

Improved catalytic activity and stability of mesostructured sulfated zirconia by Al promoter

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Abstract

Al-promoted mesostructured sulfated zirconia (Al-MSZ-5) has been successfully synthesized from the template of triblock polymer surfactant (P123) in aqueous solution. Mesostructured Al-MSZ-5 shows high thermal stability, and it can preserve its characteristic mesostructures until calcination at 650 °C. In contrast, the mesostructure of mesoporous sulfated zirconia (MSZ-5) will be destroyed during calcination at 600 °C. Catalytic data for *n*-butane isomerization show that the Al-MSZ-5 exhibits higher catalytic activity and better stability than both MSZ-5 and conventional Al-promoted sulfated zirconia (Al-SZ). The Al-MSZ-5 sample was characterized by XRD, bright-field and dark-field TEM images, N₂ adsorption isotherms, NMR, TG-DTA, IR, and numerous other techniques. The results suggest that Al-MSZ-5 has worm-like mesopores, and that the mesostructured walls contain tetragonal crystalline ZrO₂. Such unique structural features might be responsible for the observed large surface area, high catalytic activity for *n*-butane isomerization, and high thermal stability of mesostructured Al-MSZ-5.

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1. Introduction

Sulfated zirconia, as one example of solid superacids, has attracted much attention because it is potentially important for industrial reactions such as hydrocarbon isomerization, alkylation, and etherification [1–11]. However, a rapid deactivation of this catalyst has often been observed in these catalytic reactions. To improve the lifetime of sulfated zirconia in catalysis, various promoters were introduced. The addition of small amounts of Fe and Mn [12–14], and Ni [15] was found to increase the activity in *n*-butane isomerization, but the catalysts still deactivated quickly. The addition of small amounts of Pt is able to improve the stability of the catalyst [16], but Pt is too expensive. Recently, much attention has been paid to the sulfated zirconia promoted by Al (cheaper metal) since it significantly enhances the catalytic activity and stability of sulfated zirconia [17–19]. The

experimental results show that Al-promoted sulfated zirconia (3 mol% as Al₂O₃) prepared by co-precipitation method is a better catalyst for *n*-butane isomerization [17–21].

It is well known that catalysis is a surface phenomenon, and catalytic activity is strongly influenced by the surface area of the catalyst. In 1992, it has been reported that mesoporous materials with highly ordered pore structures have potential applications in catalysis, adsorption and separation of molecules because of their high surface areas, large pore volume, and tunable uniform pore structures, but they show relatively weak acid strength [22–28]. To increase the acid strength of mesoporous materials, sulfated zirconia was introduced into the mesopores such as MCM-41 [29–34], FSM-16 [35], and SBA-15 [36,37]. The SO₄²⁻/ZrO₂ incorporation approach has successfully generated materials that show stronger acid strength than conventional mesoporous materials. However, the success is limited because some pores are blocked by SO₄²⁻/ZrO₂ and the surface area of the materials is thus significantly reduced [29–37]. Most importantly, these mesoporous materials modified by sulfated zirconia show lower acid strength than conventional sulfated

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zirconia (SZ) [34]. Therefore, mesoporous sulfated zirconia with strong acid strength and large surface area is desirable.

There have been a number of successful examples for the preparation of mesoporous sulfated zirconia [38–42]. Schuth and coworkers [38] firstly have synthesized porous zirconium oxo phosphate with high surface area by a surfactant-assisted synthesis; Jentoft and coworkers [39] have successfully prepared sulfated zirconia with ordered mesopores using hexadecyltrimethylammonium bromide (CTAB) as a template; Sachlter and coworkers [40] and Kydd and coworkers [41] have reported synthesis of mesoporous sulfated zirconia by using template of neutral amines; Stein and coworkers [42] have obtained macroporous crystalline sulfated zirconium dioxide templated with colloidal crystals. Notably, although mesostructured sulfated zirconia materials have been successfully synthesized, their catalytic activities for *n*-butane isomerization are still relatively low or similar [39,40], compared with that of conventional sulfated zirconia.

More recently, we have synthesized a mesostructured sulfated zirconia, designated as MSZ-5, using a triblock copolymer, which exhibits higher catalytic activity for *n*-butane isomerization than that of conventional sulfated zirconia, but its thermal stability of mesostructures and anti-deactivation ability are still relatively poor [43]. We demonstrate here that the introduction of a small amount of Al (3 mol% as Al₂O₃) into the walls of mesostructured sulfated zirconia results in significant improvement of mesostructural thermal stability. Sample characterization shows that Al-promoted mesostructured sulfated zirconia exhibits higher catalytic activity and better anti-deactivation ability for *n*-butane isomerization than non-promoted mesostructured sulfated zirconia and conventional Al-promoted sulfated zirconia.

