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Mesoporous zirconia nanobelts: Preparation, characterization and applications in catalytical methane combustion

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ABSTRACT

Mesoporous ZrO_2 nanobelts (MZNs) have been prepared by a calcination route of ZrS_3 nanobelts in air. The nanobelts prepared at 400–600 °C are the mixtures of tetragonal and monoclinic phases, and have well-distributed mesopores (pore diameter of about 3.4–3.6 nm). As the calcination temperature increased from 400 to 1200 °C, the structures changed from tetragonal to monoclinic phase, while the morphologies turned from regular nanobelts to bead-like nanowires, and the mesopores disappeared bit by bit. Fe-doped and Fe_2O_3-loaded MZNs have been prepared to compare the catalytic activities of Fe-doped, Fe_2O_3-loaded, and pure MZNs for methane combustion. The results showed that Fe_2O_3-loaded MZNs have rather high catalytic activity, suggesting its potential application in practice. Methane combustion data over the catalysts are well fitted by a first-order kinetic expression.

1. Introduction

Methane has a much larger greenhouse effect than carbon dioxide, and the concentration of methane in the atmosphere is increasing continuously. In order to eliminate methane emission from natural gas engines and power plants as well as petroleum and petrochemical industries, complete combustion of methane becomes a must. Noble metal catalysts show high activity for methane combustion at low temperature [1–4], but limited due to their scarcity and high cost. So low-cost metal oxide or mixed metal oxide catalysts still are primary selection [5,6]. Mn-, Co-, and Fe-stabilized ZrO_2 catalysts [7] and zirconia-supported La, Mn oxides and $LaMnO_3$ perovskites [8] were once reported to have high activity for methane combustion. Recent research shows that catalytic activity can be obviously tuned by changing morphologies of catalysts or catalyst supports [9,10]. Therefore it is interesting and necessary to explore the possible shape effect of ZrO_2 as catalysts or catalyst supports.

Zirconia has been extensively used as catalysts or catalytic supports [11–14], optical waveguides [15], gate dielectric in metal-oxide semiconductor (MOS) devices [16], high-performance ceramics [17], biological materials [11], and photon absorber and photocatalyst [18,19] due to its valuable chemical and physical properties such as high melting point, high resistance to thermal shock, high dielectric constant, excellent wear resistance, biocompatibility, and wide gap band semiconductor [20]. In order to tailor these physical–chemical properties of ZrO_2, zirconia nanoparticles have been synthesized by sol–gel [21–23], hydrothermal/solvothermal [24–26], emulsion precipitation [27], and thermal decomposition [28] approaches. Zirconia nanowires [29] and rare-earth (RE)-doped zirconia nanobelts [30] have been prepared by an alumina template method and a pyrolysis of $Zr(OH)_4$: RE particles, respectively. ZrO_2 mesopore microfibers have been prepared by a Pluronic P-123 template-directed method [31,32]. However, no ZrO_2 mesopore nanobelts have been reported to date.

Here we demonstrate a novel facile route to synthesize mesopore zirconia nanobelts (MZNs), neither triblock-copolymer nor surfactants are needed, while the nanobelts were prepared into Fe-doped and Fe_2O_3-loaded MZNs catalyst for methane combustion. Firstly, ZrS_3 nanobelts were prepared by a chemical-vapor-transport (CVT) of Zr powder and S powder at 650 °C. Then the ZrS_3 nanobelts were oxidated into mesoporous ZrO_2 nanobelts in air by changing calcination temperatures. When Fe was added in process of preparing ZrS_3 nanobelts, Fe-doped MZNs could be obtained. When the mesoporous nanobelts were impregnated in ferric nitrate solution, Fe_2O_3-loaded MZNs could be obtained. The research results showed that calcination temperatures have a great influence on the crystal structures, the morphologies and pore structures of ZrO_2 nanobelts, and that Fe_2O_3-loaded MZNs reveal rather high catalytic activity for methane combustion.

