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Mesostructured sulfated zirconia with high catalytic activity in *n*-butane isomerization

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A mesostructured sulfated zirconia with a large surface area (189 m^2/g) has been successfully prepared using a triblock copolymer as a structure-directing agent. The resulting material was characterized by XRD, TEM, nitrogen adsorption, FTIR and TG/DTA, which suggested that the mesostructured sulfated zirconia was tetragonal crystalline. Catalytic testing showed that the mesostructured sulfated zirconia was much more active than conventional sulfated zirconia for *n*-butane isomerization.

KEY WORDS: mesostructured; sulfated zirconia; *n*-butane isomerization; non-ion surfactant.

1. Introduction

It is well known that sulfated zirconia (SZ), as a member of the solid superacids, has attracted much attention because it is potentially important for industrial reactions such as hydrocarbon isomerization, alkylation and etherification [1–6]. However, the relatively small surface area of SZ limits its wide application in catalytic reactions. Therefore, a strongly acidic sulfated zirconia with a large surface area has always been sought. One method of increasing the surface area is to support the SZ on mesoporous materials such as SZ/MCM-41 [7–9], SZ/SBA-15 [10] and SZ/FSM-16 [11], but the resulting materials show low catalytic activity for *n*-butane isomerization, which may be due to a decrease of their acidic strength [9].

Recently, there have been a number of successful examples of preparing mesoporous sulfated zirconia with high surface area, but these materials show relatively low activity for *n*-butane isomerization, as compared with SZ [12–14]. The low catalytic activity over mesoporous sulfated zirconia is possibly because of the absence of tetragonal crystalline phase, which is necessary for the formation of sulfated zirconia superacids [3].

In the present work, a mesostructured sulfated zirconia with a large surface area has been prepared using a block copolymer as a structure-directing agent, and characterization by X-ray diffraction (XRD) and transmission electron microscopy (TEM) suggests that the mesostructured sulfated zirconia is tetragonal crystalline. Catalytic tests show that the mesostructured sulfated zirconia is much more active than conventional sulfated zirconia for *n*-butane isomerization.

2. Experimental

2.1. Sample preparation

Mesostructured sulfated zirconia designated as MSZ-5 with a large surface area was prepared as follows. (1) 1 g of P123 ($EO_{20}PO_{70}EO_{20}$) was dissolved in 25 ml of water, followed by addition of 3.222 g of $ZrOCl_2 \cdot 8H_2O$. (2) After stirring at 60 °C for 6 h, aqueous ammonia was introduced into the solution, after which precipitation occurred. (3) The precipitate was transferred into a stainless steel autoclave, and heated at 100 °C for 24 h. (4) The resulting product was filtered off, washed repeatedly with a large amount of distilled water and dried at room temperature. (5) The as-synthesized precursor was extracted with 90% ethanol at room temperature under stirring, then the solid was filtered, washed with ethanol and dried in air at 100 °C. (6) The solid product was further immersed into 0.5 M $(NH_4)_2SO_4$ solution at room temperature for 30 min, followed by drying at 100 °C overnight and calcining at 550 °C for 3 h in air.

For comparison, conventional sulfated zirconia was made by immersing dried $Zr(OH)_4$ in 0.5 M $(NH_4)_2SO_4$ solution for 30 min, followed by calcination at 550 °C for 3 h.

2.2. Characterization

X-ray powder diffraction patterns of the samples were obtained using a Siemens D5005 instrument with CuKα radiation ($\lambda = 0.154$ nm) at 40 kV and 30 mA. TEM of the samples was carried out using a JEOL 2010 microscope. The BET surface area and pore size distribution data of the samples were obtained using a Micromeritics ASAP 2010M system at 77 K using as an adsorbent.

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Pyridine adsorption infrared spectra (IR) were measured for both samples to characterize the presence of Brønsted and Lewis acid sites. The samples were pressed into disks ($5\,mg/cm^2$), and were placed into a quartz cell (CaF_2 windows). The disks were evacuated at 400 °C for 2 h (1 torr) and then exposed to 10 torr of pyridine at room temperature, followed by evacuation at 150 °C for 30 min. IR spectra of the samples were recorded using a Nicolet Impact 410 infrared spectrometer. Thermogravimetric and differential thermal analysis (TG-DTA) was carried out using a NETZSCH STA 449C with a heating rate of 20 K/min from room temperature to 1000 °C. The samples were mounted horizontally and purged with a synthetic airflow of 100 ml/min.

