

Synthesis and characterization of nano-crystalline sulfated zirconia by sol–gel method

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Received 10 February 2003; received in revised form 24 August 2003; accepted 1 September 2003

Available online 25 September 2004

Abstract

Synthesis of nano-crystalline sulfated zirconia with crystallite size less than 20 nm using the one-step as well as the two-step sol–gel technique was carried out. Tetragonal phase of sulfated zirconia was obtained on calcination at 600 °C. All the sulfated zirconia samples were found to be active for benzoylation of toluene showing 26–41% conversion of toluene, however, samples prepared by the one-step method showed higher conversion (33–41%) as compared to the samples prepared by the two-step method (26–28%). Furthermore, in the one-step method, the introduction of sulfuric acid prior to hydrolysis, results into improved structural and textural properties in terms of higher sulfur loading, smaller crystallite size, higher surface area, average pore diameter and higher catalytic conversion for benzoylation of toluene.

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Keywords: Sulfated zirconia; Nano-crystalline; Sol–gel

1. Introduction

Sulfated zirconia is reported to possess super acidity and hold potential for catalyzing *n*-alkane isomerisation at ambient temperature [1,2] and other commercially important organic transformations like acylation, alkylation and nitration [3]. However, catalytic activity of sulfated zirconia is strongly influenced by the method of preparation [3–5], as the structural and textural features of the catalyst responsible for the catalytic activity are affected by the synthetic strategies used.

Sulfated zirconia has generally been prepared by conventional precipitation of an aqueous zirconium salt as well as an alternate method like the sol–gel technique. Both the precipitation and the sol–gel technique may result in the formation of nano-crystalline zirconia [6–8]. However, the latter is advantageous [9–11] due to its ease in controlling the homogeneity and physical characteristics during synthetic steps

of the process to form genuinely nano-crystalline materials. Furthermore, a nano-crystalline material may have a strong effect on catalytic properties due to large surface-to-volume ratio [12]. An application of nano-crystalline sulfated zirconia as a catalyst or catalyst support is promising and worth exploring due to high acidity of these solids.

The sol–gel technique can proceed by the two-step or the one-step process. In general, the two-step method is more common and involves the formation of a sol by the hydrolysis of the metal alkoxide and a three-dimensional network gel of zirconium hydroxide after condensation in the first step. This is followed by the sulfation with sulfuric acid or ammonium sulphate in the second step. However, in the one-step process, hydrolysis and sulfation is done simultaneously [13,14]. Various parameters involved during the synthesis of a gel affect its structural and textural features. In our previous study [15], we reported the effect of different parameters, such as concentration of precursor, drying temperature and calcination temperature on the structural, textural and catalytic properties of sulfated zirconia prepared by the two-step sol–gel technique. The present paper reports the synthesis of nano-crystalline sulfated zirconia by the one-step

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sol–gel technique. The effect of the order of introduction of sulfating agent (sulfuric acid) and hydrolyzing agent (water) to the zirconium *n*-propoxide precursor was also studied. For comparison, samples were also prepared by the two-step method in basic as well as neutral medium. The structural (crystallinity, binding of sulfate ions and average crystallite size) and textural (surface area, pore volume and pore size distribution) properties of thus prepared sulfated zirconia were studied. The catalytic activities of the catalysts were evaluated for the benzylation of toluene using benzyl chloride as benzylating agent and correlated with structural and textural parameters.

2. Experimental

2.1. Materials

Zirconium *n*-propoxide [Zr(OC₃H₇)₄], 70 wt.% in propanol, was procured from Sigma–Aldrich; concentrated H₂SO₄, 1-propanol, aqueous ammonia (25%), toluene and benzyl chloride were from SD Fine Chemicals, India and were used as such.

2.2. Catalyst preparation

Sulfated zirconia (SZ) samples were prepared by the one-step as well as the two-step sol–gel technique. In the one-step method, addition of sulfuric acid was done by two ways [14]: (i) an aqueous solution of concentrated sulfuric acid was added drop wise into the 30 wt.% solution of zirconium propoxide in propanol, and (ii) concentrated sulfuric acid was added to the 30 wt.% solution of zirconium propoxide in propanol–water was then added drop wise to complete the hydrolysis. The samples thus prepared are named as SZ-1 and SZ-2, respectively.

In the two-step procedure, hydrolysis of zirconium propoxide (30 wt.% solution) was done in alkaline medium with aqueous ammonia at pH 9–10 followed by drying of the resulting Zr(OH)₄ gel at ambient temperature and then at 110 °C in the first step. This was followed by sulfation with concentrated H₂SO₄ (0.5 M, 15 ml/g) in the second step. The sample is named as SZ-3.

