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One-pot hydrothermal preparation and catalytic performance of porous strontium ferrite hollow spheres for the combustion of toluene

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ABSTRACT

Strontium ferrite (SFO) hollow spheres with or without porous shells were fabricated via a novel one-pot hydrothermal route with the assistance of glucose and/or ethylenediamine. Physicochemical properties of the materials were characterized by means of a number of analytical techniques, and their catalytic performance was evaluated for the combustion of toluene. It is shown that the SFO samples possessed an orthorhombic structure and displayed a porous hollow spherical morphology with a surface area of 18–27 m^2/g. The SFO sample (SFO-3) derived hydrothermally at 170 °C with a glucose/ethylenediamine volumetric ratio of 0.3/1.0 exhibited the highest surface area and oxygen adspecies concentration and the best low-temperature reducibility. Among the SFO samples, the SFO-3 sample showed the best catalytic activity for toluene combustion, and the $T_{10\%}$, $T_{50\%}$, and $T_{90\%}$ were ca. 145, 255, and 298 °C at a space velocity of 20,000 mL/(g h), respectively. It is concluded that the good catalytic performance of SFO-3 was associated with its surface oxygen species concentration and better low-temperature reducibility.

1. Introduction

Volatile organic compounds (VOCs) emitted from industrial activities are major pollutants to the environment. Among various technologies (e.g., adsorption, absorption, biofiltration, pyrolysis, and catalytic combustion) for the control of VOC emissions, catalytic combustion is generally believed to be the most effective and promising [1]. In the past years, a large number of catalysts, such as supported noble metals, transition metal oxides, and perovskite-type oxides (ABO_3), have been developed for the removal of VOCs [2]. Due to the high oxygen mobility, abundant oxygen vacancy, and long-term stability [3], ABO_3 has been widely used as an effective solid catalyst for VOC removal [4]. Recently, $SrFeO_{3-\delta}$ (SFO) have gained much attention in the photodegradation of phenol [5] and methyl orange [6], oxidative dehydrogenation of ethane [7], methane combustion [8], and electrochemical conversion [9] of methane because of its rich oxygen deficiency, high oxygen permeability, and high electronic conductivity [4].

It has been well known that the morphology of inorganic nanoparticles is a predominant factor influencing the physicochemical property of a material [3]. Thanks for the great synthetic flexibility and controllability of crystalline growth, the solvothermal process is regarded to be a powerful strategy to fabricate hollow inorganic materials with enhanced catalytic activity, such as $CaTiO_3$ [10], $ZnSnO_3$ [11], and MFe_2O_4 (M = Zn, Co, Ni, Cd) [12]. Xu and coworkers generated $LnFeO_3$ (Ln = La, Pr–Tb) hollow spheres with porous shell via a citric acid-assisted hydrothermal route [13]. By using the templating approaches, one could obtain various hollow metal oxides [14]. For instance, adopting the hydrothermal method with carbonaceous saccharide microspheres as the template, some researchers prepared hollow Fe_3O_4@SiO_2 [15], SnO_2 [16], and MFe_2O_4 (M = Zn, Co, Ni, Cd) [12].

Except for our studies on the fabrication and catalytic properties of three-dimensionally ordered macroporous (3DOM) [17] and 3D macroporous [18] SFO for toluene combustion, however, there are few reports on the catalytic applications in the removal of VOCs. Li and Sun [19] reported that carbon spheres could be prepared from glucose at a hydrothermal temperature of 160–180 °C. According to this idea, we have recently developed a novel and facile one-pot hydrothermal strategy that exploits an in situ sacrificial template to fabricate SFO hollow spheres with or without porous shell. Herein, we report for the first time the fabrication, characterization, and catalytic performance of SFO hollow spheres for the combustion of toluene.

2. Experimental

2.1. Catalyst preparation

The SFO samples were prepared using the glucose-assisted hydrothermal strategy with metal nitrates as the precursor. In

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Table 1
Preparation conditions, crystallite sizes (*D*), BET surface areas, pore volumes, and average pore sizes of the SFO samples.

Catalyst	Solution	D^a (nm)	BET surface area (m^2/g)			Pore volume (cm^3/g)			Average pore size (nm)
			Macropore (≥50 nm)	Mesopore (<50 nm)	Total	Macropore (≥50 nm)	Mesopore (<50 nm)	Total	
SFO-0	0.5 mL EDA	123.3	0.9	10.5	11.4	0.012	0.009	0.021	9.8
SFO-1	0.5 mL EDA + 0.1 mol/L glucose	65.4	1.6	16.6	18.2	0.021	0.010	0.031	11.6
SFO-2	0.5 mL EDA + 0.3 mol/L glucose	50.5	2.2	17.0	19.2	0.030	0.006	0.036	15.1
SFO-3	1.0 mL EDA + 0.3 mol/L glucose	42.5	1.6	24.9	26.5	0.031	0.006	0.037	36.7
SFO-4	3.0 mL EDA + 0.3 mol/L glucose	41.3	1.7	8.2	9.9	0.044	0.006	0.050	26.4

[a] The data were calculated according to the Scherrer's equation using the FWHM of the (4 0 0) line for the SFO samples.

a typical preparation process, 0.01 mol of nitrates of strontium and iron were first dissolved in 25.0 mL of deionized water under magnetic stirring. After being well mixed, certain amounts of citric acid (total metal/citric acid molar ratio = 1/1), glucose (GLU), and ethylenediamine (EDA) were sequentially added to the above mixed solution, as shown in Table 1. Then, an ammonia (28 wt.%) solution was added dropwise to adjust the pH value of the mixed solution to be ca. 4.2. After being diluted to a total volume of 40.0 mL, the mixture was transferred into a 50-mL Teflon-lined stainless steel autoclave and placed in an oven for hydrothermal treatment at 170 °C for 20 h. When the autoclave was naturally cooled to room temperature (RT), the obtained precursor was first dried at 120 °C overnight and then well ground. Finally, the obtained black powders were calcined in a muffle furnace at a rate of 1 °C/min from RT to 300 °C and maintained at this temperature for 2 h, and further to 750 °C and kept at this temperature for 4 h.

