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

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ABSTRACT

Mesoporous ZrO2 nanobelts (MZNs) have been prepared by a calcination route of ZrS3 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 Fe2O3-loaded MZNs have been prepared to compare the catalytic activities of Fe-doped, Fe2O3-loaded, and pure MZNs for methane combustion. The results showed that Fe2O3-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.

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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 ZrO2 catalysts [7] and zirconia-supported La, Mn oxides and LaMnO3 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 ZrO2 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 ZrO2, 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 aluminia template method and a pyrolysis of Zr(OH)4: RE particles: RE particles, respectively. ZrO2 mesopore microfibers have been prepared by a Pluronic P-123 template-directed method [31,32]. However, no ZrO2 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 Fe2O3-loaded MZNs catalyst for methane combustion. Firstly, ZrS3 nanobelts were prepared by a chemical-vapor-transport (CVT) of Zr powder and S powder at 650 °C. Then the ZrS3 nanobelts were oxidated into mesoporous ZrO2 nanobelts in air by changing calcination temperatures. When Fe was added in process of preparing ZrS3 nanobelts, Fe-doped MZNs could be obtained. When the mesoporous nanobelts were impregnated in ferric nitrate solution, Fe2O3-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 ZrO2 nanobelts, and that Fe2O3-loaded MZNs reveal rather high catalytic activity for methane combustion.

2. Experimental

2.1. Preparation of ZrS3 nanobelt precursors

Zirconium powder (125.5 mg; Zr ≥ 99.42%, 200 meshes) and sulfur powder (139.7 mg; S ≥ 99.999%; 200 meshes) with an atomic ratio of 1:3 were mixed homogeneously, and then sealed...
in a quartz ampoule under vacuum (46 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 regents were completely converted into ZrS₃ nanobelts. The method was similar to the reported surface-assisted CVT [33], but Zr foils were not used here.

2.2. Conversion of ZrS₃ nanobelts to ZrO₂ porous nanobelts

The as-synthesized ZrS₃ nanobelts were prepared 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. ZrO₂ nanobelts with various morphologies and microstructures were formed and denoted as ZrO₂-400, ZrO₂-600, ZrO₂-700, ZrO₂-800, ZrO₂-900, ZrO₂-1000, ZrO₂-1100, ZrO₂-1200, respectively.

2.3. Preparation of ZrO₂: Fe³⁺ and Fe₂O₃-loaded ZrO₂ 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 mixtures above and sealed in a quartz ampoule under vacuum (46 mm × 10 cm, ca. 10⁻² Pa). Zr₀.₇Fe₀.₃S₃ nanobelts were synthesized according to the method above to prepare ZrS₃ nanobelts. Subsequently, the nanobelts were oxidized into Zr₀.₇Fe₀.₃O₂ mesoporous nanobelts at 600 °C for 1.5 h. Similarly, Zr₀.₈Fe₀.₂O₂ nanobelts were prepared. For preparing FeO₂-loaded ZrO₂ (FeO₂/ZrO₂) nanobelts catalysts, ZrO₂ 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 Fe₀.₂O₃/ZrO₂ nanobelt catalysts with Fe/Zr mole ratio = 0.05 and 0.25 corresponds to 2.38 mg Fe₂O₃/70.1 mg ZrO₂ and 11.3 mg Fe₂O₃/70.1 mg ZrO₂, respectively, which were named as Fe₂O₃/ZrO₂-5 and Fe₂O₃/ZrO₂-25, 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.% CH₄, 20.01 vol.% O₂, and 78.00 vol.% N₂ at a flow rate of 17 mL/min, corresponding to a space velocity of 25,500 cm³ g⁻¹ h⁻¹. The products were analyzed by an on-line gas chromatography with a 5A molecular sieve chromatogram column for separating N₂, O₂, CO and CH₄, and a Porapak Q chromatogram column for monitoring CO₂, and thermal conduction detections (TCDs).