As the one-step preparation of sulfated zirconia is in acidic medium and the two-step preparation is in alkaline medium, to study the effect of the neutral medium, sulfated zirconia sample was also synthesized in the neutral medium. Synthesis in the neutral medium is only possible by following the two-step method, where hydrolysis was done alone with water. The sulfation procedure was similar to that followed for sample prepared in alkaline medium, as described above. The sample is named as SZ-4. All the samples thus prepared were dried at ambient temperature and then at 110 °C for 12 h after filtration followed by calcination at 600 °C for 2 h in a muffle furnace in air atmosphere.

2.3. Characterization

2.3.1. X-ray powder diffraction (XRD) studies

The crystalline phase formed and the crystallinity of sulfated zirconia after calcination at 600 °C was measured by X-ray powder diffractometer (Philips X'pert) using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). The samples were scanned in 2θ range of 0–70 degree at a scanning rate of 0.04 degree s⁻¹. Crystallite size of tetragonal phase was determined from the characteristic peak ($2\theta = 30.18$ for the (1 1 1) reflection) by using Scherrer formula with a shape factor (*K*) of 0.9 [16] as below:

$$\text{Crystallite size} = K \frac{\lambda}{W} \cos \theta$$

where, $W = W_b - W_s$; W_b is the broadened profile width of experimental sample and W_s is the standard profile width of reference silica sample.

2.3.2. FT-IR spectroscopic studies

The nature of bonding of sulfate ions with zirconia surface after calcination at 600 °C was studied by FT-IR spectrophotometer (Perkin-Elmer GX). The spectra were recorded in the range 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹ as KBr pellets. Diffuse reflectance IR spectra of the samples, after in situ heating at 450 °C for determining the nature of sulfate species formed on zirconia surface, were studied by FT-IR spectrophotometer equipped with 'The Selector' DRIFT accessory (Graseby Specac, P/N 19990 series) and Automatic Temperature Controller (Graseby Specac, P/N 19930 series). The spectra of the samples, diluted with KBr (similarly as in KBr pellets), were recorded at room temperature and after in situ heating at 450 °C at a heating rate of 25 °C min⁻¹. The samples were kept at 450 °C for 30 min, thus allowing sufficient time for water vapour desorption. Typically 30 scans were co-added at a resolution of 4 cm⁻¹ under dry N₂ flow (30 cm³ min⁻¹).

2.3.3. Sulfur analysis

The bulk sulfur (wt.%) retained in sulfated zirconia samples before and after calcination at 600 °C was analyzed by C H N S/O elemental analyzer (Perkin-Elmer 2400, Sr II).

2.3.4. Surface area and pore size distribution

Specific surface area, pore volume and pore size distribution of sulfated zirconia samples calcined at 600 °C were determined from N₂ adsorption–desorption isotherms at 77 K (ASAP 2010 Micromeritics). Surface area was calculated by using BET equation; pore volume and pore size distribution were calculated by BJH method [17]. The samples were degassed under vacuum at 120 °C for 4 h, prior to adsorption measurement to evacuate the physisorbed moisture.

2.3.5. Catalytic activity for benzylation of toluene

The catalytic activity of the sulfated zirconia samples prepared was evaluated for the benzylation reaction of toluene

by benzyl chloride in liquid phase. In a single neck round bottom flask, toluene and benzyl chloride were taken in 1:1 molar ratio, and the catalyst (activated at 450 °C for 2 h) in 10:1 weight ratio with the substrate, was added to the mixture. The reaction was carried out at 100 °C with continuous stirring at 400 rpm under nitrogen atmosphere. In our previous study [15] we have observed that 4 h is the optimum time to get maximum conversion for benzylation of toluene with sulfated zirconia prepared by the two-step sol–gel method. Therefore, in the present study we analyzed the reaction mixture after 4 h by Gas Chromatography (HP6890) having HP-5 capillary column (30 m length and 0.32 mm diameter packed with silica acetate) and FID detector. Oven temperature was programmed from 50–200 °C, and N₂ (0.5 ml min⁻¹) was used as a carrier gas. The conversion was calculated on the basis of weight percent of substrate; the initial weight percent of toluene was divided by initial area percent (of GC) to get the response factor, which is multiplied with area percent after reaction, to get final weight percent of toluene remained after reaction. The conversion was calculated as follows:

$$\% \text{Conversion} = 100 \times \left[\frac{\text{initial wt.\%} - \text{final wt.\%}}{\text{initial wt.\%}} \right]$$