All of the chemicals (A.R. in purity) were purchased from Beijing Chemical Reagent Company and used without further purification.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker/AXS D8 Advance diffractometer operated at 40 kV and 40 mA using Cu Kα radiation and a Ni filter (λ = 0.15406 nm). Crystal phases were identified by referring the diffraction lines to those of the powder diffraction files – JCPDS-ICDD 2004 PDF Database. Thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) analysis were conducted in an air flow of 100 mL/min at a ramp of 15 °C/min on a Seiko 6300 TG-DTA instrument. The temperature range was RT to 900 °C. Fourier transform infrared (FT-IR) spectra of the samples in the range of 400–4000 cm^{-1} at a resolution of 0.1 cm^{-1} were measured on a Bruker Vertex 70 spectrometer. The scanning electron microscopic (SEM) images of the samples were recorded by a field emission-scanning electron microscopy (Gemini Zeiss Supra 55) operated at 10 kV, and the high-resolution transmission electron microscopic (HRTEM) images as well as the selected-area electron diffraction (SAED) patterns of the samples were collected on a JEOL-2010 instrument (operated at 200 kV). The nitrogen adsorption–desorption isotherms were measured under vacuum on a Micromeritics ASAP 2020 adsorption analyzer via N_2 adsorption at −196 °C, with the samples being outgassed at 250 °C for 2 h. The surface areas and pore size distributions were calculated according to the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. X-ray photoelectron spectroscopy (XPS, VG CLAM 4 MCD analyzer) was employed to determine the Sr 3d, Fe 2p, O 1s, and C 1s binding energies (BEs) of surface species of the samples, with Mg Kα ($h\nu$ = 1253.6 eV) as the excitation source. Before XPS analysis, the samples were pretreated in an O_2 flow of 20 mL/min at 500 °C for 1 h to remove the surface carbonate and adsorbed water. The C 1s peak at 284.6 eV was taken as a reference for the BE calibration.

Hydrogen temperature-programmed reduction (H_2-TPR) was conducted on a Micromeritics AutoChem II 2920 apparatus in the RT to 900 °C range with a sample (100 mg, 40–60 mesh) being placed in a U-shaped quartz microreactor (i.d. = 4 mm). Before each run, the sample was treated in O_2 flow (30 mL/min) at 500 °C for 1 h followed by cooling to RT under the same atmosphere. Then, the sample was reduced in a flow of 5% H_2/Ar (50 mL/min) at a heating rate of 10 °C/min, with the effluent being monitored by a thermal conductivity detector (TCD). The TCD response was calibrated against the reduction of a standard CuO sample (Alfa Aesar, 99.9995%).

2.3. Catalytic evaluation

Catalytic activities were measured in a continuously flow quartz fixed-bed microreactor (i.d. = 4 mm) at atmospheric pressure, with ca. 50 mg of the catalyst (40–60 mesh) and 0.3 g of quartz sands (40–60 mesh) being packed in the middle of the tubular microreactor. Before each measurement, the catalyst was pretreated at 80 °C for 12 h. Unless specified otherwise, the total flow rate of the reactant feed (1000 ppm toluene + O_2 + N_2 (balance)), the toluene/O_2 molar ratio, and the space velocity (SV) were 16.7 mL/min, 1/400, and ca. 20,000 mL/(g h), respectively. The flow rate was regulated by means of electronic mass flow controllers, and the 1000-ppm toluene fed to the microreactor was generated by a N_2 flow passing through a toluene-filling container placed in an ice-water

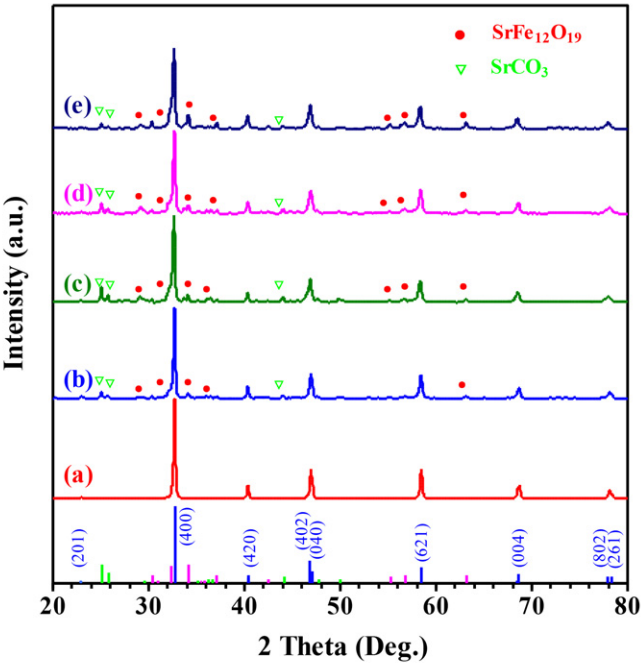

Fig. 1. XRD patterns of (a) SFO-0, (b) SFO-1, (c) SFO-2, (d) SFO-3, and (e) SFO-4.