

Synthesis and characterization of thermally stable mesostructured sulfated zirconia by a novel sulfate-assisted alcohothermal route

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Thermally stable mesostructured sulfated zirconia (MSZ) with a high surface area has been successfully prepared by a novel one-step synthetic method involving the alcohothermal processing of zirconium nitrate in the presence of ammonium sulfate. The MSZ samples were characterized using X-ray diffraction (XRD), N₂ adsorption measurements, thermal analysis (TG/DTA) and transmission electron microscopies (TEM). It is shown that the resulting mesostructured sulfated zirconia samples are tetragonal crystalline, which have a high specific surface area and a well-developed textural mesoporosity with narrow pore size distribution. Catalytic testing showed that the present mesostructured sulfated zirconia was much more active than conventional sulfated zirconia for *n*-butane isomerization.

KEY WORDS: mesostructured; sulfated zirconia; alcohothermal; ammonium sulfate; high surface area; *n*-butane isomerization.

1. Introduction

Sulfated zirconia (SZ) has attracted enormous recent interests as an environmentally friendly solid superacid due to its high catalytic activity in a number of industrially important reactions such as alkanes isomerization, alkylation and esterification [1–6]. The SZ obtained by the conventional hydroxide-sulfation method always has a relatively small specific surface area lower than 100 m² g⁻¹ [2]. However, high surface areas are often the main requirement for most alkane transformation reactions [2–5]. Hence, the usefulness of these materials is greatly compromised due to their limited specific surface area. Higher surface areas are attainable by supporting SZ materials on mesoporous materials such as MCM-41, SBA-15 and FSM-16 [7–12], but this was usually achieved at the expense of low catalytic activity for alkane isomerization, which is possibly due to a decrease of their acidic strength [10].

Recently, considerable efforts have been dedicated to the preparation of mesoporous sulfated zirconia material with a high specific surface area [13–16]. Most synthetic routes described so far are based on the surfactant-assisted methods, which typically yield products with amorphous framework walls [13–15]. Moreover, the use of the highly expensive and moisture sensitive zirconium alkoxides is required. One major problem of such materials is the structure collapse upon the surfactant removal by calcination [14]. Moreover, these materials always show relatively low activity for *n*-butane isomerization as compared with conventional sulfated zirconia [13]. The limited catalytic activity over

these materials is probably related to the absence of tetragonal crystalline phase in the amorphous framework walls, which is known to be necessary for the generation of super acidity in sulfated zirconia [15]. Hence, the development of a more convenient and practical methodology to prepare catalytically attractive mesostructured sulfated zirconia material based on a non-surfactant approach is essentially needed.

By coupling alcohothermal and supercritical fluid drying techniques, we have recently demonstrated that it is possible to prepare thermally stable ultrafine zirconia powder with a high surface area (HSA) and well-developed textural mesoporosity with a narrow pore size distribution [17,18], the formation of which has been attributed to the facile formation of a robust zirconia alcogel due to the alcohothermal processing. In the present work, we report a novel one-step non-surfactant synthetic route to mesostructured sulfated zirconia materials with a large surface area composed of tetragonal zirconia walls. The key to obtaining these materials is the formation of a mesostructured sulfated zirconia alcogel, obtained through the alcohothermal processing of an alcoholic solution of simple zirconium salts in the presence of appropriate amount of ammonium sulfate additive. Catalytic testing showed that the present alcohothermally-derived mesostructured sulfated zirconia was much more active than conventional sulfated zirconia for *n*-butane isomerization.

2. Experimental

2.1. Sample preparation

The one-step alcohothermal synthesis of mesostructured sulfated zirconia was carried out in an alcohol

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Table 1
Physicochemical properties of the MSZ materials synthesized with zirconium nitrate depending on the Zr/SO₄²⁻ ratio

Sample	Zr/SO ₄ ²⁻	C _{H₂SO₄} ^b (mol L ⁻¹)	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)	S content (wt%) ^c
MSZ-12	12	0.017	118	0.093	3.53	1.6
MSZ-8	8	0.025	143	0.108	3.24	2.0
MSZ-4	4	0.050	184	0.125	2.95	2.6
CSZ ^a	/	/	58	0.060	/	3.0

^a The reference catalyst of conventional sulfated zirconia prepared by impregnating Zr(OH)₄ with 0.5 M H₂SO₄ followed by calcination at 823 K for 3 h.