2. Experimental

2.1. Preparation of catalysts

Al-promoted mesostructured sulfated zirconia was prepared as follows: (1) 1 g of P123 (EO₂₀PO₇₀EO₂₀) was dissolved in 25 ml of water, followed by addition of ZrOCl₂·8H₂O and AlCl₃·6H₂O (3 mol% as Al₂O₃). (2) After stirring for 6 h at 45–60 °C, NH₃·H₂O was slowly added into the solution, forming the gel. (3) After stirring for 2 h, the gel was transferred to autoclaves at 100 °C. After placement for 24 h, the sample was filtered, washed with distilled water, and dried, followed by extraction of triblock polymer surfactant with ethanol at room temperature. (4) The extracted sample was further immersed in a 0.5 mol/l of (NH₄)₂SO₄ solution for 30 min, followed by calcination at 650 °C for 3 h. The sample is designated as Al-MSZ-5.

For comparison, conventional Al-promoted sulfated zirconia designated as Al-SZ (3 mol% as Al₂O₃) was prepared by immersing Al(OH)₃–Zr(OH)₄ in 0.5 mol/l of (NH₄)₂SO₄ solution for 30 min, followed by calcination at 650 °C for

3 h. The mesoporous zirconium sulfate (MZS) was synthesized as follows: hexadecyltrimethylammonium bromide (1.0934 g) was dissolved in H₂O (15 g), and Zr(SO₄)₂·4H₂O (3.554 g) dissolved in H₂O (10 g) was added. The mixture was stirred for 3 h at room temperature and then was transferred to autoclaves at 100 °C for 24 h. The product was filtered, washed with distilled water, and dried. The sample was designed as MZS. The conventional sulfated zirconia (SZ) and mesoporous sulfated zirconia (MSZ-5) were prepared using published procedures [43].

2.2. Characterization of catalysts

Powder X-ray diffraction (XRD) patterns were recorded on a Siemens D5005 diffractometer (45 kV, 40 mA) using nickel-filtered Cu K α radiation with wavelength $\lambda = 1.5406 \text{ \AA}$. Diffraction patterns were collected under ambient conditions in the 2θ range of 0.4–10° at a scanning rate of 0.6° min⁻¹ and in the 2θ range of 20–80° at a scanning rate of 4° min⁻¹. Nitrogen adsorption isotherms were obtained at –196 °C on a Micromeritics ASAP 2010 Gas Sorption and Porosimetry system. Samples were normally prepared for measurement by degassing at 150 °C under vacuum until a final pressure of 1×10^{-3} Pa was reached. Pore size distributions were calculated using the BJH method. Fourier transform infrared (FT-IR) spectroscopy was performed with a Nicolet Impact 410 infrared spectrometer using KBr pellets. The transmission electron micrograph (TEM) was taken on a JEOL 3010 microscope operating at an accelerating voltage of 300 kV. ²⁷Al NMR spectra were recorded on Varian Infinity plus 400 spectrometer and chemical shifts were referenced to Al(H₂O)₆³⁺. Thermogravimetric and differential thermal analysis (TG–DTA) were carried out on a NETZSCH STA 449C with a heating rate of 20 °C/min from room temperature to 1100 °C. The sample was mounted horizontally and purged with a synthetic airflow of 100 ml/min.

2.3. *n*-Butane isomerization

The isomerization of *n*-butane to isobutane was carried out in a fixed-bed continuous flow reactor under atmospheric pressure. 0.5 g of the catalyst was loaded into the reactor and then pretreated in flowing dry air (20 ml/min) at 450 °C for 3 h, followed by a decrease of the temperature to 250 °C. The ratio of *n*-butane/H₂ (v/v) is at 1/10 with *n*-butane weight hourly space velocity (WHSV) of 0.62 h⁻¹. An on-line gas chromatograph equipped with FID was used to analyze the reaction products.

