



# Influence of synthetic parameters on structural and catalytic properties of sulfated zirconia nanoparticles prepared by employing sulfate-containing anion surfactants via one-step route



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## ABSTRACT

A series of sulfated zirconia nanoparticles (abbreviated to SZNP) with high surface area and mesostructure have been synthesized by using sulfate-contained anion surfactants (SDS and SCS) both as a template and a sulfating agent via one-step liquid-crystal template (LCT) route. In light of N<sub>2</sub> adsorption–desorption, XRD and FT-IR analyses, it can be concluded that SDS is in favor of the mesostructure formation as well as the inhibition of ZrO<sub>2</sub> phase transformation from tetragonal to monoclinic with respect to SCS. The optimal molar ratio of Zr/S is 1:1, which lead to the largest BET surface area. It is well-demonstrated by FT-IR, NH<sub>3</sub>-TPD together with transesterification reaction that SO<sub>4</sub><sup>2-</sup> anion, originated from the hydrophilic moieties of templates, can be easily incorporated into ZrO<sub>2</sub> to form SZNP with super acidity, and the formation mechanism is also illustrated. Catalytic data exhibiting the yield of fatty acid methyl ester (FAME) in transesterification of soybean oil with methanol is in the following order: SZNP<sub>12-(550)-1.0</sub> > SZNP<sub>16-(550)-1.0</sub> > TSZ<sub>(550)</sub>.

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## 1. Introduction

Sulfated zirconia (abbreviated to SZ), discovered by Holm and Bailey [1] and recognized as a solid super acid (the acidity is far stronger than 100% H<sub>2</sub>SO<sub>4</sub>), has attracted considerable attention in heterogeneous catalysis due to the fact that SZ exhibits high catalytic activity for many important industrial and organic reactions [2–4]. Furthermore, it was demonstrated that the catalytic activity of mesoporous sulfated zirconia (MSZ) is far higher than that of traditional sulfated zirconia (TSZ) due to the synergistic effect of uniform pore size, high porosity and large surface area [5–8]. Therefore, in the past two decades, many researchers focused on the synthesis of MSZ with high surface area via various methods [9–16]. In light of these previous documents, the synthesis routes of MSZ can be generally classified into one-step and two-step. Compared with two-step, one-step synthesis route has attracted much attention due to the advantages of avoiding sulfating step and simplifying the overall synthesis procedure to a great extent [2,3,13]. Nanosized SZ with mesostructure has been prepared by using a simple calcination [14]. Schüth et al. [15] reported that MSZ has been synthesized via a one-step LCT route by employing cation template CTAB as a structure-directing agent for the first time. Cheng et al. [16] reported that MSZ has been fabricated by using CTAB and Zr(SO<sub>4</sub>)<sub>2</sub> as a template and a zirconium source. Fripiat and coworkers

firstly reported that mesoporous zirconia rather than MSZ has been synthesized by using anion surfactant SDS as a template [17,18]. Recently, Ozawa et al. [19] reported a one-step route for the synthesis of SZ powder by using SDS and Zr(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> as a template and a zirconium source, respectively. However, mesostructure was not formed at all, as confirmed by their small angle XRD analysis. More importantly, BET surface area of the sample calcined at 600 °C for 1 h was only 24 m<sup>2</sup>/g [19].

In this paper, we reported a new facile one-step route for the synthesis of sulfated zirconia nanoparticles (abbreviated to SZNP) with mesostructure and high surface area by using sulfate-containing anion surfactants both as a template and a sulfating agent via one-step liquid-crystal template (LCT) [20,21] for the first time. The effects of synthetic parameters (the alkyl chain length of template, calcination temperature as well as the molar ratio of Zr/S) on the structure of resulting materials were investigated in detail.

## 2. Experiment

### 2.1. Materials

Zirconium n-propoxide [Zr(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>] with 70 wt.% in n-propanol and soybean oil were purchased from Sigma-Aldrich and Kunming Chang-feng company, respectively. Sodium dodecyl sulfate (C<sub>12</sub>H<sub>25</sub>OSO<sub>3</sub>Na, SDS), sodium cetyl sulfate (C<sub>16</sub>H<sub>33</sub>OSO<sub>3</sub>Na, SCS), concentration hydrochloric acid (c-HCl, 36 wt.%) and anhydrous methanol were obtained from Shanghai chemical reagent company of China.