^b The concentration of H₂SO₄ in ethanol in the reaction system for the alcohothermal synthesis.

^c Sulfur content in the catalysts was estimated from the TG data based on the weight loss.

solution at 393 K with a zirconium compound (Zr(NO₃)₄·5H₂O) and appropriate amount of ammonium sulfate ((NH₄)₂SO₄) as additive with a Zr/SO₄²⁻ molar ratio of 12/1–4/1. Typically, Zr(NO₃)₄·5H₂O (8.58 g, 0.02 mol) was dissolved at 333 K in absolute ethanol (80 mL) to form a clear solution, and then a solution of sulfuric acid (1.67 ~ 5 mmol) dissolved in ethanol (20 mL) was added. The mixture was stirred at 333 K for 0.5 h and put into a 100 mL autoclave with a Teflon[®] liner. After sealed, the autoclave was maintained at 393 K for 4 h, and then allowed to cool to room temperature. A translucent alcogel was thus obtained. The alcogel was aged at room temperature for about 1 h followed by air-drying at 393 K for 12 h. Calcination of the resulting xerogel sample was conducted ranging from 673 to 1023 K in a muffle oven under air for 3 h. The resultant samples named as MSZ followed by a number (denotes the Zr/SO₄²⁻ molar ratio in the calcined catalysts) are summarized in table 1.

For comparison, conventional sulfated zirconia (denoted as CSZ) was prepared by impregnating Zr(OH)₄ with 0.5 M H₂SO₄ [2]. Briefly, one gram of dried Zr(OH)₄ was impregnated with 10 mL H₂SO₄ solution for 2 h with stirring, then filtered, dried at 373 K for 24 h, followed by calcination at 823 K for 3 h. The resulting solid has a BET surface area of 58 m² g⁻¹ and a sulfur content of 3 wt%.

2.2. Characterization

The X-ray powder diffraction (XRD) of the catalysts was carried out on a Germany Bruker D8Advance X-ray diffractometer using nickel filtered Cu K α radiation at 40 kV and 20 mA. The textural parameters have been measured using the BET method by N₂ adsorption and desorption at 77 K in a Micromeritics TriStar system. Simultaneous thermal gravimetric and differential thermal measurements (TG/DTG and DTA) were performed on a Perkin-Elmer 7 Series Thermal Analyzer apparatus in air flow (30 ml/min), using Al₂O₃ as a reference and with a heating rate of 10 K/min. For each experiment, 10–15 mg of sample was used. Transmission Electron Microscopy (TEM) was recorded digitally with

a Gatan slow-scan charge-coupled device (CCD) camera on a JEOL 2011 electron microscope operating at 200 kV. The samples were prepared by dispersing the powder products as a slurry in acetone, which was then deposited and dried on a holey carbon film on a Cu grid. Sulfur content in the catalysts was estimated from the TG data based on the weight loss.

2.3. Activity tests

The isomerization of *n*-butane to isobutane was carried out in a fixed-bed continuous flow reactor under atmospheric pressure. The catalyst samples were pelleted and sized to 40/60 mesh. Approximately 0.50 g of the catalyst was loaded into the reactor and then pretreated in flowing dry air (20 ml/min) at 450 °C for 3h, followed by a decrease to 250 °C, then a mixture of *n*-butane and H₂ (1:10 molar ratio) was fed at *n*-butane weight hourly space velocity (WHSV) of 0.3 h⁻¹. The reaction products were analyzed with an on-line gas chromatograph (Type GC-122, Shanghai) equipped with a FID.

3. Results and discussion

The XRD patterns of the present sulfate-assisted alcohothermally derived sulfated zirconia samples prepared with varied Zr/SO₄²⁻ mole ratio after calcination at 823 K are given in figure 1(a–c). The presence of a single diffraction peak in the small-angle region is indicative of a disordered mesostructure. In contrast, the XRD pattern for the comparative zirconia sample prepared by alcohothermal method in the absence of ammonium sulfate (not shown) exhibits no diffraction peak in the small angle range, suggesting the essential role of ammonium sulfate in the formation of mesoporosity. It can be seen that the intensity of diffraction peaks in the small angle range is greatly strengthened when the Zr/SO₄²⁻ mole ratio is decreased from 12 to 8, indicating the improved mesoporosity with increasing amount of ammonium sulfate at low SO₄²⁻ doping levels. However, the decrease in intensity of the low-angle diffraction peak is observed when a lower Zr/SO₄²⁻