3. Results and discussion

3.1. Structure and morphology

Fig. 1a and b indicates the SEM images of the ZrS₃ nanobelts. A typical nanobelt has a rectangular section of about 22 × 66 nm² (inset in Fig. 1b), and a length of about 25 μm (Fig. 1a). Fig. 1c shows the XRD pattern of the ZrS₃ nanobelts, indexed as monoclinic ZrS₂ (PCPDF ICDD No. 30-1498). Fig. 1d exhibits TG–DSC curves of ZrS₃ 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 ZrS₃. Therefore, ZrS₃ is almost oxidized to ZrO₂ above 400 °C, and completely to ZrO₂ without sulfur above 700 °C. In fact, the ZrO₂ nanobelts prepared above 400 °C for 1.5 h do not almost contain sulfur by EDX analysis (Figs. S1 and S2, Supporting information). It is possible to have enough time to release sulfur completely under the preparation condition.

The XRD patterns of ZrO₂ 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-) ZrO₂ (PCPDF ICDD No. 80-0965) and monoclinic (m-) ZrO₂ (PCPDF ICDD No. 78-1807), and t-ZrO₂ phase dominates. As the temperature increases, the peaks 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-ZrO₂, but m-ZrO₂ 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 ZrO₂ [34].

Fig. 3a–e shows the SEM images of the ZrO₂ nanobelts prepared at 400–900 °C. The products at 400–700 °C still exhibit belt-like structures, and the size approaches that of the prismatic ZrS₃ nanobelts. At the stage, because ZrS₃ is oxidated and SO₂ give off, the mesoporous nanobelts form. When temperature gets at 800–900 °C, the ZrS₃ nanobelts are converted into porous ZrO₂ 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 ZrO₂ 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 ZrO₂, respectively. Fast Fourier transform (FFT) pattern (inset in Fig. 4a) from the HRTEM image can be completely indexed as tetragonal ZrO₂. Fig. 4c is the TEM image of another ZrO₂ 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 ZrO₂, respectively. Fast Fourier transform (FFT) pattern (inset in Fig. 4c) from the HRTEM image can be completely indexed as monoclinic ZrO₂. Therefore, the coexistence of t- and m-ZrO₂ 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-
For practical applications, BET analysis has been carried out. Fig. 5 shows nitrogen adsorption/desorption isotherms of various ZrO$_2$ nanobelts prepared at 400, 600, 900, and 1200 °C. From the adsorption curves of Fig. 5, the amount of N$_2$ slowly increases as the relative pressure rises, and the steep capillary condensation steps occur in the relative pressure of 0.9–1.0, not exhibiting any limiting adsorption at high relative pressure. According to the original IUPAC classification [35], the isotherms are classified as type IV isotherms with H3 type hysteresis loops. However, according to the extended classification of adsorption isotherms [36], the isotherms are classified as type IIb isotherms. These results indicate typical slit-shaped mesopore performance, and the mesopore should be voids between particles in the aggregates, not framework-confined mesoporosity. When decomposed temperature gets above 900 °C, the ZrO$_2$ nanobelts are partly sintered so that they have low surface area and porous capacities. BJH calculations for the pore-size distribution are derived from desorption data. The average pore diameters and BET specific surface area are included in Table 1. The products prepared at 400 and 600 °C have high surface areas and well-distributed mesopores (pore diameter of about 3.4–3.6 nm), comparable with the zirconia mesoporous microfibers prepared by using P123 [31].