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## 2.2. Synthesis of sulfated zirconia

In this article, the following general procedures were used to synthesize sulfated zirconia nanoparticles with high surface area and mesostructure, in which  $Zr(OC_3H_7)_4$  and anion surfactants (SDS or SCS) were employed as a zirconium source and as a structure-directing agent, respectively. In a typical synthesis batch, 0.05 mol of template (SDS or SCS) was added into 200 ml of deionized  $H_2O$  with vigorously stirring at room temperature (RT). After the template (SDS or SCS) was completely dissolved, the calculated  $Zr(OC_3H_7)_4$  was added into the above mixture solution to keep the molar ratio of Zr/S between 0.5 and 4.0. Next to, the pH value of mixture solution was adjusted by using HCl solution (1.0 M) to 3.0, and the mixture was continuously stirred for 0.5 h. After that, the mixture was aged at RT for 20 h and thermally treated at 80 °C for 5 days under static conditions in sequence. Subsequently, the reaction product was filtered, washed with the mixture solution consisting of deionized water and isopropanol and dried at 110 °C for 12–24 h. Finally, the dried samples were calcined at 550 °C in air for 3 h. Sulfated zirconia samples synthesized with SDS and SCS via this route were designated as  $SZNP_{12-(x)-y}$  and  $SZNP_{16-(x)-y}$ , respectively, in which “x” and “y” was represented calcination temperature and the molar ratio of Zr/S.

For comparison purposes, a sulfated zirconia sample was synthesized by using traditional two-step method. In a typical synthesis batch, 20 ml of  $Zr(OC_3H_7)_4$  was added into 200 ml  $H_2O$ . Next to, the pH value of mixture solution was adjusted by using HCl solution (1.0 M) to 3.0 and the mixture solution was continuously stirred for 0.5 h. Then, the resulting mixture was aged at RT for 20 h and thermally treated at 80 °C for 5 days under static conditions in turn. After that, the white reaction product  $Zr(OH)_4$  was filtered, washed with the mixture solution of deionized water and isopropanol, and dried at 110 °C for 12–24 h. Subsequently, the dried zirconium hydroxygen was ground and added into  $H_2SO_4$  solution (1.0 M) with stirring (20 ml/g  $Zr(OH)_4$ ) for 2 h. Then, the sulfated product was filtered and dried again at 110 °C for 12–24 h. Finally, the dried sample was calcined at 550 °C in air for 3 h. The sulfated zirconia sample synthesized by this two-step method was nominated as  $TSZ_{(550)}$ .

## 2.3. Characterization

X-ray diffraction (XRD) patterns were performed on a Rigaku D/max-1200 diffractometer using Cu  $K\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ), operating at 40 kV and 30 mA. BET surface area and  $N_2$  adsorption-desorption isotherms were carried out on a Micromeritics-ASAP-2000 apparatus at  $-196 \text{ }^\circ\text{C}$ . All samples were degassed at 250 °C for 2 h prior to analysis. BET specific surface area was calculated from adsorption data in the relative pressure range from 0.05 to 0.25. TEM images were obtained on a JEM-2010 HR transmission electron microscope, operating with an accelerate voltage of 200 kV. FT-IR spectra of the samples in the form of KBr pellets were recorded by using a Nicolet 560 IR spectrometer.

## 2.4. Catalytic activity tests

Transesterification of soybean oil with methanol was performed in a stirred batch reactor with samples withdrawn periodically for analysis, and the yield of fatty acid methyl esters (FAME) was determined by a flame ionization detection (FID) of gas chromatography (GC) equipped with a capillary column (Agilent DB-5HT, 30 m  $\times$  0.32 mm  $\times$  0.10  $\mu\text{m}$ ).