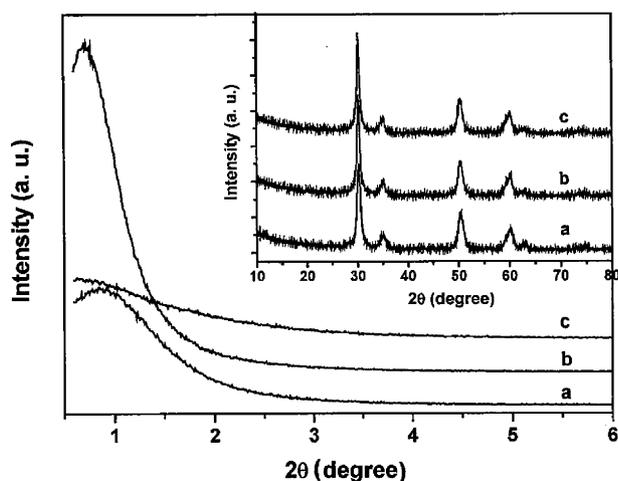


Figure 1. Powder XRD patterns of calcined MSZ samples prepared from alcohothermal method with various Zr/SO_4^{2-} ratio: (a) $Zr/SO_4^{2-} = 12$; (b) $Zr/SO_4^{2-} = 8$; (c) $Zr/SO_4^{2-} = 4$. The inset displays the diffraction patterns of the samples in the wide-angle regions.

mole ratio of 4 is used in the synthesis procedure. In the wide-angle regions of the XRD patterns (inset to figure 1) the as-prepared products exhibit reflection peaks assignable to well-defined tetragonal zirconia.

Figure 2 presents the N_2 adsorption-desorption isotherms and pore-size distributions for mesostructured sulfated zirconia samples obtained by calcination at 823 K. The nitrogen adsorption-desorption isotherms for all samples as shown in figure 2a exhibit type IV-like isotherms with a sharp inflection at $P/P_0 \approx 0.5$ (type H2 hysteresis) [19]. The pore size distributions are shown in figure 2b. The pore diameters are very narrow in distribution, and the pore size at the maximum of the distribution is systematically shifted from 3.53 to 2.95 nm against the Zr/SO_4^{2-} ratio used for the synthesis of the present MSZ materials. Table 1 lists the textural properties for the alcohothermal-derived sulfated zirconia samples prepared with varied Zr/SO_4^{2-} mole ratio. Note that the zirconia sample prepared in the absence of ammonium sulfate under otherwise identical conditions shows a type I isotherm, a wide pore size distribution and a low BET surface area of ca. $50 \text{ m}^2 \text{ g}^{-1}$ [18]. Both pore volumes and pore sizes are much larger for the samples prepared in the presence of ammonium sulfate. Based on the t -plot analysis, the contribution from micropores to the measured surface areas and pore volumes are negligible for the MSZ samples prepared in the presence of ammonium sulfate. It is therefore very clear that the mesoporous sulfated zirconia materials with a large surface area could be readily obtained when the alcohothermal reaction of zirconium nitrate was carried out in the presence of ammonium sulfate additive.

In figure 3, the surface area and pore volume of the mesostructured sulfated zirconia product ($Zr/SO_4^{2-} = 4$) prepared by the present sulfate-assisted alcohothermal approach is plotted against the calcination temperature