2. Experimental

2.1. Preparation of ZrS_3 nanobelt precursors

Zirconium powder (125.5 mg; Zr $\geqslant$ 99.42%, 200 meshes) and sulfur powder (139.7 mg; S $\geqslant$ 99.999%; 200 meshes) with an atomic ratio of 1:3 were mixed homogeneously, and then sealed

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in a quartz ampoule under vacuum (Φ6 mm × 10 cm, ca. 10^{-2} Pa). The quartz ampoule was then placed in a conventional horizontal furnace with a temperature gradient of ca.10 K cm^{-1} from center to edge, and the end with the mixture powers were put at the center of the furnace. In the following the furnace was heated to 650 °C and maintained at the temperature for 5 h. Finally, the reagents were completely converted into ZrS_3 nanobelts. The method was similar to the reported surface-assisted CVT [33], but Zr foils were not used here.

2.2. Conversion of ZrS_3 nanobelts to ZrO_2 porous nanobelts

The as-synthesized ZrS_3 nanobelt precursors were placed in the center of an unsealed quartz ampoule and then the ampoule was put at the center of the furnace and oxidized spontaneously in air at 400, 600, 700, 800, 900, 1000, 1100, and 1200 °C for 1.5 h. ZrO_2 nanobelts with various morphologies and microstructures were formed and denoted as ZrO_2-400, ZrO_2-600, ZrO_2-700, ZrO_2-800, ZrO_2-900, ZrO_2-1000, ZrO_2-1100, ZrO_2-1200, respectively.

2.3. Preparation of ZrO_2: Fe^{3+} and Fe_2O_3-loaded ZrO_2 nanobelts

Zirconium powder (101.1 mg; 99.42%), and iron powder (26.6 mg; 99.5%) were first ground to homogeneous mixtures. After that, sulfur powder (152.4 mg; 99.999%) were added to the mixture above and sealed in a quartz ampoule under vacuum (Φ6 mm × 10 cm, ca. 10^{-2} Pa). $Zr_{0.7}Fe_{0.3}S_3$ nanobelts were synthesized according to the method above to prepare ZrS_3 nanobelts. Subsequently, the nanobelts were oxidated into $Zr_{0.7}Fe_{0.3}O_2$ mesopore nanobelts at 600 °C for 1.5 h. Similarly, $Zr_{0.8}Fe_{0.2}O_2$ nanobelts were prepared. For preparing Fe_2O_3-loaded ZrO_2 (Fe_2O_3/ZrO_2) nanobelts catalysts, ZrO_2 nanobelts prepared at 600 °C for 1.5 h were impregnated in an aqueous solution containing the requisite amount of ferric nitrate, then the mixtures were dried at 100 °C, and calcined in air at 600 °C for 1 h. The Fe_2O_3/ZrO_2 nanobelt catalysts with Fe/Zr mole ratio = 0.05 and 0.25 corresponds to 2.38 mg Fe_2O_3/70.1 mg ZrO_2 and 11.3 mg Fe_2O_3/70.1 mg ZrO_2, respectively, which were nominated as Fe_2O_3/ZrO_2-5 and Fe_2O_3/ZrO_2-25, respectively.

2.4. Characterization and activity test

The as-synthesized products were characterized by an X-ray diffractometer (XRD; Shimadzu XRD-6000) with graphite monochromatized Cu Kα1-radiation, scanning electron microscope (SEM; S-4800) and high-resolution electron microscopy with a point resolution of 0.19 nm (HRTEM; JEOL model JEM-2100). Thermogravimetry–differential scanning calorimetry (TG–DSC) curves were recorded on Netzsch STA-499C thermal analyzer. Nitrogen adsorption–desorption isotherms were obtained at 77 K on a Micromeritics ASAP 2020 apparatus after degassing of the samples at 300 °C for 2 h, and Brunauer–Emmett–Teller (BET) specific surface area was calculated using BET adsorption data acquired at in the relative pressure range from 0.06 to 0.2, and the pore size distribution was calculated from the nitrogen desorption isotherm by the Barrett–Joyner–Halenda (BJH) method.

The catalytic activities of the catalysts for methane combustion were measured in a quartz-tube plug flow reactor using 40 mg of catalysts (for each test) in a gas mixture of 1.99 vol.% CH_4, 20.01 vol.% O_2, and 78.00 vol.% N_2 at a flow rate of 17 mL/min, corresponding to a space velocity of 25,500 $cm^3\ g^{-1}\ h^{-1}$. The products were analyzed by an on-line gas chromatography with a 5A molecular sieve chromatogram column for separating N_2, O_2, CO and CH_4, and a Porapak Q chromatogram column for monitoring CO_2, and thermal conduction detections (TCDs).