3. Results

3.1. X-ray diffraction

Fig. 1 shows XRD patterns of Al-MSZ-5 in both small- and wide-angle regions. The presence of a single diffraction

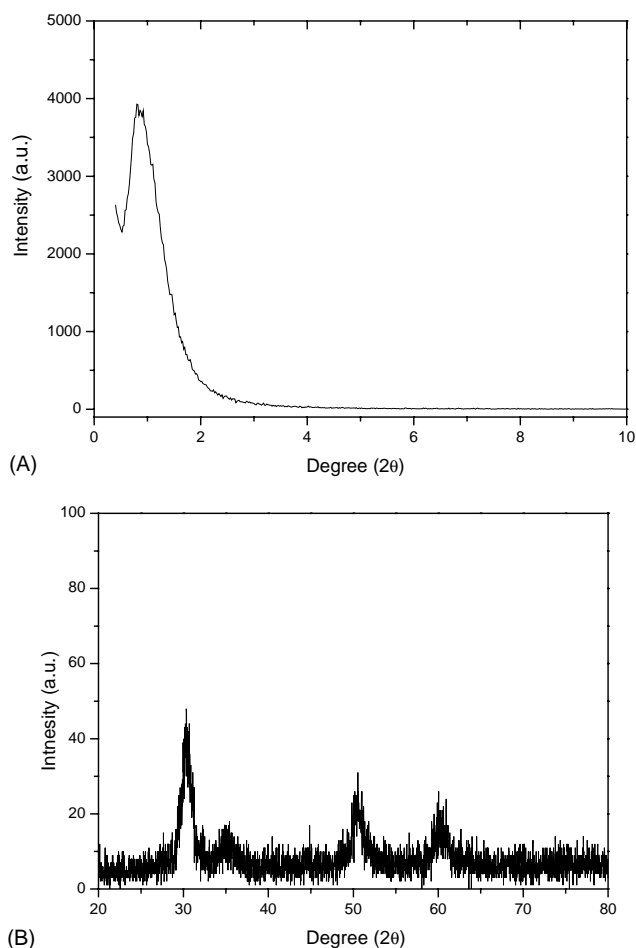


Fig. 1. (A) Small-angle and (B) wide-angle XRD patterns of Al-MSZ-5.

line at ca. 0.84° (Fig. 1A) in the small-angle region is indicative of a disordered mesostructure. In the wide-angle region of the XRD patterns (Fig. 1B), Al-MSZ-5 exhibits diffraction peaks at ca. 30° , 35° , 50° and 60° , assigned to tetragonal phase of crystalline ZrO_2 . These results suggest that crystalline tetragonal ZrO_2 exists in the mesostructured walls of Al-MSZ-5.

Fig. 2 shows XRD patterns of various samples. The as-synthesized mesoporous zirconium sulfate shows three reflections (ca. 2.1° , 3.7° and 4.2°) in the small angle region, but no reflections can be observed at wide angles (Fig. 2A). These results suggest that MZS is an ordered mesoporous material with amorphous walls. Nevertheless, after calcination at 550°C for 3 h, the peaks in the small-angle region disappear completely, indicating that MZS has lost its mesostructure (Fig. 2B). This may be due to incomplete condensation of the walls in the synthesis of MZS [38]. In contrast, mesostructured sulfated zirconia [43] shows higher thermal stability, and it can preserve its mesostructure during calcination at 550°C (Fig. 2C). However, calcination at 600°C leads to the loss of its mesostructure (Fig. 2D). Interestingly, after a little Al is introduced into the mesostructured sulfated zirconia (Al-MSZ-5), its mesostructure is

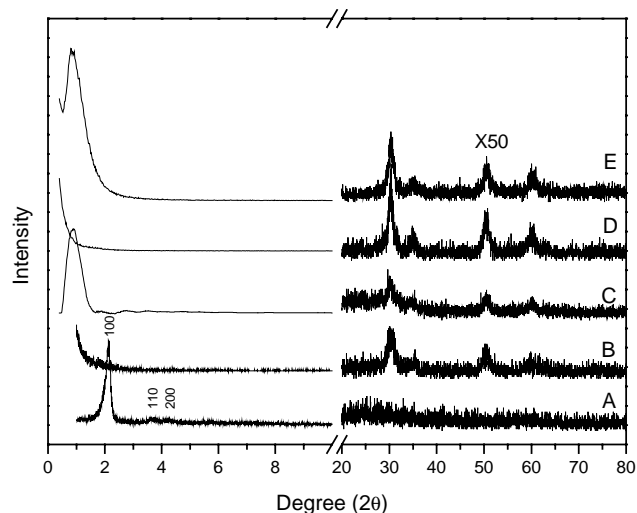


Fig. 2. Small-angle and wide-angle XRD patterns of (A) as-synthesized MZS, (B) MZS calcined at 550°C for 3 h, (C) MSZ-5, (D) MSZ-5 calcined at 600°C for 3 h, and (E) Al-MSZ-5 calcined at 650°C for 3 h.

stable over 650°C (Fig. 2E). Obviously, the presence of Al species can stabilize the mesostructure remarkably.