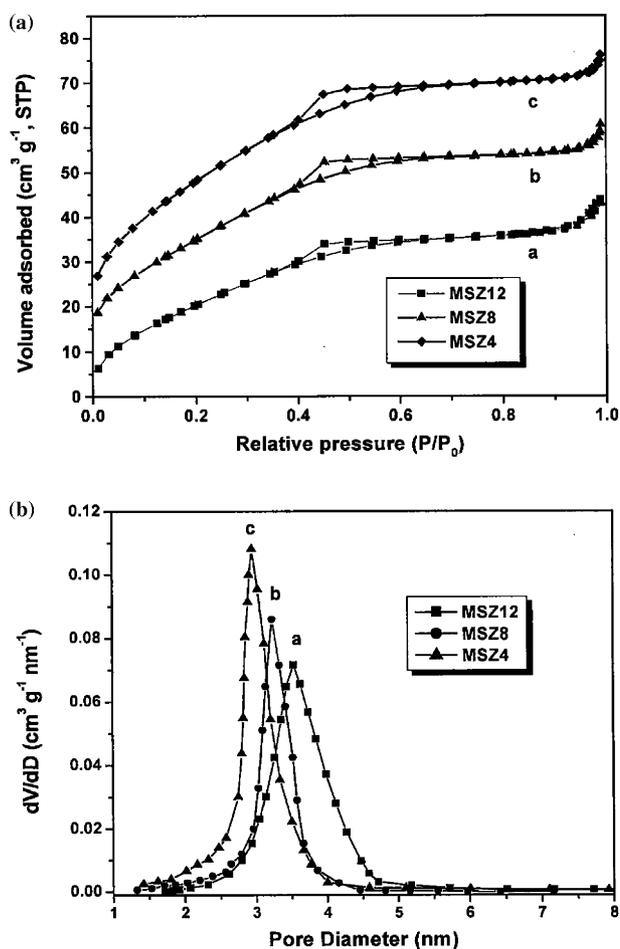


Figure 2. Nitrogen adsorption/desorption isotherms (a) and BJH pore-size distributions (b) for the alcohothermally derived mesostructured sulfated zirconia samples prepared with varied amounts of ammonium sulfate addition calcined at 823 K for 3 h. (a) $Zr/SO_4^{2-} = 12$; (b) $Zr/SO_4^{2-} = 8$; (c) $Zr/SO_4^{2-} = 4$.

in the range between RT and 1023 K, respectively. For comparison, the variation behavior of the surface area as well as the pore volume of the conventional sulfated zirconia sample synthesized by a conventional H_2SO_4 -impregnation method is also plotted. It is seen that the conventional sample suffers from a severely rapid decrease in the surface area and pore volumes upon calcination at temperature higher than 673 K, which is consistent with previous reported data for a common sulfated zirconia sample [2]. In sharp contrast, the MSZ-4 material has much larger surface area and pore volume than the reference sample even after calcination at temperatures above 923 K. It should also be noted that the mesoporosity could be retained even after heating the sample in air at temperatures up to 1023 K. Table 2 summarized the textural evolution of the new sulfated zirconia material upon thermal treatments, suggesting the remarkable thermal stability of the mesostructured sulfated zirconia as-prepared by the present alcohothermal method.

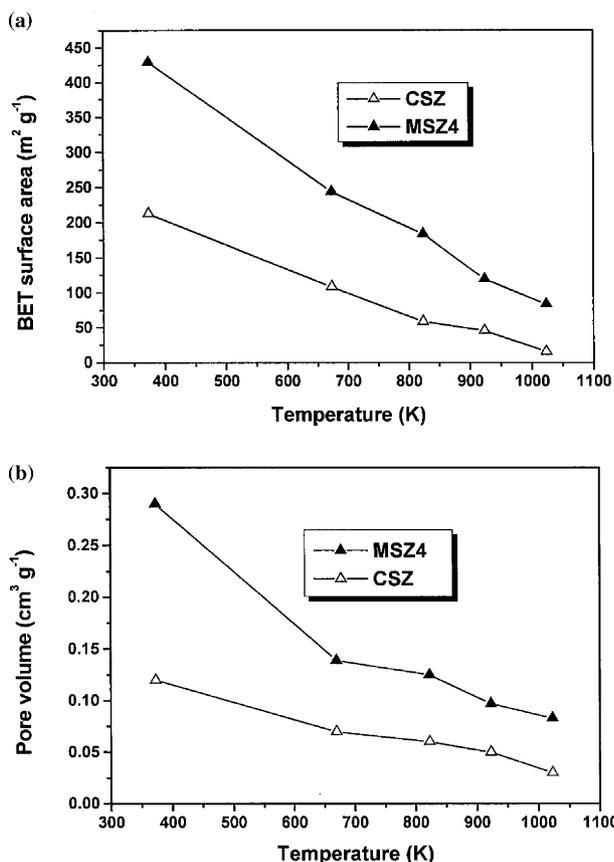


Figure 3. BET surface area (a) and pore volume (b) of sulfated zirconia samples calcined at various temperatures: the present MSZ-4 sample (ω) prepared with Zr/SO_4^{2-} mole ratio of 4 and the conventional sulfated zirconia sample (ϖ), respectively.