3. Results and discussion

3.1. Structural properties

3.1.1. Crystalline phase and crystallite size

X-ray diffraction pattern of sulfated zirconia samples, after calcination at 600 °C (Fig. 1), showed the presence of only tetragonal phase with $2\theta = 30.18$ [(1 1 1) reflection], 50.2 and 60.2 in all the samples. Crystallite size determined from X-ray diffraction data (Table 1) showed that all sulfated zirconia samples, prepared by the one-step as well as the two-step sol–gel technique, were of nano-crystalline nature with crystallite size in the range of 11–16 nm. The crystallite size of SZ-2 (11 nm) is lower than SZ-1 (14 nm) in the one-step preparation, and SZ-3 (11 nm) is lower than SZ-4 (16 nm) in the two-step preparation.

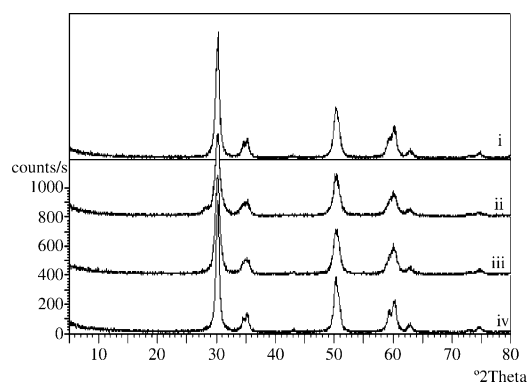


Fig. 1. X-ray diffraction pattern of SZ samples; (i) SZ-1, (ii) SZ-2, (iii) SZ-3, and (iv) SZ-4.

3.1.2. FT-IR studies

The FT-IR spectra of sulfated zirconia sample (SZ-2) calcined at 600 °C (Fig. 2a) showed the IR bands of SO₄²⁻ group in the region of 1200–900 cm⁻¹, with peaks at 1242, 1142, 1073, 1045 and 998 cm⁻¹, characteristic of inorganic chelating bidentate sulfate, which are assigned to asymmetric and symmetric stretching frequencies of S–O and S–O bonds [18]. The partially ionic nature of the S–O bond is responsible for the Bronsted acid sites in sulfated zirconia samples [15]. A broad peak at around 3400 cm⁻¹ and an intense peak at 1632–1628 cm⁻¹ (not shown in Fig. 2a) were also observed and were attributed to the ν_{O–H} stretching and δ_{O–H} bending mode of water, respectively, associated with zirconia and sulfate group. Similar spectra were obtained for SZ-1, SZ-3 and SZ-4 samples.

DRIFT spectra of dehydrated sample (SZ-2) after in situ activation at 450 °C under N₂ atmosphere shows a band at 1405 cm⁻¹, characteristic for covalently bonded S=O group,

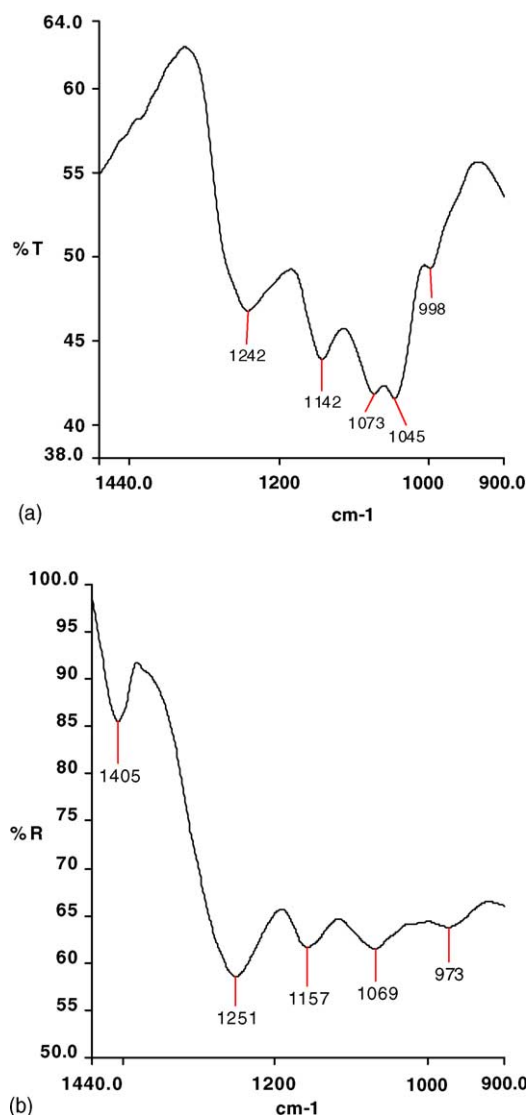


Fig. 2. (a) FT-IR spectra of SZ-2 at ambient temperature, and (b) DRIFT spectra of SZ-2 after in situ activation at 450 °C.

