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Electrospun mesoporous zirconia ceramic fibers for catalyst supporting applications

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ABSTRACT

Mesoporous zirconia has been widely used as supporting materials, absorption materials, catalysts and high temperature insulating materials. While seldom has taken a consideration of the mesoporous fiber structure. In the present work, mesoporous zirconia ceramic fibers were fabricated by electrospinning method with CTAB as the template. The thermal decomposition and crystallization process of the mesoporous zirconia fibers were fully studied by TG/DSC, IR spectra and XRD. The highest surface area of the mesoporous zirconia fibers was about 120 m^2/g. With mesoporous zirconia fibers as the supporting materials, tungstate supported on zirconia fibers catalyst showed that the specific activity of bromination of phenol red was 1.26 mmol h^{-1} g^{-1}. The results confirmed that zirconia fibers with the mesoporous structure would be a promising candidate as a supporting material.

1. Introduction

Zirconia has been extensively studied for its widespread utilization as structural and functional materials. Due to the high temperature melting point, low thermal conductivity, high chemical stability and high thermal expansion, zirconia with yttrium oxide as the phase stabilizer has been used in thermal barrier [1] and thermal insulating [2] areas. Oxygen ion vacancies were created by yttria dopant zirconia which increased the selective oxygen ion conductivity and thus making zirconia commonly used oxygen sensors [3]. Zirconium dioxide has also been used as catalyst for various reactions [4] and absorbents for organic pollutants [5,6]. Furthermore, both acidic and basic properties existed on the surface of zirconia make it an acid-base bifunctional oxide [7]. For the high temperature stability and characteristic surface properties, zirconia has also been used as a promising supporting material in a wide temperature range [8–10].

Porous structure especially the mesoporous structure was widely focused when zirconia was applied as functional materials. For catalysts, catalyst supporting material and absorbent material, mesoporous structure could obviously increase the surface area and further enhance catalytic activity, surface active sites and absorption sites. Porous structure could also obviously decrease the thermal conductivity when zirconia was used as high temperature insulating material [11]. In the past decades, both of hard templates [12] and soft templates [13–15] have been used for the preparation of mesoporous zirconia. While most of the works were concentrated on the particles with various range from nanometer to micrometer and seldom have taken a consideration of the porous fiber structure.Two disadvantages of the particles are the hard separation from solution at low temperature and the coalescence at high temperature, thus making ceramic fiber a promising candidate in wide temperature range for its easy separation from solution and high temperature stability.

In the present study, mesoporous zirconia ceramic fibers were prepared by electrospinning method with CTAB as the template. The porous ceramic fibers pyrolysis and formation process were fully discussed. With mesoporous zirconia fibers as the supporting material, tungstate was supported on the ceramic fiber for bromination of phenol red. The specific activity of catalyst showed that mesoporous zirconia ceramic fibers were a promising candidate as supporting material.

2. Experimental section

2.1. Materials

Basic zirconium carbonate (BZC, ZrO_2 ≥ 40%), glacial acetic acid (CH_3COOH, ≥ 99.5%), anhydrous methanol (CH_3OH, ≥ 99.5%), cetyltrimethyl ammonium bromide (CTAB, ≥ 99%), dichloromethane (CH_2Cl_2, ≥ 99%), polyethylene oxide (PEO, Mw ~ 1000,000, Aladdin), ammonium metatungstate (≥ 99%, Aladdin), ammonium bromide (NH_4Br, ≥ 99%), bromophenol red (≥ 97%), H_2O_2 (≥ 30% in water)

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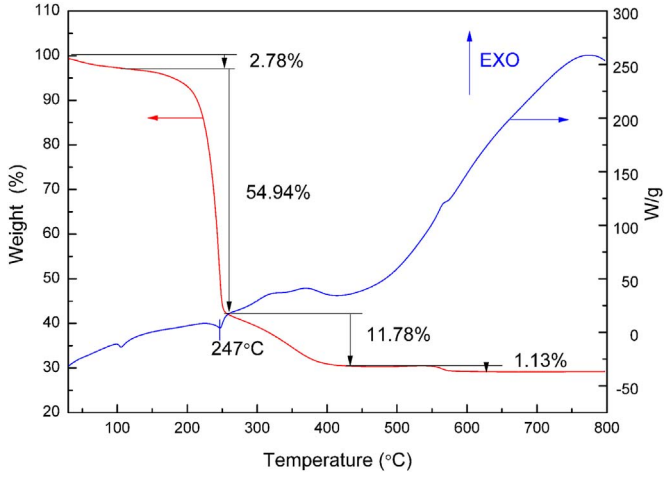

Fig. 1. TG/DSC curves of the precursor fibers in air.