3.3. Catalytical activity for methane combustion

Fig. 6a and b reveal the SEM images of the Fe$_2$O$_3$-loaded ZrO$_2$ pore nanobelts with Fe/Zr mole ratio = 0.05 and 0.25, respectively. A few Fe$_2$O$_3$ nanoparticles can be observed on the surface of the nanobelts. Because ferric-nitrate-impregnated ZrO$_2$ is decomposed in air at 600 °C, we consider that ferric nitrate is converted into Fe$_2$O$_3$. EDX analysis confirms further that Fe$_2$O$_3$ was loaded on ZrO$_2$ porous nanobelts, and no sulfur is observed (Fig. S3, Support information). XRD patterns (Fig. 7a and b) indicate the coexistence of Fe$_2$O$_3$ (JCPDS Card No.84-0311) and tetragonal and monoclinic ZrO$_2$. Fig. 6c and d display the SEM images of Zr$_{0.8}$Fe$_{0.2}$O$_2$ and Zr$_{0.7}$Fe$_{0.3}$O$_2$ porous nanobelts, respectively. XRD patterns (Fig. 7c and d) indicate coexistence of tetragonal and monoclinic ZrO$_2$. EDX analysis confirms that Fe$^{3+}$ was doped in ZrO$_2$ nanobelts, and no sulfur was observed (Fig. S4, Support information). Fig. 8a
and b shows nitrogen adsorption/desorption isotherms and pore diameter distributions of Fe$_2$O$_3$/ZrO$_2$-5 and Zr$_{0.7}$Fe$_{0.3}$O$_2$ nanobelts, respectively. Both isotherms can be still categorized as type IV with H3 type hysteresis loops [35]. The average pore diameters and BET specific surface area are included in Table 1.

Fig. 9a shows the influence of the reaction temperature on the methane conversion over the mesoporous ZrO$_2$-based nanobelts catalysts. On the whole, as temperature rises, the methane conversion increases. Fe$_2$O$_3$/ZrO$_2$-25 activates methane combustion at 400 $^\circ$C and gives complete CH$_4$ conversion at 650 $^\circ$C, showing well catalytic performance, whereas Zr$_{0.8}$Fe$_{0.2}$O$_2$ activates the reaction at about 500 $^\circ$C, showing poor catalytic performance close to that of ZrO$_2$-600. Fe$_2$O$_3$/ZrO$_2$-25 possesses higher catalytic activity than Fe$_2$O$_3$/ZrO$_2$-5 while Fe$_2$O$_3$-loaded MZNs posses higher catalytic activity than Fe-doped and pure MZNs. It shows that Fe$_2$O$_3$ is an active species (Fe$_2$O$_3$ species has been confirmed by XRD), and MZNs mainly are dispersive supporters. Our results do not agree to the fact that Fe-doped ZrO$_2$ catalyst is more helpful to methane conversion than pure ZrO$_2$ [7]. It probably origins from the differences of crystal structures of catalysts, because our catalysts are the mixed phases of Fe-doped t- and m-ZrO$_2$, whereas the catalysts in literature [7] are Fe-doped cubic ZrO$_2$. CO$_2$ selectivities with methane conversion above 9% are shown in Fig. 9b. As reaction temperature rises, the selectivities to CO$_2$ increase except ZrO$_2$-600. The CO$_2$ selectivity over ZrO$_2$-600 is 100% at 550 $^\circ$C, whereas it is about 49% at 600 $^\circ$C, in the following it rises with increase of reaction temperature, which is repeatedly confirmed. In fact, the selectivity need not rise monotonously with increasing the reaction temperature, the phenomenon appears in other catalytic reaction [8], which may depend on essence of catalyst.

The mechanism of the methane oxidation on the surface of a perovskite catalyst was explained by the participation to the surface reaction of two oxygen species, the adsorbed oxygen and the bulk lattice oxygen, respectively. At low temperature, the reaction
Fig. 4. TEM (inset: FFT pattern of corresponding HRTEM image) and HRTEM images of a single ZrO$_2$ nanobelt prepared at 600 °C. (a and b) Mesoporous nanobelt of t-ZrO$_2$; (c and d) mesoporous nanobelt of m-ZrO$_2$.

Fig. 5. N$_2$ adsorption–desorption isotherms and corresponding pore size distribution curves (inset) for ZrO$_2$ nanobelts prepared at (a) 400, (b) 600, (c) 900, and (d) 1200 °C.
occurs between non-dissociated adsorbed oxygen and gaseous methane (Eley–Rideal mechanism), whereas at higher temperatures, the surface process is following a Mars-van Krevelen mechanism that involves atomic oxygen originated from catalyst lattice [37–39]. In fact, metal oxide catalysis still follows the mechanism [40]. So the reaction rate equation is generalized as a pseudo-first-order expression when oxygen excess [38,39]:

