



Research paper

Facile synthesis of micro-mesoporous alumina-zirconia nanocrystals with tailoring texture

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HIGHLIGHTS

- Micro-mesoporous alumina-zirconia nanocrystals are prepared by vapor-induced route.
- The Al incorporation improves the textural properties of the composites.
- The largest surface area of 313 m²/g is obtained.
- The samples possess stable tetragonal structure of zirconia.
- The samples show large pore volumes in the range of 0.18–0.39 cm³/g.

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ABSTRACT

Micro-mesoporous alumina-zirconia nanocrystals with controllable textural properties are prepared using tri-block copolymer F127 as a template via one-pot vapor-induced pathway. The BET surface area and pore volume of the samples increase with rising aluminum content. When the Al/Zr molar ratio is 0.6, the sample exhibits highest surface area of 313 m²/g of which 118 m²/g in the form of micropores after high temperature calcination. Moreover, the incorporation of Al species enhances the structural stability of zirconia in tetragonal phase.

1. Introduction

Mesoporous zirconia materials have been the subject of intense research in various areas such as separation, adsorption, sensors, catalysis and solar cells, because of their attractive structural diversity, acidic-basic and redox properties [1–3]. Accordingly, great efforts have been focused on the synthesis of the mesoporous zirconia through the sol-gel process [4], precipitation [5] and the evaporation-induced self-assembly methods [6]. However, there are many thermal stable problems such as pore blockage and phase transition for the synthesized mesoporous zirconia during heat-treatment, which usually results in the reduction of the specific surface area followed with the decrease of catalytic activity. There is an effective approach to improve structure stability of mesoporous zirconia by doping with different metal oxides (Y₂O₃, MgO, CaO, Al₂O₃, etc.) as a structure stabilization agent [7], because of the stabilization achieved by introducing divalent or trivalent cations into zirconia [8]. Among these metal oxide dopants, it is of

great interest and importance to prepare aluminum doped mesoporous zirconia. The alumina/zirconia composites which will combine the intrinsic properties of both zirconia and alumina will show improved structural properties such as high surface area, especially with zirconia in tetragonal phase. These are favorable to achieve good application effects in many fields such as catalysis and adsorption. It was reported that the aluminum-doped mesoporous zirconia synthesized by the evaporation induced self-assembly (EISA) method with a block copolymer (F127) as the template stabilizes tetragonal phase [7]. They showed disordered wormhole-like mesoporous structure and a specific surface area of 172 m²/g. The synthesis of super-microporous alumina-zirconia materials with a high surface area of 216 m²/g were recently reported via self-assembled strategy using surfactants as templates [9]. The above results illustrate that the introduction of Al can obviously enhance the specific surface area of the materials. Ghotbiet al. reported that the microporous spherical alumina/zirconia materials with a high surface area of 125 m²/g were obtained by alkaline etching of solid

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solution [10]. However, the single pore structure (either mesopore or micropore) mentioned above is difficult to meet the special needs of multiscales. Therefore, the synthesis of micro-mesoporous alumina-zirconia nanocomposites is a worthwhile effort, which will be expected to apply in shape selectivity catalysis for required molecules. However, so far few studies have been reported in the literature synthesizing micro-mesoporous alumina-zirconia nanocrystals.

Here, micro-mesoporous alumina-zirconia nanocrystals with triblock copolymer F127 as a template are developed by a facile one-pot vapor-induced synthesis route. The synthesized composites exhibit high surface area, phase structure stability and controllable pore size.

2. Experimental procedure

In a typical procedure, 2.36 g of F127 is dissolved into 17 ml anhydrous ethanol accompanied by stirring about 10 min. Then 0.077–0.46 g of aluminum isopropoxide and 1.44 g of zirconium *n*-butoxide are slowly added to the above solution respectively. The molar ratio of aluminum to zirconium is in the range of 0.1–0.6. After being further stirred for 15 min, the mixed solution is poured into the glass container which is placed inside the Teflon-lined hydrothermal chamber in which 12 ml deionized water is previously placed. Thus the water does not contact the solution and the fierce hydrolysis reaction is avoided. Then the hydrothermal chamber is sealed into the autoclave that is heated at 140 °C for 24 h. The obtained white solid products are washed twice with ethanol and further isolated by centrifugation to remove the excess substances, which is followed by drying the products in an oven at 60 °C overnight. Finally, the samples are calcined at 400 °C for 5 h in air respectively. The prepared micro-mesoporous alumina-zirconia nanocrystals are named as AZ-*x*, where *x* is Al/Zr molar ratio ranging from 0.1 to 0.6.

Small-angle and wide-angle X-ray powder diffraction are performed on a Shimadzu XRD-6000 instrument (Cu K α radiation). The crystal sizes of the samples are estimated from the corresponding XRD peaks at 30.2°, 50° and 60° by Scherrer Formula. Textural properties of the samples are obtained from N₂ adsorption-desorption isotherm measurements at 77 K with a Quantachrome analyzer. The surface areas are calculated by Brunauer-Emmett-Teller formula. The pore size and pore volume analyses of all samples are derived from the adsorption branched of the isotherms by the non-local density functional theory (NLDFT). The micropore surface areas are calculated by the t-plot method micropore analysis. Transmission electron microscope (JEM-2100F) and scanning electron microscope (TESCAN MIRA3) are used to observe the surface morphology of the selected sample. Energy dispersive spectroscopy (EDS) allowed the determination of the elemental composition and contents that are present in the sample.