3.2. Transmission electron microscopy

The bright-field TEM image of Al-MSZ-5 (Fig. 3A) exhibits worm-like mesopores. The selected-area electron diffraction pattern (Fig. 3A inset) has verified the presence of crystalline tetragonal ZrO_2 in the mesostructured walls of Al-MSZ-5, displaying characteristic diffuse electron diffraction rings. Moreover, the dark-field TEM image of the same area (Fig. 3B) shows a lot of light dots, indicating the presence of crystalline ZrO_2 . This confirms that the mesostructured walls of Al-MSZ-5 contain nanocrystalline tetragonal zirconia.

3.3. N_2 adsorption–desorption isotherm

Fig. 4 shows the N_2 adsorption–desorption isotherm of Al-MSZ-5. It is very interesting to note that the isotherm exhibits a typical adsorption curve of type IV. An increasing step occurs in the curve at a relative pressure $0.5 < P/P_0 < 0.7$, which is assigned to the contribution of mesoporous structures. Correspondingly, pore size estimation for Al-MSZ-5 shows the pore distribution at a mean value of 4.5 nm, in good agreement with the TEM results.

Furthermore, the BET surface area and pore volume of Al-MSZ-5 are as high as $190\text{ m}^2/\text{g}$ and $0.26\text{ cm}^3/\text{g}$, respectively. In contrast, we have prepared conventional SZ and Al-SZ, showing the BET surface area and pore volume at $85\text{--}115\text{ m}^2/\text{g}$ and $0.09\text{--}0.12\text{ cm}^3/\text{g}$, these values are much lower than those of Al-MSZ-5. The parameters of BET surface area, pore volume, and pore diameter of various samples including Al-MSZ-5, Al-SZ, and SZ are summarized in Table 1.

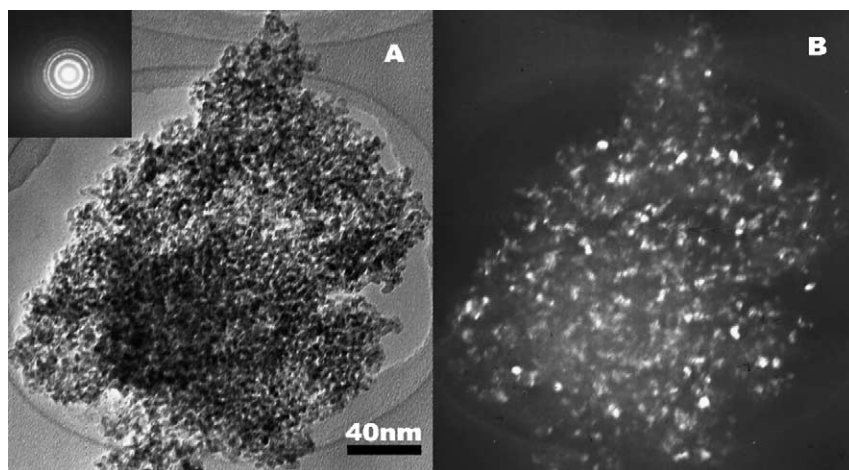


Fig. 3. TEM images of Al-MSZ-5: (A) bright-field image (inset electron diffraction patterns obtained on the image area), and (B) dark-field image on the same area.

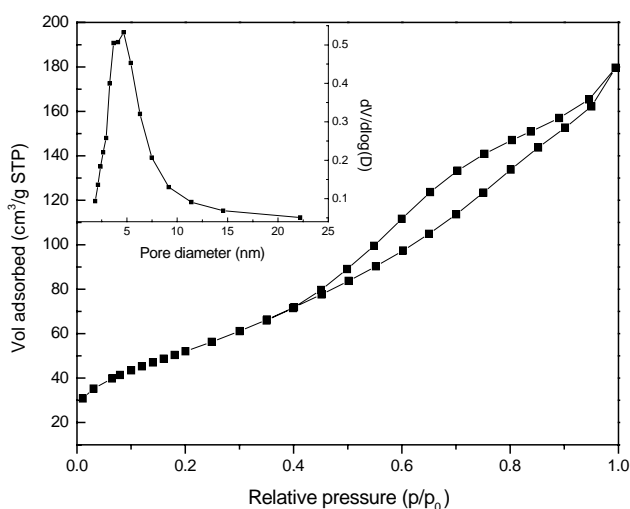


Fig. 4. N₂ adsorption/desorption isotherms and pore size distribution of Al-MSZ-5.