Figure 4 shows the thermal analysis of the sulfated zirconia xerogel sample prepared with Zr/SO_4^{2-} mole ratio of 4. The TG curve of the corresponding mesostructured sulfated zirconia xerogel presents at least three weight loss features over the whole range of temperature studies. The first below 150 °C is associated with endothermic response in DTA and is attributed to the desorption of physisorbed species related to losses of water. The second weight loss processes between 200 and 500 °C are highly exothermic and are assigned to the combustion and continuous decomposition of the covalently anchored ethoxy- groups over the surface of the sample. Similar results have been reported on the

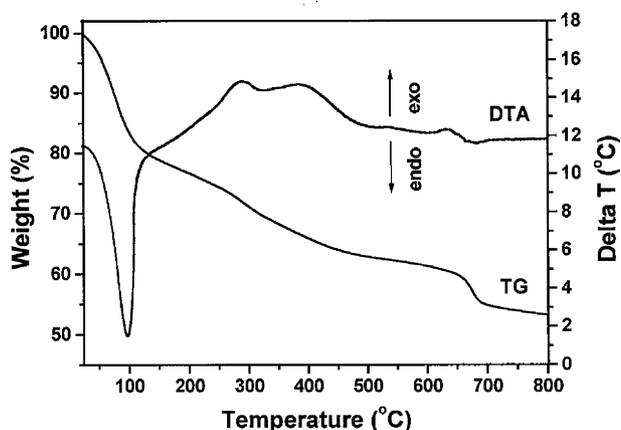


Figure 4. Thermal analysis (TG/DTA) data of the MSZ-4 sample obtained by the alcoholthermal method: heating rate 10 °C min⁻¹ in a 30 ml min⁻¹ flow of dry air; reference sample α -alumina.

zirconia precipitates obtained by thermal decomposition of zirconium alkoxides in organic media [18], where small amounts of alky groups covalently bonded to the surface oxygen atoms of the zirconia particles have been detected. The final weight loss feature centered at 680 °C is due to decomposition of SO_4^{2-} species on the sample, which leading to the ultimate formation of SO_3 moieties [7]. Based on the amount of weight loss, it is estimated that MSZ-4 contains 2.6 wt% of sulfur content, which is slightly lower than that of conventional sulfated zirconia (3.0 wt% of sulfur content).

The TEM images for the 823 K calcined samples prepared from the sulfate-assisted alcoholthermal approach show the presence of a network of mesopores with uniform size. As shown in figure 5, the MSZ-4 sample prepared with Zr/SO_4^{2-} mole ratio of 4/1 show typical wormhole like porous structure. The selected area electron diffraction patterns, shown as insets to figure 5, verified the presence of well-defined crystalline tetragonal zirconia in the mesostructured framework. These results clearly show that the pore walls of the as-made mesostructured products consist essentially of tetragonal zirconia.

Solvothermal process has been demonstrated to be a powerful technique for generating novel materials with unusual properties using low cost raw materials under mild conditions [20]. We have previously demonstrated that the alcoholthermal treatment of a simple alcoholic solution of $Zr(NO_3)_4 \cdot 5H_2O$ allows the facile formation of a robust zirconia alcogel which affords the fabrication of tetragonal zirconia aerogel with a high surface area [17]. On the other hand, it has been well known that the hydrolysis of $Zr(SO_4)_2 \cdot 4H_2O$ in water produces polymeric $[Zr(OH)_2SO_4OH_2]$ units that are capable of cross-linking through sulfate bridges [21,22]. It is therefore reasonable that similar polymeric units can be formed in the zirconia- $(NH_4)_2SO_4$ alcogel system. The essential role of $(NH_4)_2SO_4$ is to promote the gel-crosslinking reaction of the zirconium polymeric species in ethanol

Table 2

The thermal evolution of the textural properties of the alcoholthermally-derived MSZ-4 sample

Calcination temperature	BET surface area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Pore Diameter (nm)
As-synthesized	429	0.290	2.90
673 K	244	0.139	2.90
823 K	184	0.125	2.95
923 K	120	0.097	3.05
1023 K	84	0.083	3.20

