xie, & Zheng, 2012; Wu, Li, & Overbury, 2012). The assembly methods of nanoparticles affect not only the electrical, optical, and magnetic properties (Li, Shen, Tang, Liu, & Chen, 2014), but also the thermal stability of the materials. A 3D-structured catalyst generally exhibits greater resistance to thermally collapse, which is an important feature for thermocatalysis. Moreover, in terms of surface texture, CeO_2 with a large specific surface area and well-developed porosity shows good catalytic activity (Guo et al., 2010; Li, Zhang, Chen, Luo, & Lu, 2011).

To improve the catalytic activity of CeO_2, intensive efforts have been devoted to designing nanostructured CeO_2. Methods of controlled syntheses involve the addition of structure-directing agents, doping with other elements, and acid/base leaching. Among these approaches, organic acid assisted-synthesis is particularly attractive. Owing to the high oxygen affinity of rare earth elements, cerium tends to coordinate with oxygen-containing carboxyl groups; thus, organic acids can regulate the surface states of ceria precursors. Deori, Gupta, Saha, and Deka (2014) synthesized 3D-

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Table 1
Labeling scheme and description of samples.

Sample	Organic acid	HNO_3 treatment time (h)	Calcination temperature (°C)
Ace	Acetic acid	–	–
Ace500	Acetic acid	–	500
Pro500	Propionic acid	–	500
But500	*n*-Butyric acid	–	500
Ole500	Oleic acid	–	500
Ace(E0.5)500	Acetic acid	0.5	500
Ace(E1)500	Acetic acid	1	500
Ace(E2)500	Acetic acid	2	500

structured CeO_2 using oleic acid to stabilize the (100) plane. Zhou et al. (2008) synthesized uniform CeO_2 nanoflowers with the assistance of oleic acid and oleylamine. The obtained nanoflowers featured a large surface area, high porosity, and high activity for CO oxidation.

In addition, inorganic acid post-treatments have been used as an effective strategy to modify metal oxides. Ates and Hardacre (2012) illustrated that HCl treatments increased the micropore volume of natural zeolites through dealumination and the creation of defects. Peng et al. (Peng et al., 2016; Si, Wang, Peng, & Li, 2015) used HNO_3 to selectively remove A-site ions from ABO_3 perovskites. The modified perovskites possessed a larger surface area, higher porosity, and lattice oxygen mobility, which contributed to excellent performance in NO_x storage and reduction.

Herein, we investigate the effects of organic and inorganic acids on CeO_2 microstructures and develop new strategies to prepare CeO_2 materials with prominent VOC catalytic performances. The new strategy of combining organic acid assisted-synthesis and inorganic acid post-treatment is simple, effective, and inexpensive. To estimate the potential for VOC abatement, toluene catalytic combustion was examined as a probe reaction. Relationships between the physicochemical properties of the CeO_2 and the toluene combustion performances are discussed in detail.

Experimental

Synthesis

All reagents were of analytical purity and used without any further purification. In a typical synthesis, 6.5 g of $Ce(NO_3)_3 \cdot 6H_2O$ was dissolved in a mixed solution including 60 mL of ethylene glycol (EG), 8 mL of deionized water and 2.9 g of polyvinylpyrrolidone (PVP k30). A 1 mL portion of acetic acid (or propionic acid, *n*-butyric acid, oleic acid) was added under stirring to form a transparent solution. The mixed solution was transferred to a 100 mL Teflon-lined autoclave and heated at 200 °C for 3.5 h. After the hydrothermal reaction, the purple precipitate was separated by centrifugation, then washed with deionized water and ethanol alternatively. The sample was dried at 80 °C overnight to obtain CeO_2 precursor and CeO_2 was obtained after calcinating at 500 °C for 1 h.

A 1.0 g portion of the ceria precursor was added into 100 mL of 0.1 mol/L HNO_3 solution and stirred constantly for 0.5, 1, or 2 h. The obtained yellow sample was washed with deionized water and ethanol several times before drying at 80 °C overnight. The dried sample was calcinated at 500 °C for 1 h to obtain the etched CeO_2.