3. Results and discussion

3.1. Structure and morphology

Fig. 1a and b indicates the SEM images of the ZrS_3 nanobelts. A typical nanobelt has a rectangular section of about 22 × 66 nm^2 (inset in Fig. 1b), and a length of about 25 μm (Fig. 1a). Fig. 1c shows the XRD pattern of the ZrS_3 nanobelts, indexed as monoclinic ZrS_3 (PCPDF ICDD No. 30-1498). Fig. 1d exhibits TG–DSC curves of ZrS_3 nanobelts in air from room temperature to 1200 °C with a rate of 10 °C/min. The weight loss in the range of 166–234.5 °C (2.24 wt.%), 324–381 °C (24.64%), and 545–700 °C (2.24%) corresponds to part decomposition, oxidation, and remnant sulfur oxidation of ZrS_3. Therefore, ZrS_3 is almost oxidated to ZrO_2 above 400 °C, and completely to ZrO_2 without sulfur above 700 °C. In fact, the ZrO_2 nanobelts prepared above 400 °C for 1.5 h do not almost contain sulfur by EDX analysis (Figs. S1 and S2, Support information). It is possible to have enough time to release sulfur completely under the preparation condition.

The XRD patterns of ZrO_2 nanobelts prepared at 400, 600, 700, 800, 900, 1000, 1100, and 1200 °C for 1.5 h are shown in Fig. 2. The reflection peaks of the products at 400 °C (Fig. 2a) reveal that they are the mixtures of tetragonal (t-) ZrO_2 (PCPDF ICDD No. 80-0965) and monoclinic (m-) ZrO_2 (PCPDF ICDD No. 78-1807), and t-ZrO_2 phase dominates. As the temperature increases, the peak at 30.35°, indicating tetragonal phase, reduces gradually, and disappears until 1200 °C, i.e. the products completely turns into monoclinic phase. So the products at 400–1000 °C are still the mixed phases of t-and m-ZrO_2, but m-ZrO_2 phase dominates after 800 °C. Because reflection peaks between t (1 1 2) and m (2 2 0) overlap, and between t (2 1 1) and m (−3 0 2) overlap, the products at 400 °C show stronger peaks at 50.5° and 60°. As the tetragonal phase decreases, the peaks at 50.5° and 60° are debased. The results approach those of annealed ZrO_2 [34].

Fig. 3a–e shows the SEM images of the ZrO_2 nanobelts prepared at 400–900 °C. The products at 400–700 °C still exhibit belt-like structures, and the size approaches that of the primal ZrS_3 nanobelts. At the stage, because ZrS_3 is oxidated and SO_2 give off, the mesoporous nanobelts form. When temperature gets at 800–900 °C, the ZrS_3 nanobelts are converted into porous ZrO_2 nanobelts with a pinhole on one end. The nanobelts are composed of the particles with a diameter of about 45 nm (Fig. 3d and e). The macropores and pinholes origins from shrinking act of materials at high temperature. When temperature gets at 1000 °C, the nanobelts split into a few parallel bead-like nanowires (Fig. 3f), which originates from sintering and shrinking of the materials. When temperature gets above 1100 °C, the nanobelts are completely converted into bead-like nanowires, as shown in Fig. 3g and h.

Fig. 4a is TEM image of individual ZrO_2 nanobelt prepared at 600 °C, showing a lot of wormlike (or slit-shaped) holes on the surface. Fig. 4b shows corresponding HRTEM image. Fringe spacings of 0.36 and 0.30 nm accord with spacings of (1 0 0) and (1 0 1) planes of tetragonal ZrO_2, respectively. Fast Fourier transform (FFT) pattern (inset in Fig. 4a) from the HRTEM image can be completely indexed as tetragonal ZrO_2. Fig. 4c is the TEM image of another ZrO_2 nanobelt, and the HRTEM image is shown in Fig. 4d. Fringe spacings of 0.53 and 0.52 nm accord with those of (0 1 0) and (0 0 1) planes of monoclinic ZrO_2, respectively. Fast Fourier transform (FFT) pattern (inset in Fig. 4c) from the HRTEM image can be completely indexed as monoclinic ZrO_2. Therefore, the coexistence of t- and m-ZrO_2 nanobelts is further confirmed.

3.2. Surface area and pore-size distributions

To investigate the statistical data (surface area and pore-size distributions) derived from these porous nanobelts, which are crit-