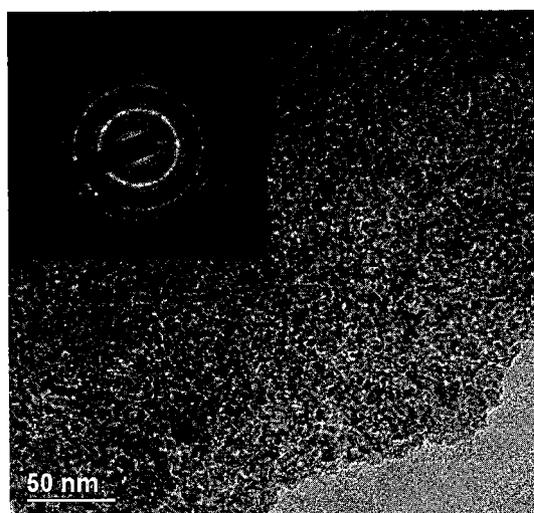


Figure 5. TEM images for the calcined MSZ-4 sample prepared by the alcohothermal method. The inset shows the electron diffraction patterns for this sample.

and afford the formation of a robust gel network based on the crosslinking via sulfate bridges, which may well account the present formation of mesostructured sulfated zirconia under alcohothermal conditions.

Catalytic activities determined for the catalytic cracking of *n*-butane at 250 °C over the zirconia samples were given in figure 6, where the performance of the catalysts calcined at 823 K was examined as a function of the initial $\text{Zr}/\text{SO}_4^{2-}$ molar ratio used in the precursor solution. Figure 6a depicts the variation of the rate of *n*-butane isomerization as a function of time on stream. The conversion profiles show strong activity decay during the first 30 min on stream, followed by a slower deactivating region. Similar initial high rates of conversion for *n*-butane isomerization has already been reported by Mou *et al.* for various mesoporous molecular sieve supported SZ materials [8–10]. One can also see that for the present MSZ samples prepared by the alcohothermal method, *n*-butane conversion increased in the order of $\text{Zr}/\text{SO}_4^{2-} = 12 < 8 < 4$. This result can be rationalized by considering the surface area and the amount of sulfate present as functions of the initial $\text{Zr}/\text{SO}_4^{2-}$ molar ratio, as shown in table 1. Moreover, it is noticeable that the zirconia samples prepared from the present alcohothermal method displays much higher initial catalytic activity for *n*-butane conversion than the reference catalyst of sulfated zirconia prepared by a conventional hydroxide- H_2SO_4 impregnation method. Additionally, the selectivity to isobutane (Figure 6b) over MSZ samples is also slightly higher than that over conventional sulfated zirconia sample. The pronounced performance for *n*-butane isomerization demonstrates clearly that the present new mesostructured sulfated zirconia material is strongly acidic, suggesting that it is an excellent candidate catalyst for alkanes transformations.

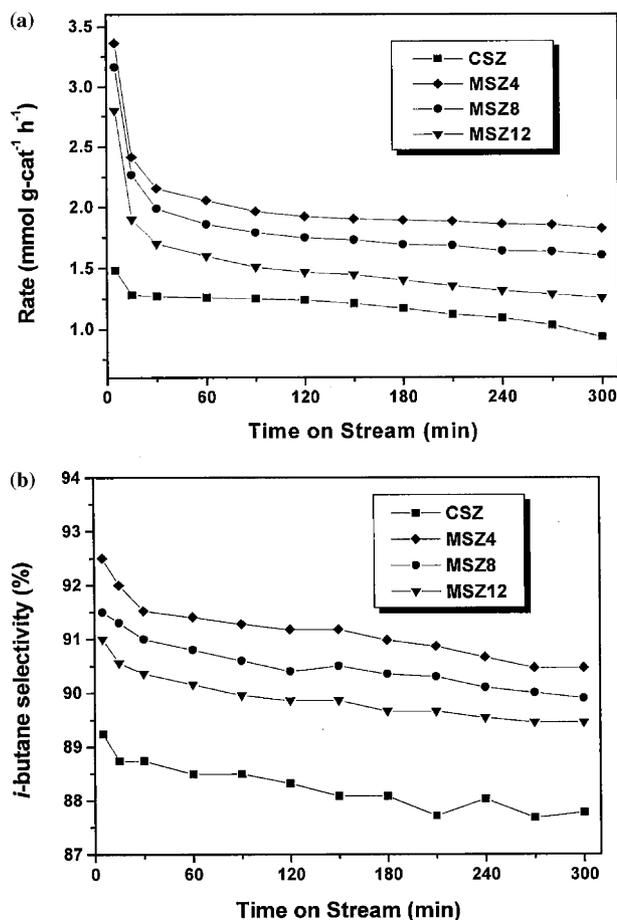


Figure 6. Rate of *n*-butane isomerization (a) and selectivity to isobutane (b) as a function of time on stream for MSZ samples and CSZ reference catalyst at 250 °C.