Table 1
Characterization of sulfated zirconia

Sample code	Crystalline phase	Crystallite size (nm)	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (Å)	Sulfur (%) before calcination	Sulfur (%) after calcination (600 °C)
SZ-1	T	14	101	0.152	58	3.49	1.3
SZ-2	T	11	118	0.190	62	3.78	1.6
SZ-3	T	11	101	0.087	35	4.35	1.4
SZ-4	T	16	81	0.081	42	5.23	1.3

which display Lewis acid sites in sulfated zirconia samples [18]. Similar spectra were obtained for SZ-1, SZ-3 and SZ-4 samples. It shows that removal of water molecules brings S=O double bond character in sulfate group. The peak area of 1405 cm⁻¹ band is in the range of 2.0–2.3 A cm⁻¹ for three (SZ-1, SZ-2 and SZ-3) samples, which shows the almost similar Lewis acid character in these three samples. However, the fourth, SZ-4, prepared in neutral medium shows higher (3.0 A cm⁻¹) peak area representing slightly higher Lewis acid character. Furthermore, less intensity of 1405 cm⁻¹ band (2–3 A cm⁻¹ peak area) reflects the presence of sulfate groups predominantly as Bronsted acid sites.

3.1.3. Sulfur analysis

Table 1 shows the data of sulfur analysis before and after calcination at 600 °C. It shows that the sulfur retained after calcination was in the range of 1.3–1.6 wt.% in both the one-step and the two-step processes; however, percent loading was higher in one-step (36–42%) than in the two-step (25–32%) samples. Sample SZ-2 showed the maximum (42%) and SZ-4 showed the minimum (25%) of sulfur loading after calcination at 600 °C.

3.2. Textural properties

N₂ adsorption–isotherm at 77 K measured for sulfated zirconia calcined at 600 °C (Fig. 3) was found to be of type IV, which is generally observed for mesoporous solids. However, there is a large increase in adsorption at higher relative pressure (p/p_0) showing the presence of larger size mesopores in the samples. The inflection point at around $p/p_0 = 0.4$ shows the capillary condensation within the mesopores

after the formation of monolayer. However, it is not sharp in all the samples, which reflects that the pores are not of uniform size and have broad distribution. Hysteresis observed for three samples (SZ-1, SZ-3 and SZ-4), is of type H2, except sample SZ-2, which showed a broad hysteresis of type H3, reflecting the presence of large mesopores, evidenced by the highest pore volume (0.19 cm³/g) and the average pore diameter (62 Å) and also the lack of well-defined pore structure in this sample. The surface area calculated from adsorption–isotherm using BET equation (Table 1) was in the range of 81–118 m²/g. Among all samples, SZ-2 has the highest surface area, pore volume and pore size, and SZ-4 has the lowest surface area. In general, one-step samples showed higher pore volume and pore size as compared to two-step samples. The pore size distribution in SZ-2 was observed to be very broad from 20 to 120 Å; however, in other three samples it ranges from 20 to 60 Å (Fig. 4). The peculiar textural properties of SZ-2 clearly indicates the effect of the order of the introduction of sulfuric acid prior to hydrolysis on the textural property of sulfated zirconia.

3.3. Catalytic activity

Table 2 shows the catalytic activity of the samples for the benzylation of toluene. In general, samples prepared by the one-step method show higher conversion (33–41%) in comparison to the samples prepared by the two-step synthesis (26–28%). Furthermore, among the samples prepared, SZ-2 shows higher catalytic activity, which may be explained in terms of its different structural and textural properties. We have observed [15] that benzylation of toluene with sulfated zirconia is catalyzed by ionic sulfur species. As discussed

