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## Eco-friendly synthesis of nanocrystalline zirconia with tunable pore size



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## ABSTRACT

Microporous/mesoporous zirconia materials have been successfully synthesized by controlling hydrolysis rate without adding acid or base and calcining under mild conditions, and characterized by XRD, TEM and N<sub>2</sub> adsorption-desorption. The results show that the as-synthesized materials are super-microporous (pore size in the range of 1–2 nm) as using dimethyl distearyl ammonium chloride as the template, but mesoporous (pore size > 2 nm) when didodecyl dimethyl ammonium chloride and bisoctyl dimethyl ammonium chloride are employed. By changing the carbon chain length of the templates, the average pore sizes of the zirconia samples are tailored, and a range of pore sizes from 1.2 to 4.2 nm is obtained.

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## 1. Introduction

Since the first successful synthesis of well-ordered mesoporous silica materials in the 1990s [1,2], many efforts have been directed towards the synthesis of both mesoporous (pore size > 2 nm) and microporous (pore size < 2 nm) transition metal oxide analogues of these exciting new materials [3–6]. The first microporous transition metal oxide molecular sieve was reported in 1997 using soft templating pathway [7]. Then with same synthesis route, different kinds of microporous non-silica materials such as TiO<sub>2</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Ta<sub>2</sub>O<sub>5</sub>, and Fe<sub>2</sub>O<sub>3</sub> were synthesized. Among them, zirconia was widely employed as catalyst or catalyst support and extensively studied owing to its acidic-basic surface and unique redox properties [8]. Over the past two decades, a variety of approaches have been developed for the preparation of microporous zirconia materials, but their syntheses normally require the presence of acid or base to adjust pH value of the surfactant solution [9–11]. The use of acid and base generally produces a large amount of wastes, which is not environmentally friendly. Furthermore, the procedures required multiple steps and were time-consuming. Recently, our laboratory has developed the super-microporous alumina-based materials via an evaporation-induced self-assembly (EISA) pathway [12,13], which presents a new route to obtain super-microporous metal oxides. Supermicropores, first introduced by Dubinin [14], was defined as nanopores with pore

sizes ranging from 1 nm to 2 nm. This family of nanoporous materials can fill the gap between micropores and mesopores, since the pore size of conventional zeolites (typical microporous materials) does not exceed the boundary of 1 nm and that of mesoporous materials is larger than 2 nm. To date, little work concerns to the synthesis of super-microporous zirconia materials without any additional acid or base, especially from super-micropore to mesopore.

Here, we report a facile synthesis of porous zirconia materials which enables control of pore structure, including pore diameter, using eco-friendly surfactants by the EISA method. More importantly, the whole process is self-adjusting to organize the network-forming zirconium oxide species without any acid or base additive. Pore structures of these synthesized zirconia range from super-micropore to mesopore, and average pore size can be tuned from 1.2 to 4.2 nm by varying the length of surfactants' carbon chain. This fundamental knowledge could be exploited in the design of tailored porous materials.

## 2. Experimental section

## 2.1. Materials

Dimethyl distearyl ammonium chloride (M<sub>av</sub>=586, (C<sub>18</sub>H<sub>37</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>NCl), Didodecyl dimethyl ammonium chloride (M<sub>av</sub>=418, (C<sub>12</sub>H<sub>25</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>NCl), Bisooctyl dimethyl ammonium chloride (M<sub>av</sub>=305, (C<sub>8</sub>H<sub>17</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>NCl), Zirconium *n*-propoxide

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( $[\text{Zr}(\text{OC}_3\text{H}_7)_4]$ , 70 wt% in 1-propanol) were purchased from Aldrich.

## 2.2. Synthesis procedure

All chemicals were used as received without further purification. Typically, 2.0 g surfactant was dissolved in 20 mL of waterless ethanol. As the surfactant was completely dissolved, 0.01 mol zirconium *n*-propoxide ( $[\text{Zr}(\text{OC}_3\text{H}_7)_4]$ , 70 wt% in 1-propanol) was added. Upon rapid stirring at room temperature about 4 h, the resulting transparent-sol mixture underwent solvent evaporation at 40 °C in air for two days and subsequently dried in an oven at 100 °C for one day. Then the as-prepared samples were heated at a ramping rate of 1 °C/min to 350 °C, 400 °C and 500 °C in the air for 5 h. The materials were abbreviated as Zr-X-T, where X and T represented number of carbons in the alkyl chain and the final calcination temperature, respectively.

## 2.3. Characterization

Powder X-ray diffraction patterns were recorded on a Shimadzu XRD-6000 diffractometer using Ni-filtered Cu K $\alpha$  (0.154 nm) radiation. Transmission electron microscopy (TEM) experiments were performed on a JEOL 2011 microscope operated at 200 kV. N<sub>2</sub> adsorption was conducted on a Quantachrome analyzer at –196 °C. Before measurements, the samples were degassed at 300 °C in vacuum for 5 h. The BET method was used to calculate the specific surface areas. The pore size distributions were derived from the adsorption branches of the isotherms using the DFT (density functional theory) method.