2.3. Catalytic tests

The isomerization of *n*-butane to isobutane was carried out in a fixed-bed continuous flow reactor under atmospheric pressure. The catalyst (0.35 g) 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 to 250 °C. The ratio of *n*-butane/H_2 (v/v) was 1/10 with *n*-butane weight hourly space velocity (WHSV) of 0.89/h. An on-line gas chromatograph equipped with an FID was used to analyze the reaction products.

3. Results and discussion

Figure 1 shows the dependence of catalytic activity for *n*-butane isomerization on reaction time over SZ and MSZ-5. Interestingly, MSZ-5 exhibits high catalytic activity (2.79 mmol/g/h at the beginning). In contrast, SZ shows relatively low catalytic activity (1.45 mmol/g/h). These results indicate that MSZ-5 is much more active than SZ. Additionally, we also find that the selectivity for isobutane over MSZ-5 is slightly higher than that over SZ.

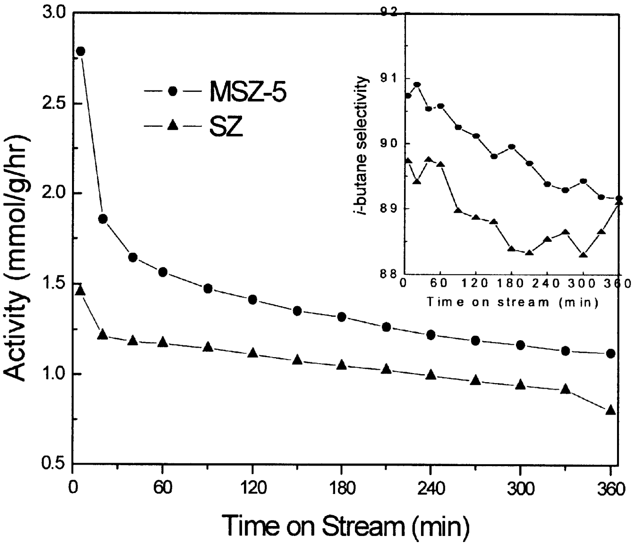

Figure 1. Catalytic activity and selectivity (inset) of SZ (▲) and MSZ-5 (●) at 250 °C.

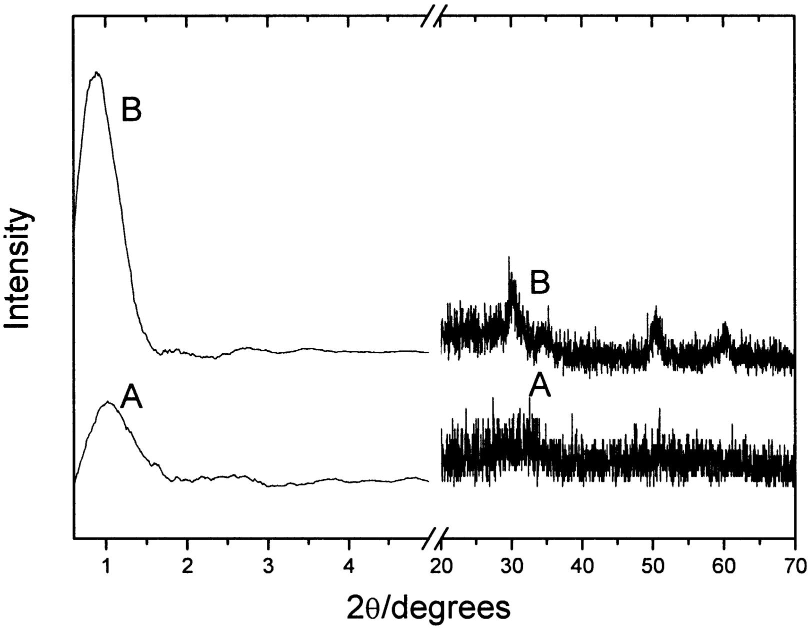

Figure 2. Small-angle and wide-angle XRD patterns of (A) as-synthesized and (B) as-calcined mesostructured sulfated zirconia (MSZ-5).

Figure 2 shows the results of small-angle and wide-angle XRD of as-synthesized and as-calcined mesostructured sulfated zirconia. The as-synthesized sample exhibits a broad peak at 1.01° in the small-angle XRD and a very broad peak at 25–35° in the wide-angle XRD (figure 2(A)). The peak at 1.01° is assigned to mesostructure, and the very broad peak at 25–35° is assigned to the amorphous nature of zirconia. However,

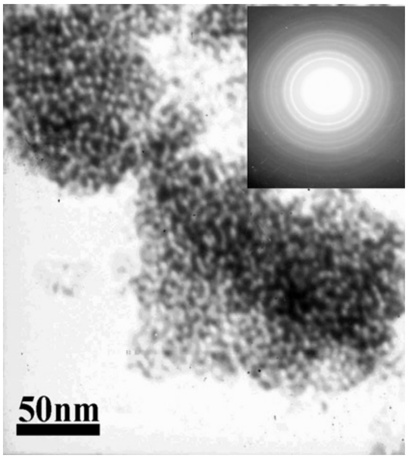

Figure 3. TEM image and selected electron diffraction pattern (inset) of MSZ-5.

