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Preparation and characterization of mesoporous tetragonal sulfated zirconia

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Abstract

Mesoporous tetragonal sulfated zirconia with high surface area and narrow pore-size distribution was prepared using $Zr(O\text{-}nPr)_4$ as zirconium precursor, sulfuric acid as sulfur source and triblock copolymer poly(ethylene glycol)–poly(propylene glycol)–poly(ethylene glycol) (P123) as the template. The samples were characterized by X-ray diffraction, N_2 sorption, TEM, and NH_3-TPD. A phase transformation from monoclinic sulfated zirconia to tetragonal sulfated zirconia is observed. The product shows strong acidity.

Keywords: Sulfated zirconia; Mesoporous; TEM; Phase transformation; Acidity

Mesoporous metal oxides have gained great interest in catalysis and the preparation of mesoporous Al_2O_3 [1], WO_3 [2], TiO_2 [3], Cr_2O_3 [4], etc. has been reported recently. Most of these mesoporous materials have been prepared by liquid-crystal template (LCT) method. The hard template method also has been reported, however, the mesoporous structure of the metal oxides may partially collapse during the calcination and removal of the template. Therefore, LCT method is still an effective route to create mesoporous transition metal oxide with high surface area, narrow pore-size distribution, and high thermal and hydrothermal stabilities.

In heterogeneous catalysis solid acid catalyst is widely used. Among them, tetragonal sulfated zirconia has been well documented as a catalyst with strong acidity which shows high catalytic activity in many reactions such as dehydration [5], alkylation [6,7], isomerization [8,9], esterification [10], etc. under mild conditions. However, sulfated zirconia prepared with conventional methods normally contains intracrystalline pores with relatively low surface area and wide pore-size distribution [11,12]. It is expected that mesoporous tetragonal sulfated zirconia may improve the catalytic activity due to its high surface area and porous structure. A number of research works have been reported on the study of mesoporous zirconia and sulfated zirconia [6,13–16], however, these products usually have wide pore-size distribution and low stability of the pore structure upon calcination. In addition, tetragonal sulfated zirconia normally has a phase transformation to its monoclinic counterpart after calcination at high temperature. Here we report the

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preparation of tetragonal sulfated zirconia with relatively narrow mesopore distribution through an unique phase transformation from monoclinic sulfated zirconia prepared via LCT route using $Zr(OC_3H_4)_4$ as zirconia source and triblock copolymer P123 as template.

1. Experimental

In a typical preparation, 2 g of P123 was dissolved in 10 g of ethanol by stirring magnetically for 4 h and 10 mmol of $Zr(OC_3H_4)_4$ was added under anhydrous condition. The mixture was further stirred for 12 h and then hydrolyzed by passing a flow of air with 100% humidity at 298 K under stirring for ca. 4 days. After complete hydrolization, the template was extracted with ethanol and the solid was dried in air at room temperature for several days. The product obtained was treated in 0.5 mol/L H_2SO_4 for 3 h (15 mL 0.5 mol/L H_2SO_4/1 g ZrO_2). Finally, the as-synthesized solid was calcined at different temperature for 3 h.

2. Results and discussion

To determine suitable calcination temperature, the as-synthesized solid treated with 0.5 mol/L H_2SO_4 was calcined at different temperatures. The XRD patterns of these samples are shown in Fig. 1. When calcined at 650 °C, the sample exhibits nearly pure monoclinic phase of zirconia (JCPDS No. 83-0944). The diffraction intensities of tetragonal phase of zirconia (JCPDS No. 81-1545) increase with increasing calcination temperature. When calcination temperature reaches 750 °C, the tetragonal phase of zirconia was dominant with very small amount of monoclinic phase of zirconia. A detailed investigation of the effects of calcination temperature around 750 °C and calcination time on the crystalline phase formed shows that it is impossible to completely transform the minor monoclinic phase of zirconia to tetragonal phase. Hence, the final product is obtained by treating at 750 °C for 3 h.

The N_2 adsorption–desorption isotherms of the obtained sulfated zirconia is shown in Fig. 2. The shape of the isotherm belongs to type IV and shows mesostructure. The pore-size distribution curve calculated from either adsorption or desorption branch has a sharp peak at about 3.60 nm, and the BET surface area is 119 m^2/g which is much larger than that of the bulk sulfated zirconia [17]. Compared to the reported tetragonal zirconia [13,18], the sample prepared in this work has much narrower pore-size distribution.

In order to visually observe the morphology and porosity of the mesoporous tetragonal sulfated zirconia, transmission electron microscopy (TEM) and high resolution TEM (HRTEM) were employed. Fig. 3(a) shows that the sulfated zirconia is comprised of the particles with average size of ca. 50 nm. The crystalline nature of tetragonal zirconia can be observed in Fig. 3(b), in which the d space of 0.361 nm found is corresponded to the (1 0 0) of tetragonal phase of zirconia (JCPDS No. 81-1545). The image of Fig. 3(c) indicates that the sample prepared in this work contains irregularly arranged mesopores within particles. The diameters observed from TEM study are