3.4. NMR spectroscopy

Fig. 5 shows ²⁷Al MAS NMR spectra of Al-MSZ-5 and Al-SZ. Both samples exhibit a sharp peak at around -5.0 ppm and a broad peak centered at around 18 ppm, though the peak widths and peak intensities are different. This is slightly different from the result reported by Gao and coworkers that gives only a sharp resonance signal at

3.7 ppm corresponding to octahedral Al species [18]. However, the Al-promoted tungstated zirconia prepared by Mou and coworkers also shows two resonance signals at around 0 and 30 ppm in ²⁷Al MAS NMR spectroscopy [44]. They suggest that the resonance at around 0 ppm is correspondent to the octahedral Al species and they assign the broad resonance centered at around 30 ppm to Al species in disordered state. Therefore, we suggest that the chemical shift at around -5.0 ppm should be attributed to octahedral Al sites and the broad shoulder peak centered at around 18 ppm is due to Al species in disordered state. Obviously, the Al species in Al-MSZ-5 are similar to those in conventional Al-SZ.

3.5. Thermal analysis

Fig. 6 shows TG curves of Al-SZ and Al-MSZ-5. Both exhibit two weight losses at 25–250 and 800–1100 °C, which are assigned to the removal of water and the decomposition of sulfate, respectively. However, it is noteworthy that the weight loss of Al-MSZ-5 sample is greater than that of Al-SZ. Below 300 °C, Al-MSZ-5 and Al-SZ lose 5.4 and 3.9 wt.%, respectively. In the region of 800–1100 °C, the weight loss of Al-MSZ-5 and Al-SZ are at 5.4 and 4.2%, respectively. These results indicate that Al-MSZ-5 contains more sulfate species than Al-SZ, which is important for sulfated zirconia with more strong acidic sites because sulfate species are a key for the formation of strong acid strength [9,11,18].

Table 1

Characterization data of SZ, Al-SZ, and Al-MSZ-5

Samples	Calcination temperature (°C)	BET area (m ² /g)	Pore volume (cm ³ /g)	Sulfate content ^a (wt.%)	Sulfate density (SO ₄ ²⁻ /nm ²)	Surface coverage (%)
SZ	650	84	0.09	3.5	2.6	65.0
Al-SZ	650	115	0.12	4.2	2.3	57.5
Al-MSZ-5	650	190	0.26	5.4	1.8	45.0

^a Sulfate content is estimated by TG.

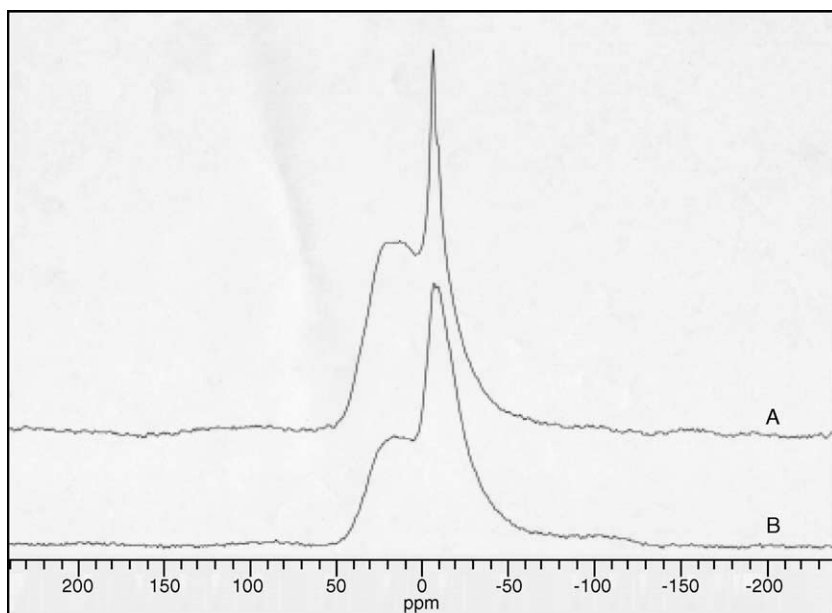


Fig. 5. ^{27}Al MAS NMR spectra of (A) Al-SZ and (B) Al-MSZ-5.