the as-calcined sample (MSZ-5) shows a peak at 0.89° in small-angle XRD and obvious peaks at ~30, 35, 50 and 60° in wide-angle XRD (figure 2(B)). The peaks in wide-angle XRD are characteristic of tetragonal phase of crystalline ZrO_2, suggesting that calcination of the as-synthesized mesostructured sulfated zirconia results in formation of crystalline ZrO_2 tetragonal phase, which is very important for the preparation of sulfated zirconia superacids [3].

The TEM image of MSZ-5 (figure 3) is spotted with worm-like pores. Selected-area electron diffraction patterns (figure 3 inset) recorded for the same sample confirm that the mesostructured walls are composed of tetragonal phase, displaying characteristic diffuse electron diffraction rings.

Figure 4 shows N_2 adsorption/desorption isotherms of MSZ-5. A hysteresis loop at high relative pressure is observed, which is related to the capillary condensation associated with mesopores. Correspondingly, BJH pore size distribution for MSZ-5 [15] shows a mean value at 5.1 nm (figure 4 inset). Furthermore, a high BET surface area of 189 m^2/g is observed for MSZ-5, which is much larger than that for conventional SZ (80–100 m^2/g) [4,14].

Figure 5 shows IR spectra of pyridine-adsorbed MSZ-5 and SZ catalysts. Both samples exhibit obvious bands at 1450 and 1540 cm^{-1}, which are typical of Brønsted and Lewis sites, respectively. Notably, the intensities of the 1540 and 1450 cm^{-1} bands of MSZ-5 are much stronger than those of SZ, indicating that MSZ-5 has many more exposed Brønsted and Lewis acidic sites than SZ.

Figure 6 shows the TG curve of as-calcined mesotructured sulfated zirconia (MSZ-5), showing two weight-loss features: the first below 300 °C is due to the evaporation of physically adsorbed water and other molecules, and the second between 580 and 900 °C is assigned to decomposition of SO_4^{2-} species on the sample, forming SO_3 [7]. Based on the amount of weight loss, we have estimated that MSZ-5 contains 7.4 wt% of sulfate ions, which is higher than that of conventional sulfated zirconia (6.2 wt% of sulfate ions).

As observed in figure 2, MSZ-5 possesses peaks assigned to both mesostructured phase and crystalline tetragonal phase. There are two main possibilities for the observation of such structures: the materials are merely physical mixtures of independent mesostructured phase and crystalline tetragonal phase or they are truly bifunctional in that mesostructured walls are crystalline tetragonal phase. The following evidence strongly argues for 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

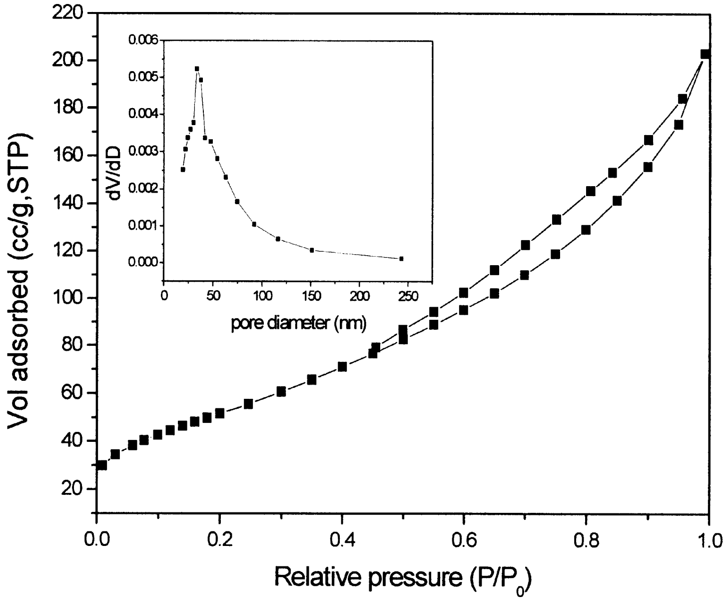

Figure 4. N_2 adsorption/desorption isotherm and BJH pore size distribution plot (inset) of MSZ-5.