The labeling scheme of the samples subjected to different treatments is given in Table 1.

Characterization

X-ray diffraction (XRD) was performed on an X'Pert Pro diffractometer (PAN Analytical, The Netherlands) with Cu Kα radiation. The data were collected under ambient conditions in a 2θ range of 10°–90° at a scan rate of 0.1°/s. The N_2-sorption isotherms were collected at 77 K on an ASAP 2020 instrument (Micromeritics, USA). All samples were pretreated under a vacuum at 250 °C for 4 h prior to measurements. The specific surface area was calculated by the BET method. The total pore volume was estimated from the N_2 uptake capacity at a P/P_0 of ca. 0.99; the mesopore and micropore volumes were derived from BJH and *t*-plot analysis, respectively. The mesopore and micropore size distributions were estimated by the BJH and DFT methods. The morphology was characterized by imaging with a scanning electron microscope (SEM, Hitachi S-3400N, Japan) and a transmission electron microscope (TEM, Tecnai G2 F20, FEI, USA) with selected area electron diffraction (SAED). X-ray photoelectron spectroscopy (XPS) was measured on an ESCALAB 250XI spectrometer (Thermo, USA) with Al Kα ($h\nu$ = 1486.6 eV) radiation as the excitation source. The binding energy of samples was calibrated to the C 1s peak at 284.6 eV.

Toluene-temperature programmed desorption (toluene-TPD) was performed on a Micromeritics Autochem II 2920 instrument. The prepared CeO_2 (50 mg) materials were loaded onto quartz reactor and pretreated at 400 °C for 0.5 h under a 5% O_2/Ar flow to remove carbon contamination and adsorbed H_2O, followed by cooling to 100 °C under a pure He flow (50 mL/min). Toluene vapor was introduced by He flow and pulsed until the samples were saturated. The temperature was dropped below 50 °C under a pure He flow for 1 h, followed by heating to 800 °C at a rate of 10 °C/min. The toluene and CO_2 were continuously monitored by a mass spectrometer (OmniStar, Pfeiffer Vacuum, Germany) at m/z 91 and 44, respectively.

Toluene combustion activity

A 100-mg portion of the CeO_2 (40–60 mesh) was loaded into a quartz microreactor (inner diameter 8 mm). The total gas flow rate was 33.4 mL/min, corresponding to a gas hourly space velocity of 20,000 mL/(h g_{cat}). Prior to measurement, the sample was preheated at 250 °C for 1 h under a constant air flow, followed by slowly cooled to 120 °C. After reaching a stable condition, the experiment was performed from 120 to 280 °C under a toluene/air flow with a toluene concentration of 4 g/m^3. The conversion of toluene from the outlet of the reactor was determined with a gas chromatograph (Agilent 6820, USA) equipped with a FID detector. The reaction temperature was monitored by a thermocouple placed in the middle of catalyst bed.

Results and discussion

CeO_2 synthesized with different organic acids

The XRD patterns of the CeO_2 precursor and CeO_2 materials are shown in Fig. 1. The diffraction patterns observed at 2θ angles of 28.3°, 32.9°, 47.1°, and 56.2°, were indexed to (111), (200), (220), and (311) planes, respectively. All the XRD patterns were attributed to the cubic phase of the ceria fluorite structure (JCPDS No. 43-1002). The CeO_2 materials synthesized from different organic acids featured almost identical XRD patterns. The precursor (Ace) showed weaker and broader XRD patterns, indicating poor crystallinity.

The SEM images in Fig. 2(a)–(d) show the monodisperse micro/nanostructures of the CeO_2 materials. The morphologies varied considerably depending on the type of organic acid used in the synthesis. In the case of Ace500 synthesized with acetic acid, we obtained quasi-spherical particles with diameters of ~180 nm and holes on their surface (indicated by arrows in Fig. 2(a)). Pro500 showed a novel morphology, with spheres featuring one or two large holes on their surface (as shown by the arrow in

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