3.6. IR spectroscopy

Fig. 7 shows IR spectra of Al-SZ and Al-MSZ-5. Both samples exhibit obvious bands at 1033, 1072, 1147, and 1274 cm^{-1} that are assigned to typical frequencies for chelating bidentate sulfate ion coordinated to zirconium cation [11], indicating that sulfur species in Al-MSZ-5 and Al-SZ is very similar.

3.7. *n*-Butane isomerization

Fig. 8 shows catalytic activities for *n*-butane isomerization over various samples, and Table 2 presents activities at reaction times of 5 and 180 min. Notably, mesoporous sulfated zirconia with amorphous walls (MSZ) exhibits low catalytic

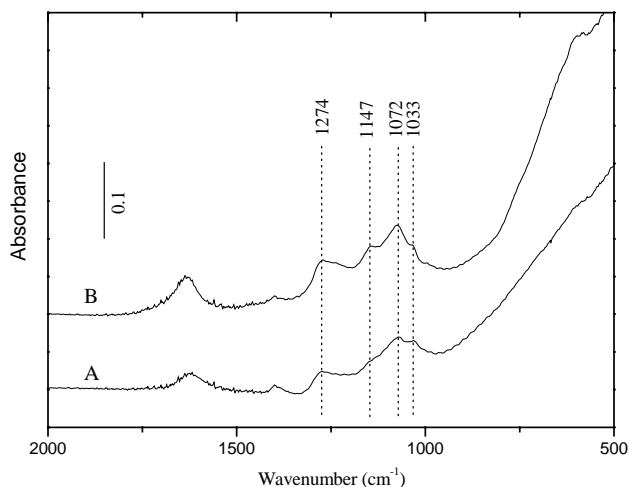


Fig. 7. IR spectra of (A) Al-SZ and (B) Al-MSZ-5.

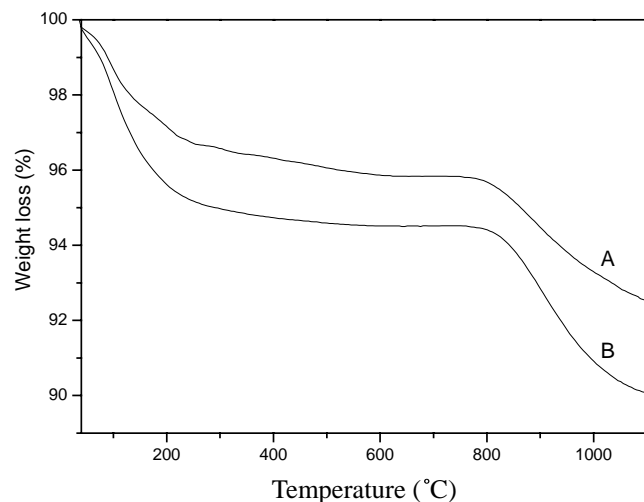


Fig. 6. TG curves of (A) Al-SZ and (B) Al-MSZ-5.

activity ($<1\text{ mmol/g h}$), although its surface area is relatively high ($202\text{ m}^2/\text{g}$) [39]. In contrast, conventional sulfated zirconia with tetragonal crystalline phase (SZ) gives high activity, reaching to the values of $1.45\text{--}2.13\text{ mmol/g h}$ after 5 min,

Table 2
Catalytic activities for 5 and 180 min on various samples

Samples	References	Calcination temperature ($^{\circ}\text{C}$)	Activity (mmol/g h)	
			5 min	180 min
SZ	[43], this work	550	1.45	1.05
SZ	[43], this work	650	2.13	1.43
MSZ	[39]	540	<1.0	<1.0
MSZ-5	[43], this work	550	2.79	1.32
Al-SZ	[17–21], this work	650	3.79	2.71
Al-MSZ-5	This work	650	4.29	3.26