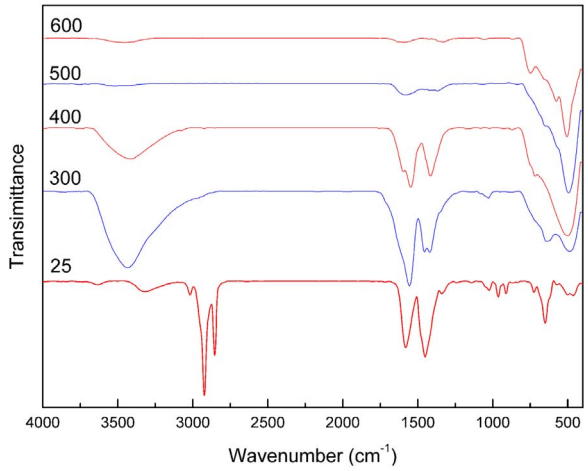

Fig. 2. IR spectra of the precursor fibers heat treated at different temperatures.

Table 1
Assignment for precursor fibers at room temperature.

Wavenumber (cm^{-1})	Assignment
2922	CH_2 antisym.str.
2853	CH_2 sym.str.
1580	C-O antisym.str.
1451	C-O sym.str.
1338	CH_3 sym.def.
1024	CH_3 rock
963	C-C Str.
911	C-C Str.
725	CH_2 rock
650	CO_2 Sym. Def.
502	Zr-O Str.
461	Zr-O Str.

and distilled water were used as starting materials without further purification.

2.2. Preparation of mesoporous zirconia fibers

BZC (5.00 g) was diluted in CH_3COOH (2.50 g) and CH_3OH (5.90 g) with continuous magnetic stirring at 60 °C until the mixture was transparent. CTAB (5.91 g), CH_2Cl_2 (6.88 g), and 4.0 g 0.1% PEO methanol solution were added to the above mixture to obtain the electrospinning solution. Electrospinning was carried out with the voltage of 20 kV at room temperature. The distance between nozzle and collector was 20 cm, and the feeding rate was 2.0 mL/h. The obtained precursor fibers were heated at the rate of 1 °C/min to different temperatures in air.

2.3. Preparations of WO_4^{2-}/ZrO_2 fibers catalysts

Fibers heat treated at 300 °C were used as the supporting material. Generally, 0.1 g fibers were impregnated with series of 20 mL x wt% aqueous ammonium metatungstate followed by evaporating water at 50 °C, drying at 100 °C for 12 h to get the final catalysts. x wt% was the concentration of WO_4^{2-} based on the fibers. The catalysts were referred as xWZ.

2.4. General procedure for bromination of phenol red over WO_4^{2-}/ZrO_2 fibers catalysts

A 50 mL tube was charged with 30 mL of 0.05 mM phenol red aqueous solution; 0.1 M NH_4Br and 11.3 mM H_2O_2 were added to the solution. 10 mg xWZ was then added to the reaction mixture under sever stirring. Sample (1.5 mL) was diluted every 10 min and the solid catalyst was removed before monitoring each UV–vis spectrum. The concentration of bromophenol blue was calculated and monitored at 591 nm with extinction coefficient of 72.8 $mmol^{-1}$ cm^{-1}.

2.5. Characterization

Thermogravimetry and differential scanning calorimetry (TG/DSC, SDT Q600 v8.3 Build 101, TA, US) measurements of the precursors were performed at a heating rate of 10 °C/min from room temperature to 800 °C in air. Fourier transformation infrared (FT-IR, ALPHA-T, Bruker, Germany) spectrum recorded in the region of 4000–400 cm^{-1} was measured with a RT-DLATGS spectrometer using the KBr pellet method. X-ray diffraction (XRD, D8 Advance, Bruker, Germany) data collection was performed with Cu-Kα radiation using a graphite monochromator in the range of 10–90°. Scanning electron microscope (SEM, S-4800, Hitachi, Japan) was used to observe the surface morphologies and microstructures of the fibers and catalysts. Elemental analyses of the samples were undertaken, using X-ray photoelectron spectroscopy (XPS, Thermo Fisher scientific, ESCALAB250, US) and Al-Kα radiation. The morphology was characterized by scanning electron microscopy (SEM; Hitachi, S-4800), the transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) which were taken with a JEOL JEM-2100F transmission electron microscope. The UV–vis absorption spectrum was obtained on a Philips Cary-50 spectrometer, operated in the wavelength range of 300–700 nm using a matched pair of 1 cm quart cuvettes. The surface area, average pore size and the pore volume were characterized by N_2 adsorption-desorption at 77 K measured by JW-K analyser (Beijing Jingwei Gaobo Sci-Tech. Ltd., China) after the samples were evacuated at 100 °C for 8 h under vacuum. The pore size distribution and the pore volume were determined via the density functional theory (DFT) method with the relative pressure (P/P_0) from 0.05 to 0.3.