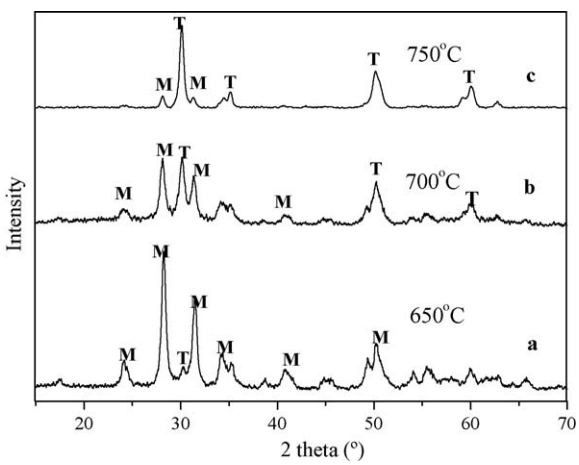

Fig. 1. The XRD patterns of the as-synthesized sample treated with 0.5 mol/L H_2SO_4 calcined at different temperature for 3 h. M and T represents monoclinic phase of ZrO_2 and tetragonal phase of ZrO_2, respectively.

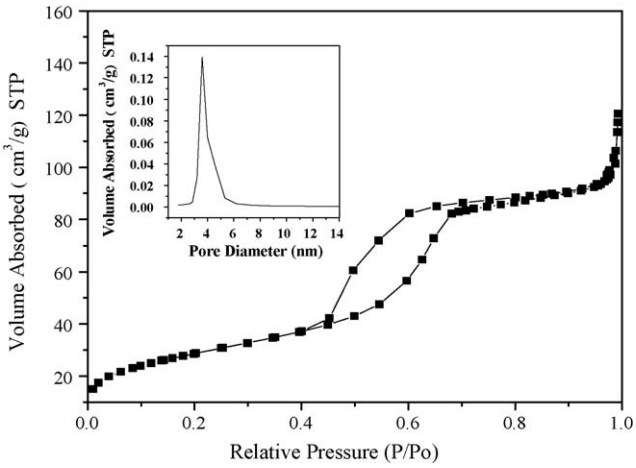

Fig. 2. The N_2 adsorption–desorption isotherm and the pore-size distribution curve of the sample calcined at 750 °C.

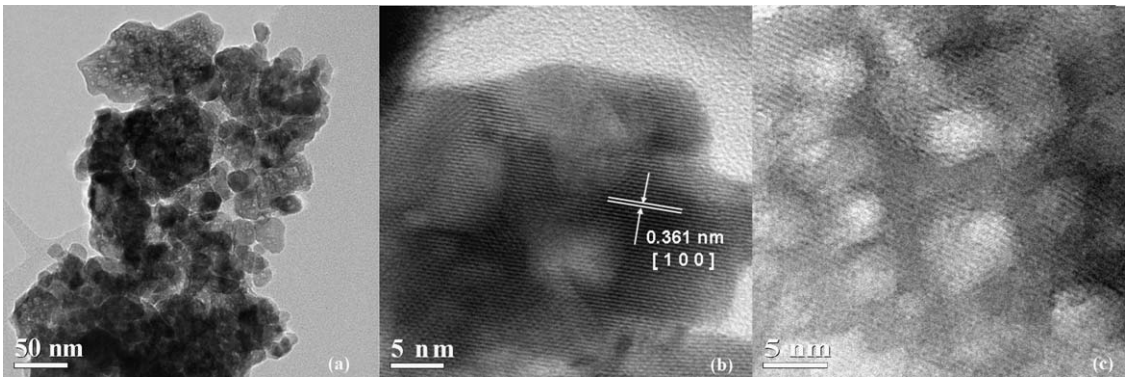

Fig. 3. TEM (a) and HRTEM (b and c) images of the sample calcined at 750 °C.

consistent with those found in the N_2 adsorption measurement. Although the synthesis of zirconia nanoparticles with size of less than 20 nm has been reported, the BET surface area of the particles was still small because of their non-porous structure [19,20]. The irregularly arranged mesopores within particles in our sample contributes its high surface area.

XRD pattern in small angle region shows no apparent peaks, indicating the mesostructure of the product is of low order although the porous property can be well proved by the N_2 adsorption–desorption isotherm and TEM. The sulfur

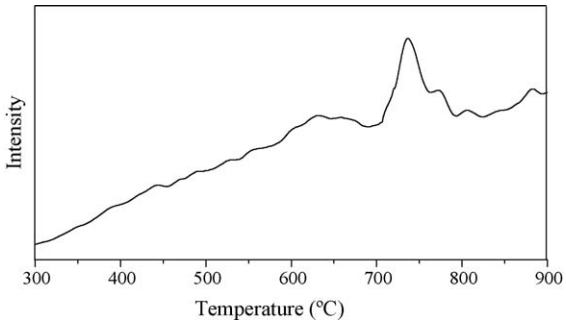

Fig. 4. The NH_3-TPD curve of the sample calcined at 750 °C.

content of tetragonal sulfated zirconia is 3.60 wt%. NH_3-TPD shows mainly a peak around 736 °C (Fig. 4), which indicates strong acidity. The catalytic properties of the mesoporous tetragonal sulfated zirconia are under further investigation.

In conclusion, a phase transformation from monoclinic sulfated zirconia to tetrahedral sulfated zirconia was found through the calcination of the monoclinic phase prepared by the LCT method at 750 °C. The product has a surface area of 119 m^2/g with relatively narrow mesopore distribution and strong acidity.

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