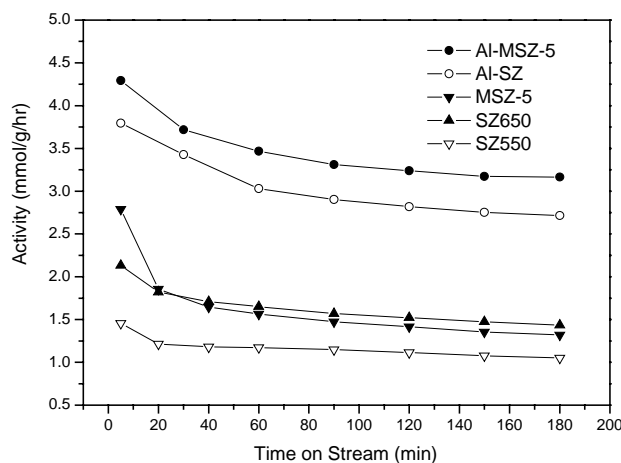


Fig. 8. Catalytic activity vs. reaction time on stream in *n*-butane isomerization.

even if the surface area is relatively low (84–112 m²/g). Obviously, the presence of tetragonal crystalline phase in sulfated zirconia is one of the most important factors for high activity in *n*-butane isomerization.

Furthermore, we find that calcination temperature has a great effect on the activity of the catalyst for *n*-butane isomerization, and that the calcination at 650 °C is suitable for preparation of sulfated zirconia. For example, SZ calcined at 650 °C (2.13 mmol/g h after 5 min) is more active than SZ calcined at 550 °C (1.45 mmol/g h after 5 min).

It is worthy to note that Al-SZ shows higher activity and stability than SZ, indicating that the Al promoter plays a positive role in *n*-butane isomerization, in agreement with the results reported previously [17–21]. Most importantly, it is observed that Al-promoted mesostructured sulfated zirconia with tetragonal crystalline ZrO₂ exhibits both the highest activity (4.29 mmol/g h after 5 min) and the best anti-deactivation ability (3.26 mmol/g h after 180 min) among all samples.

4. Discussion

4.1. Thermal stability of mesostructures

It is well known that calcination temperature is very important for the formation of superacidic sites during preparation of sulfated zirconia [9,11]. Generally, calcination at 650 °C is suitable for the conventional sulfated zirconia, but this temperature cannot be applied to the preparation of mesoporous sulfated zirconia, because the stability of mesostructures for these materials is lower than 650 °C. For example, thermal stability of ordered mesostructured sulfated zirconia with amorphous walls (MSZ) is conserved up to 550 °C [39]. Mesostructures of sulfated zirconia with tetragonal crystalline phase templated by hexadecane amine [40] and triblock polymer surfactant [43] are sta-

ble at 550–600 °C. Therefore, improvement of mesostructured thermal stability is greatly important for preparation of mesostructured sulfated zirconia with high catalytic activity.

Interestingly, Al-promoted mesostructured sulfated zirconia with tetragonal crystalline ZrO₂ is remarkably stable for calcination at 650 °C. In comparison, all other mesostructured materials failed under these conditions. It is quite clear that the thermal stability of mesostructure for Al-MSZ-5 is the highest among all the mesostructured sulfated zirconia samples examined. Obviously, the presence of Al species can stabilize the mesostructure effectively. One possibility is that the presence of Al species could prevent the formation of large crystallites, thus stabilizing the tetragonal phase. The estimation of crystalline size for non-promoted mesoporous zirconia calcined at 600 °C and Al-promoted mesoporous zirconia calcined at 650 °C by using Scherrer's equation is at 8 and 6 nm, respectively. A similar phenomenon has been found by other groups [20,45–47]. They reported that the effect of alumina was to prevent the formation of large crystallites, resulting in the stable tetragonal phase [20,45–47].

4.2. Catalytic activity for *n*-butane isomerization

Many factors can influence catalytic activity of sulfated zirconia catalysts for *n*-butane isomerization such as preparation procedure, crystalline phase of zirconia, calcination temperature, sulfate species, surface area, activation temperature, and water content [9,43,48–54]. Usually, the tetragonal phase of ZrO₂ is believed to be a key for the formation of superacids [9]. As observed in Table 2, ordered mesoporous sulfated zirconia with amorphous walls exhibits relatively low activity (<1.0 mmol/g h), whereas mesostructured sulfated zirconia with tetragonal crystalline ZrO₂ shows high activity (1.43–4.29 mmol/g h). These results confirm the importance of the tetragonal phase of zirconia for the formation of superacids.