\[ r = k_m P_{CH_4}, \]

where \( r \) represents the reaction rate of methane consumption, \( k_m \) is rate constant, and \( P_{CH_4} \) is partial pressure of methane (Pa). The Arrhenius formulate of the rate constant is

\[ k_m = k_{m0} \exp(-E_a/RT), \]

where \( R \) represents universal gas constant, \( T \) is reaction temperature (K), and \( E_a \) is an active energy (kJ/mol). Based on the influence of the reaction temperature on the methane conversion (Fig. 9a) and a pseudo-homogeneous plug-flow model of the experimental reactor [38,41], the corresponding Arrhenius plots (at 500–650 °C) are presented in Fig. 10. The pre-exponential factors \( (k_{m0}) \) and activation energies \( (E_a) \) are obtained by linear regression of these lines. The conversion ratios for methane combustion and kinetic parameters are included in Table 1. The catalytic activity of ZrO₂-600 is higher than that of ZrO₂ particles [8], which may be ascribed to high specific surface area of ZrO₂-600. The activity of Fe₂O₃/ZrO₂-25 is slightly lower than LCCA (La₀.₉Ce₀.₁CoO₃) [39], but comparable with LaMnO₃ [8]. The activation energy of methane combustion over Fe₂O₃/ZrO₂-25 is 97.9 kJ mol⁻¹, close to that of LaMnO₃ [8], and the activity approaches that of LaMnO₃. The catalytic activities are not directly related to the activation energies, because the reaction rates depend on two factors of the activation energies and the pre-exponential factors. The phenomenon also appeared in catalytic methane combustion over LCCA and LSCA [39].

### 4. Conclusions

In the paper, we introduce a new method to prepare mesoporous nanobelts of ZrO₂, and the morphology and microstructures of the nanobelts can be controlled by calcination temperatures. The

<table>
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<tr>
<th>Nanobelt catalysts</th>
<th>( D ) (nm)</th>
<th>( S ) (m²/g)</th>
<th>( T_{50} ) (°C)</th>
<th>( T_{100} ) (°C)</th>
<th>( E_a ) (kJ mol⁻¹)</th>
<th>( k_{m0} ) (mol s⁻¹ Pa⁻¹ kg⁻¹)</th>
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<tr>
<td>ZrO₂-400</td>
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<td>650</td>
<td>700</td>
<td>105</td>
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<td>3.8 and 40.8</td>
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<td>ZrO₂-1200</td>
<td>14.4 and 24.7</td>
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<td>88.8</td>
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<td>650</td>
<td>97.9</td>
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<td>LCCA [39]</td>
<td>427</td>
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<td>LSCA [39]</td>
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<td>745(T₉₉)</td>
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\( D \): Average pore diameters; \( S \): BET specific surface area; \( T_{50} \), \( T_{99} \), and \( T_{100} \): reaction temperature of conversion ratio up to 50%, 99%, and 100%; \( E_a \) is an active energy; \( k_{m0} \) is a pre-exponential factors; [8] and [39]: Refs. [8] and [39]; ZLaMn-16 is 16 wt.% LaMnO₃/ZrO₂; LCCA: La₀.₉Ce₀.₁CoO₃; LSCA: La₀.₈Sr₀.₂CoO₃.

Fig. 6. SEM images of Fe₂O₃-loaded ZrO₂ nanobelts: (a) Fe/Zr mole ratio = 0.05 (Fe₂O₃/ZrO₂-5), and (b) Fe/Zr mole ratio = 0.25 (Fe₂O₃/ZrO₂-25). The ZrO₂ nanobelts were prepared at 600 °C. SEM images of (c) Zr₀.₈Fe₀.₂O₂ and (d) Zr₀.₇Fe₀.₃O₂ porous nanobelts.
Catalytic activities for methane combustion over these catalysts are evaluated, showing that Fe2O3/ZrO2-25 have rather high catalytic activity and selectivity to CO2, which could be used in practical methane combustion. In addition, the MZNs as supports of new catalysts are probably applied to other catalytic reaction.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.micromeso.2011.03.019.

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