4. Conclusions

In summary, we have successfully demonstrated the novel synthesis of thermally stable mesostructured sulfated zirconia with a high surface area by a mild alcohothermal synthetic approach. The phases, morphology and microstructure of the derived sulfated zirconia samples were characterized using combined techniques of XRD, TG/DTA, N_2 adsorption measurements, and TEM. The results showed that the as-prepared mesostructured sulfated zirconia is tetragonal crystalline. Catalytic evaluations show that the present mesostructured sulfated zirconia materials are much more active than conventional sulfated zirconia for *n*-butane isomerization.

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References

- [1] A. Corma, *Chem. Rev.* 95 (1995) 559.
- [2] X. Song, A. Sayari, *Catal. Rev. Sci. Eng.* 38 (1996) 320.
- [3] T. Jin, T. Yamaguchi and K. Tanabe, *J. Phys. Chem.* 90 (1986) 4797.
- [4] K. Arata, *Appl. Catal. A* 146 (1996) 3.
- [5] V. Adeeva, H.Y. Liu, B.Q. Xu and W.M.H. Sachtler, *Top. Catal.* 6 (1998) 61.
- [6] Y.D. Xia, W.M. Hua, Y. Tang and Z. Gao, *Chem. Commun.* (1999) 1899.
- [7] Q.H. Xia, K. Hidajat and S. Kawi, *J. Catal.* 205 (2002) 318.
- [8] C.L. Chen, S. Cheng, H.P. Lin, S.T. Wong and C.Y. Mou, *Appl. Catal. A* 215 (2001) 21.
- [9] C.L. Chen, T. Li, S. Cheng, H.P. Lin, C.J. Bhongale and C.Y. Mou, *Micropor. Mesopor. Mater.* 50 (2001) 201.
- [10] Y.Y. Sun, L. Zhu, H. Lu, R. Wei, S. Lin, D. Jiang and F.S. Xiao, *Appl. Catal. A* 237 (2002) 21.
- [11] T. Lei, W.M. Hua, Y. Tang, Y.H. Yue and Z. Gao, *J. Nol. Catal. A* 170 (2001) 195.
- [12] H. Matsushashi, M. Tanaka, H. Nakamura and K. Arata, *Appl. Catal. A* 208 (2001) 1.
- [13] Y.Y. Huang, T.J. McCarthy and W.M.H. Sachtler, *Appl. Catal. A* 148 (1996) 135.
- [14] U. Ciesla, S. Schachi, G.D. Stucky, K.K. Unger and F. Scucchi, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 541.
- [15] X. Yang, F.C. Jentoft, R.E. Jentoft, F. Girgsdies and T. Ressler, *Catal. Lett.* 81 (2002) 25.
- [16] Y. Sun, L. Yuan, W. Wang, C.L. Chen and F.S. Xiao, *Catal. Lett.* 87 (2003) 57.
- [17] J.C. Hu, Y. Cao, J.F. Deng and K.N. Fan, *Chem. Lett.* 5 (2001) 398.
- [18] Y. Cao, J.C. Hu, Z.S. Hong, J.F. Deng and K.N. Fan, *Catal. Lett.* 81 (2002) 107.
- [19] K.S.W. Sing, *Pure Appl. Chem.* 54 (1982) 201.
- [20] Y. Jiang, Y. Wu, S.Y. Zhang, C.Y. Xu, W.C. Yu, Y. Xie and Y.T. Qian, *J. Am. Chem. Soc.* 122 (2000) 12383.
- [21] J. Livage, M. Henry and C. Sanchez, *Prog. Solid State Chem.* 18 (1988) 259.
- [22] J.A. Navio, G. Colón, P.J. Sánchez-Soto and M. Macias, *Chem. Mater.* 9 (1997) 1256.