## 3. Results and discussion

$N_2$  adsorption-desorption isotherms and Barrett-Joyner-Halenda (BJH) pore size distribution curves of  $SZNP_{12-(110)-1.0}$  and  $SZNP_{12-(550)-1.0}$  are presented in Fig. 1. According to IUPAC classification,  $N_2$  adsorption-desorption isotherm of  $SZNP_{12-(110)-1.0}$  is found to be of type IV [22,23].

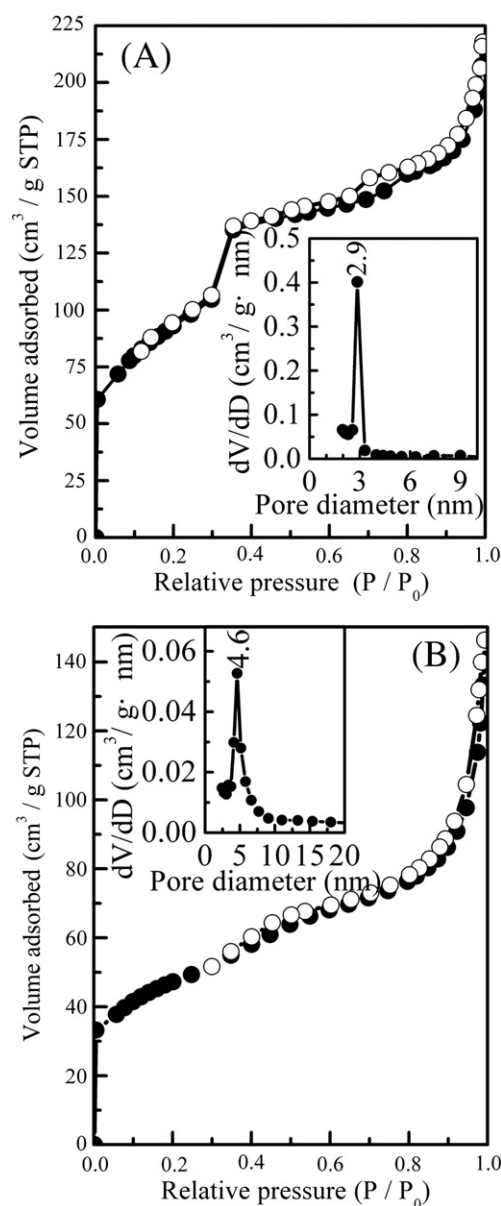


Fig. 1.  $N_2$  adsorption-desorption isotherms and BJH pore size distribution curves (inset) of (A)  $SZNP_{12-(110)-1.0}$  and (B)  $SZNP_{12-(550)-1.0}$ .

Three distinct regions in the adsorption isotherm are detected for  $SZNP_{12-(110)-1.0}$ . The first increase in  $N_2$  adsorption at relative pressure  $P/P_0 < 0.1$  is due to multilayer adsorption on the surface, while the second increase at  $P/P_0 = 0.3-0.5$  arises from capillary condensation in the mesopores with nitrogen multilayers adsorbed on the inner surface [24]. The third adsorption step at  $P/P_0 > 0.9$  is characteristic of textural interparticle macroporosity [25]. A narrow BJH pore size distribution together with average pore diameter of 2.9 nm is observed for  $SZNP_{12-(110)-1.0}$  (Fig. 1A inset). However, the presence of a single diffraction peak in  $2\theta$  region below  $2^\circ$  (Fig. S1) is an indicative of disordered mesostructure [26,27]. It was documented that the position of inflection point is closely related to a diameter in the mesopore range and the corresponding sharpness indicates the uniformity of mesopore size distribution [28–30]. In light of these results, it can be deduced that  $SZNP_{12-(110)-1.0}$  is a typically disordered mesoporous materials. As can be seen by comparing Fig. 1, the second step in  $N_2$  adsorption of  $SZNP_{12-(550)-1.0}$  is still preserved, although the sharpness is far lower than that of  $SZNP_{12-(110)-1.0}$ , thus indicating some mesostructures within the sample are still maintained. The difference between  $SZNP_{12-(550)-1.0}$

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