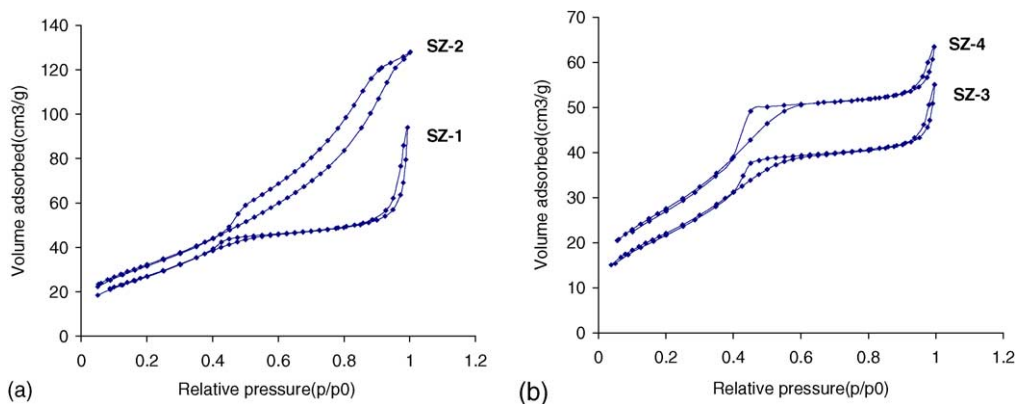


Fig. 3. N₂ Adsorption–desorption isotherms: (a) one-step samples, and (b) two-step samples.

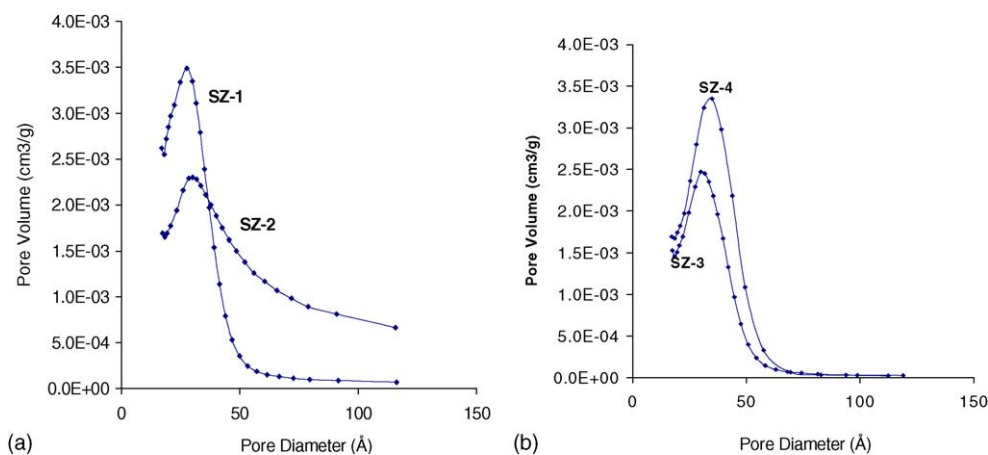


Fig. 4. Pore size distribution: (a) one-step samples, and (b) two-step samples.

Table 2
Catalytic activity of sulfated zirconia for benzylation of toluene

Catalyst	Conversion (wt.%)
SZ-1	33
SZ-2	41
SZ-3	26
SZ-4	28

Toluene:benzyl chloride = 1:1 M ratio; catalyst:toluene = 10:1 ratio-by-weight; reaction temperature = 100 °C; reaction time = 4 h.

above, FT-IR data clearly shows that most of the surface sulfur is present as ionic species, i.e., as Bronsted acid sites. The sample SZ-2 is observed to have higher sulfur loading compared to other samples (Table 1). Furthermore, higher surface area of SZ-2 (118 m²/g) also leads to better dispersion of sulfur species on the surface of the sample. The higher average pore diameter (62 Å) observed for SZ-2 may also facilitate the easy diffusion of the reactants and the products from the pores of the catalyst. Therefore, the higher catalytic benzylation activity of sample SZ-2 compared to other samples can be attributed to its higher sulfur retention, higher surface area along with larger average pore size diameter. Tichit [14] also reported higher *n*-hexane conversion with similarly prepared sulfated zirconia by the one-step method in comparison to others prepared by different routes.

4. Conclusion

Sulfated zirconia samples prepared by sol–gel technique using the one-step as well as the two-step strategies, are nanocrystalline having tetragonal phase. Structural and textural properties of samples prepared by both the methods are comparable; however, in the one-step method, sample prepared by adding sulfuric acid in zirconium alkoxide precursor before the addition of water showed improved structural and textural properties in terms of higher sulfur loading, small crystalline size, higher surface area, pore volume and thus, higher catalytic conversion. Therefore, this study reveals that the one-step strategy for preparing the sulfated zirconia may

be considered a better technique in comparison to the commonly used two-step technique.

Acknowledgements

Authors are thankful to NMITLI for financial support, Director P.K. Ghosh for encouragement, and to Dr.(Mrs.) Pragyna Bhatt, Mr. V.B.Boricha, Mr. Jince Sebastian, and C.D. Chudasama for instrumental analytical support.

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