3. Results and discussion

Fig. 1 shows the nitrogen adsorption-desorption isotherms and the corresponding pore size distribution of the micro-mesoporous alumina-zirconia materials. All samples exhibit type IV isotherms with the H2-shaped hysteresis loops (Fig. 1A) at $p/p_0 = 0.5$ – 0.99 , which is typical characteristic of mesoporous materials. It can be seen that the sharp increase of the nitrogen adsorption amounts at low relative pressure ($p/p_0 < 0.1$) in the adsorption branches of the composites could be ascribed to the results of the filling of micropores [11], indicating a relevant development of microporosity in the samples. The generation of certain microporosity in the samples could mainly be ascribed to incorporating Al species into zirconia and inhibiting from the growth of nanocrystal particles. It can be seen from Table 1 that the BET surface areas of AZ-*x* ($x = 0.1$ – 0.6) samples nearly show a clear increase trend with enhancing the amount of the added aluminum. But their micropore surface areas and pore volumes relatively seem to be insensitive to the Al/Zr molar ratio after the initial increase for AZ-0.1 to AZ-0.2. These results suggest that compared with the higher Al/Zr molar ratio

zirconium ions could be more easily replaced by aluminum to form rich microporosity at low Al contents. In addition, a decrease in micropore surface area for AZ-0.5 relative to AZ-0.4 could be explained as the formation of mesoporous alumina. It is found that the sample AZ-0.6 exhibits the largest BET surface area of 313 m²g⁻¹ of which 118 m²/g in the form of micropores after high temperature calcination, which are much higher than that of the samples previously reported [7,9,12]. Correspondingly, the NLDFT pore size distributions of all samples are displayed in Fig. 1B. As can be seen, AZ-*x* samples show narrow peaks in the range of 1.30–1.50 nm, reflecting the existence of microporosity in the products. Meanwhile, smaller mesopore sizes centered at around 2.5 nm and larger mesopore sizes centered at about 8.8 nm are observed from Fig. 1B. These results indicate that the introducing Al into zirconia plays an important role on the generation of micro-mesoporosity in the materials. It is noticeable that the micro-mesoporous alumina-zirconia products possess larger specific surface areas and pore volumes than that of the Al-free material (Table 1), reflecting their improved textural properties.

Fig. 2A depicts the wide-angle X-ray diffraction (W-XRD) patterns of the prepared micro-mesoporous alumina-zirconia nanocrystals after high temperature thermal treatment. It demonstrates that the composites exhibit well crystalline, even though with higher Al/Zr molar ratio, consisting only of tetragonal phase of zirconia without any trace of alumina crystals. This suggests that aluminum-doped zirconia nanocrystals synthesized not only maintain crystallinity, but also enhance the stability of zirconia in tetragonal phase through the addition of alumina to zirconia. It can be explained that Al³⁺ ions randomly substitute Zr⁴⁺ ions, forming solid solutions with zirconia [13]. Fig. 2C illustrates the W-XRD diffraction peaks of zirconia sample in the absence of Al, the sample AZ-0.1 calcined at 400 °C and the sample AZ-0.1-600 obtained after the calcination of 600 °C, to reveal further their stability of tetragonal structure. It can be seen that W-XRD patterns of the zirconia sample prepared without aluminum species present the coexistence of tetragonal and monoclinic phases (Fig. 2C f, h). Moreover, zirconia sample calcined at 600 °C without Al shows more monoclinic fraction than that of the product calcined at 400 °C (Fig. 2C f, h), which indicates that tetragonal structure of zirconia is more unstable at the higher calcination temperature. AZ-0.1 calcined at 400 °C relative to the Al-free materials exhibits pure tetragonal phase in zirconia (Fig. 2C a, f). When increasing the calcination temperature to 600 °C, W-XRD pattern peaks of sample AZ-0.1-600 show more intense but still maintain pure tetragonal phase compared with sample AZ-0.1 (Fig. 2C a, g). These results further suggest that the incorporation of Al can enhance the structural stability of zirconia in tetragonal phase by inhibiting the phase transformation. Therefore, this result showed the characteristics, such as stability in tetragonal phase comparing published work [7]. It is also found that the XRD peaks of the samples become gradually weaker and wider with increasing aluminum dopant (Fig. 2A). This indicates that introducing aluminum ions into zirconia structure gradually causes a decrease in not only crystallinity but also crystal size (Table 1) for the composite nanomaterials, as a result of increasing oxygen vacancy defect content in the solid solution by substitution of Zr⁴⁺ by Al³⁺ ions [10]. From the small-angle X-ray diffraction (S-XRD) patterns shown in Fig. 2B, it can be seen that almost all samples doped with aluminum species exhibit characteristic peak located around 1–2°, which is a part of the mesoporous structure. In addition to, the diffraction peak of sample AZ-0.1 shows weaker than that of the other samples, indicating less pore volume generated in the sample (Table 1). It is noted that when increasing the Al/Zr molar ratio from 0.4 to 0.6, the diffraction peaks of the samples slightly shift to high angles (Fig. 2B c, d), and then shift to low angles accompanied by a gradual disappearance of the peak (Fig. 2B e). This result can be correlated with the change of their crystallinity and the reduction of their crystal sizes arising from increasing aluminum contents, as indicated by W-XRD patterns in Fig. 2A and the data as shown in Table 1. In addition, randomly stacking of the great number of small nanocrystals can

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