As shown in Fig. 8, all sulfated zirconia samples have tetragonal crystalline ZrO₂, but their activities are still greatly different. For example, if one increases the calcination temperature from 550 to 650 °C, the initial activity of SZ increases from 1.45 to 2.13 mmol/g h, indicating the importance of calcination temperature. Under the same calcination temperature of 550 °C, mesostructured sulfated zirconia prepared from triblock polymer surfactant exhibits higher activity than conventional SZ, indicating the importance of the surface area of the catalyst. Interestingly, Al-promoted sulfated zirconia (Al-SZ) shows much higher catalytic activity and better anti-deactivation ability than conventional SZ, indicating the importance of Al promoter. Particularly, Al-promoted mesostructured sulfated zirconia shows the highest activity in all samples. This is reasonably assigned to the combination of advantages of large surface area, tetragonal crystalline, suitable calcination temperature, and positive effect of Al promoter in mesostructured sulfated zirconia.

4.3. The phase of mesostructured sulfated zirconia

The phase of mesostructured sulfated zirconia is generally characterized by XRD and TEM bright-field images. For example, Sachlter and coworkers [40] have prepared mesoporous sulfated zirconia from the organic template of hexadecane amine. Characterization of the sample by XRD and TEM bright-field images suggests that the walls of mesoporous sulfated zirconia contain partially tetragonal crystalline ZrO_2 [40]. As observed in Fig. 1, Al-MSZ-5 possesses peaks assigned to both mesostructured phase and crystalline tetragonal ZrO_2 . There are two main possibilities for the observation of such structure: The materials may be merely physical mixtures of independent mesostructured phase and crystalline tetragonal ZrO_2 or they may be truly bifunctional materials whose mesostructured walls are crystalline tetragonal ZrO_2 . The following pieces of evidence strongly argue for Al-MSZ-5 as a pure phase. (1) It has been reported that mesoporous sulfated zirconia with amorphous nature exhibits lower catalytic activity in *n*-butane isomerization than that of SZ with crystalline tetragonal ZrO_2 . If Al-MSZ-5 were a physical mixture of mesostructured Al-promoted sulfated zirconia with amorphous walls and Al-promoted sulfated zirconia with crystalline tetragonal phase, its catalytic activity should be lower than that of conventional Al-SZ. (2) TEM bright-field image of Al-MSZ-5 shows worm-like mesopores (Fig. 3A), and the electron diffraction patterns recorded on the same sample shows that the mesostructured walls are crystalline tetragonal ZrO_2 . (3) TEM dark-field image of Al-MSZ-5 recorded on the same area as bright-field image shows many bright spots, indicating that pieces of tetragonal crystalline zirconia are embedded in the walls of Al-MSZ-5.

4.4. Sulfur species on mesostructured sulfated zirconia

It has been reported that an abundance of surface sulfate species may correspond to an increase in surface active sites for the same series of catalysts [18], and the sulfate content of SZ, MSZ-5, and Al-MSZ-5 is presented in Table 1. In our case, the sulfur content is analyzed by the TG method. Notably, although Al-MSZ-5 shows higher sulfate content, it gives lower sulfate density ($1.8SO_4^{2-}/nm^2$) and sulfate coverage (45%) than SZ ($2.6SO_4^{2-}/nm^2$, 65%) and Al-SZ ($2.3SO_4^{2-}/nm^2$, 57%). The sulfated density for monolayer coverage is $4.0SO_4^{2-}/nm^2$ [55,56], and the sulfated zirconia with monolayer coverage of sulfate species would have high catalytic activity [57]. Overlayer sulfates would decrease the stabilization of the tetragonal phase and hinder the isomerization activity [58,59]. For Al-promoted mesostructured sulfated zirconia, in our case its sulfate density is much lower than that of monolayer coverage. Therefore, it is possible to greatly increase sulfate density on the surface of Al-MSZ-5 by various experimental procedures such as changing the concentration of sulfated reagent, even up to close to monolayer coverage. That is, it is possible to im-

prove the catalytic activity for *n*-butane isomerization significantly if Al-MSZ-5 with sulfate density close to monolayer coverage could be synthesized. Work to determine whether the Al content (3 mol% as Al_2O_3) is the optimal concentration of aluminum is ongoing.

5. Conclusion

Al-promoted mesostructured sulfated zirconia has been successfully synthesized from the template of triblock polymer surfactant of P123. N_2 adsorption isotherms show that the sample has a large surface area, reaching to $190 m^2/g$. Catalytic data for *n*-butane isomerization shows that Al-promoted mesostructured sulfated zirconia has higher catalytic activity and stability than both non-promoted mesostructured sulfated zirconia and conventional Al-promoted sulfated zirconia.

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