## 3. Results and discussion

Fig. 1 is the N<sub>2</sub> adsorption-desorption isotherms of the calcined zirconia samples synthesized with surfactants of different alkyl chain lengths and their corresponding pore size distribution curves. The isotherm of Zr-18 is type I isotherm and does not show hysteresis in the desorption branch, indicating that the micropores are formed. Pore diameters are calculated by the DFT method, which produces values centered at around 1.2 nm. Whereas the isotherms of the samples synthesized with smaller alkyl chain lengths (C=8, 12) exhibit a large hysteresis loop, which are the typical characteristic of mesoporous materials, namely type IV isotherms assigned to mesoporous structure. A DFT analysis of the desorption branch of the isotherm indicates that Zr-8 and Zr-12

**Table 1**  
BET and micropore surface areas for zirconia calcined at different temperatures.

| Sample    | S <sub>BET</sub> (m <sup>2</sup> /g) | t-Method micropore surface area (m <sup>2</sup> /g) | Pore volume (cm <sup>3</sup> /g) | Average pore size (nm) <sup>a</sup> |
|-----------|--------------------------------------|---|----------------------------------|-------------------------------------|
| Zr-8-350  | 173                                  | 55  | 0.17                             | 4.2                                 |
| Zr-12-350 | 165                                  | 83  | 0.17                             | 2.6                                 |
| Zr-18-350 | 178                                  | 139   | 0.13                             | 1.2                                 |
| Zr-18-400 | 79                                   | 42  | 0.08                             | 1.5                                 |
| Zr-18-500 | 50                                   | – <sup>b</sup>                                      | 0.06                             | 3.5                                 |

<sup>a</sup> The pores were measured by DFT method, the fitting error is below 0.5%.

<sup>b</sup> No micropore is observed.

possess a mean pore size of 4.2 nm and 2.6 nm, respectively. This suggests that the super-micropores transform to the mesopores with decreasing the alkyl chain length. It can be seen in Table 1 that, as the alkyl chain length is 18 carbons, the physisorption measurements reveal the largest BET surface area of 178 m<sup>2</sup>/g. The BET surface area is 173 m<sup>2</sup>/g for Zr-8 and 165 m<sup>2</sup>/g for Zr-12. It is also found that the BET surface area has little influence with increasing the alkyl chain length, but the micropore surface area increases. For samples Zr-18 (Fig. 2 and Table 1), the BET surface area and pore volume of the samples decrease with increasing calcination temperatures, while the mean pore size increases. The evolution of pore size is attributed to the partial degradation of the walls surrounding micropores leading to an extended network of pores [12].

Fig. 3 shows the wide-angle X-ray diffraction pattern. It is revealed that there is no phase transformation during the annealing, and the as-made zirconia walls are exclusively crystallized into the tetragonal phase. It also can be observed that the higher the calcination temperature is, the sharper the diffraction peak exhibits, which suggests the growth of the crystalline in the framework during annealing.

Fig. 4 exhibits the TEM image of super-microporous zirconia sample calcined at 400 °C. The disordered wormhole-like structure can be found. Electron diffraction patterns (insets in Fig. 4) confirm that the walls are polycrystalline, which is consistent with the wide-angle XRD results.

In our synthesis, no extra acid or base is added. Nevertheless, this does not mean that the hydrolysis and condensation process is uncontrolled. The hydrolysis of zirconium alkoxide engenders an acidic ambience for the self-assembly process and acts as the inhibitor of the hydrolysis-condensation process of zirconium species [8]. It has been found with silicate materials that the pore diameter is related to the alkyl chain length of the surfactant used in the synthesis [15,16]. The question as to whether there is also a

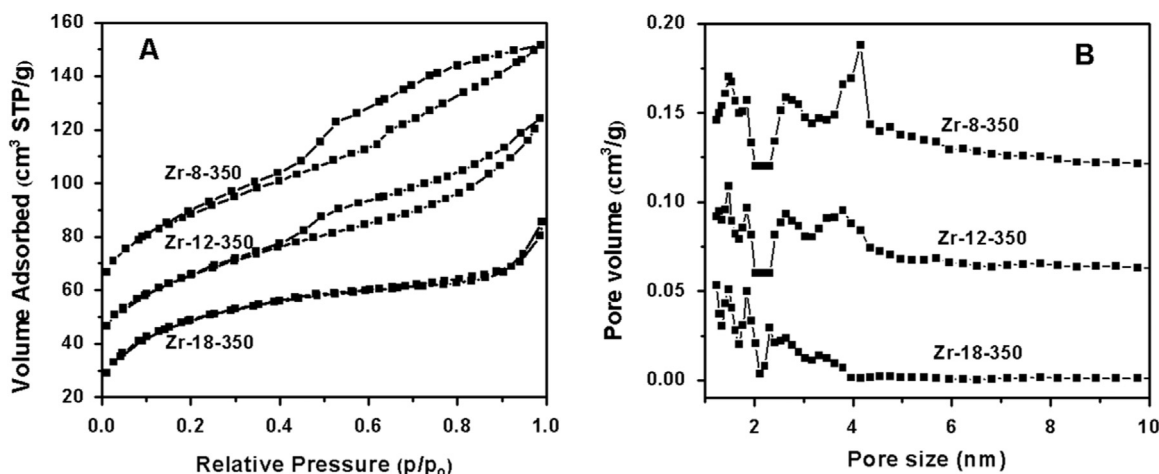


Fig. 1. Nitrogen adsorption-desorption isotherms (A) with corresponding pore size distribution curves (B) of Zr-X samples calcined at 350 °C.

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