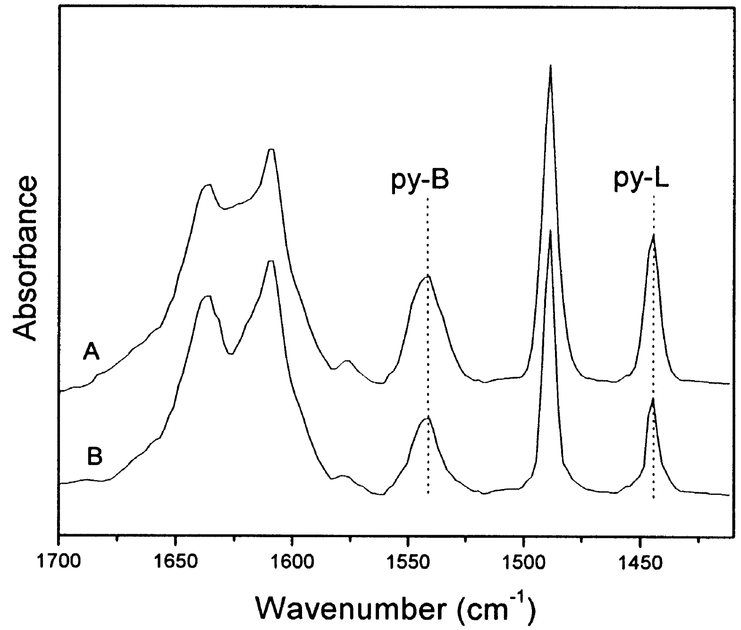

Figure 5. IR spectra of pyridine adsorbed on (A) MSZ-5 and (B) SZ.

than SZ with crystalline tetragonal phase. If MSZ-5 were a physical mixture of mesostructured sulfated zirconia with amorphous wall and sulfated zirconia with crystalline tetragonal phase, its catalytic activity should be lower than that of conventional SZ. (2) TEM images of MSZ-5 show worm-like mesopores (figure 2), and the electron diffraction patterns recorded on the same sample show that the mesostructured walls are crystalline tetragonal phase. (3) Scanning electron micrographs recorded using a JEOL 6700F instrument show that MSZ-5 is a pure phase. (4) IR spectra of pyridine adsorbed on MSZ-5 indicate many more acidic sites than on conventional SZ.

Additionally, we also used other polymer surfactants such as F127 ($EO_{106}PO_{70}EO_{106}$) to prepare novel materials of mesostructured sulfated zirconia, and these materials also show similar catalytic activity to that of MSZ-5 in *n*-butane isomerization.

4. Conclusions

A mesostructured sulfated zirconia with a large surface area has been successfully prepared using triblock copolymer surfactants, and catalytic tests show

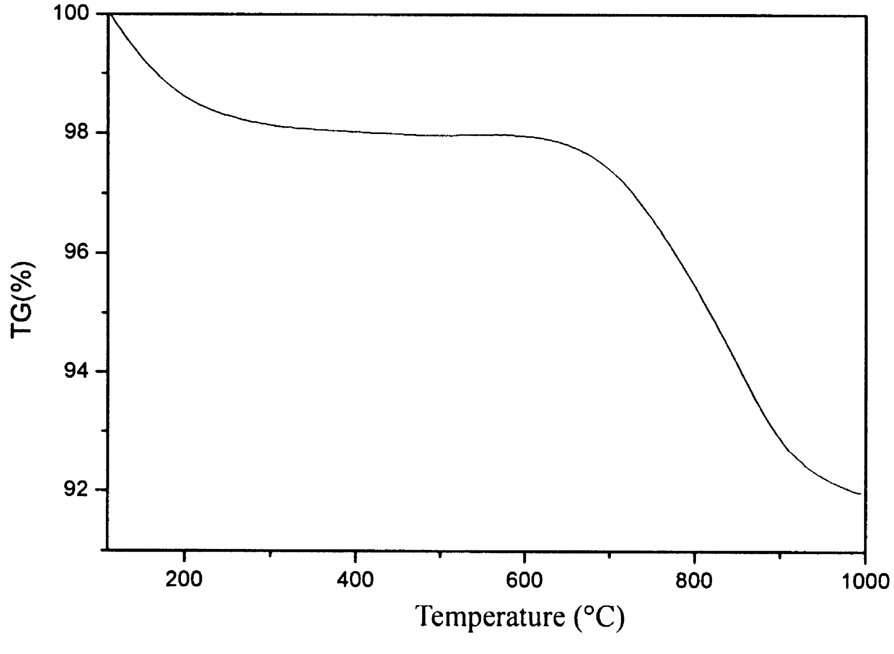

Figure 6. TG curve of MSZ-5.

that the mesostructured sulfated zirconia is much more active than conventional sulfated zirconia for *n*-butane isomerization.

Acknowledgments

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