doi:10.1246/cl.2011.760

A Mesoporous Sulfated Zirconia–Silica Material with High Hydrothermal Stability and Acid Catalytic Activity

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A mesoporous sulfated zirconia–silica material with high hydrothermal stability was prepared by a two-step hydrothermal treatment process in a pH range of 1.65–3. This material still showed high surface area, large pore volume, and uniform structure after steam treatment at 800 °C for 5 h. In cumene cracking, the material exhibited relatively steady catalytic activity even after steam treatment at 600 °C for 2 h.

Mesoporous materials with uniform and adjustable pore size and high surface area have been extensively noticed, since the appearance of MCM-41 in 1992.[1] However, compared to zeolites, these mesoporous matarials show relatively poor hydrothermal stability and low activity, which hinders their further industrial applications. To improve and enhance practical applications of the mesoporous materials, great efforts have been made,[2–8] increasing thickness of mesoporous walls,[2,3] improving the framework crosslinkage,[4] introducing heteroatoms,[5] post-treatment grafting,[6] high-temperature synthesizing,[7] and preparation of mesoporous aluminosilicates with framewok crystallinity.[8] All these mesoporous materials have exhibited improvement of hydrothermal stability either by treatment in boiling water or in steam. Compared to MCM-41 materials, SBA-15 type materials with larger pore diameter and thicker pore walls show higher hydrothermal stability to a certain extent, but weak acidity is far from satisfactory. Many attempts were made to resolve the problem. Xiao et al.[9] have reported relatively high hydrothermal stability through introducing Zr and S, and Pan et al.[7] have prepared highly ordered mesoporous materials with extremely high hydrothermal stability by high-temperature hydrothermal treatment to increase the inorganic framework crosslinking and incorporation of Al. Despite this progress, most Al or Zr species were not incorporated into the framework, so the acidity was still relatively weak compared with the crystalline zeolites used in industry. Previously, it was reported that a direct synthesis of Zr-SBA-15 with a high Zr loading,[10] subsequently, one-pot synthesis of $SO_4^{2-}/ZrO_2–SiO_2$ materials with well-ordered mesoporous structure were successfully performed.[11] The materials prepared by the above method have shown relatively high stability and stronger acidity. However, the catalyst was easily deactivated in the reaction whether it was steamed or not, which hindered industrial application. Thus, to obtain a mesoporous acidic catalytic material with high hydrothermal stability and relatively steady activity has still been a challenging project.

In this work, we prepared a mesoporous material with highly hydrothermal stability and relatively steady catalytic activity by high-temperature hydrothermal treatment in a reaction mixture with low pH. The mesoporous sulfated zirconia–silica material indicated highly acidic catalytic performance and stability in cumene cracking before and after being steamed at high temperature of 600 °C.

The mesoporous sulfated zirconia–silica material was prepared by two-step crystallization. $Zr(NO_3)_4 \cdot 3H_2O$ and cetyltrimethylammonium bromide in ethanol solution was precrystallized at 110 °C for 3.5 h. The precrystallized Zr precursor was mixed with tetraethyl orthosilicate (TEOS) and poly block copolymer surfactant Pluronic P123 in H_2SO_4 solution. The pH value of the final mixture was adjusted to 1.65–3 under stirring continuously. A gel was formed and the hydrothermal synthesis was carried out at 180 °C for 24 h. The as-synthesized product was filtered, washed, dried, and calcined in air flow at 600 °C for 3 h to obtain the final sample with Zr/Si molar ratio from 0.3 to 2.1. Herein, the molar ratio of 1.3 was taken for example, which was labeled as NMSM, and the sample after hydrothermal treatment was named NMSM-600 or NMSM-800, which were hydrothermally treated in steam at 600 and 800 °C, respectively. Conventional sulfated zirconia–silica materials were prepared according to the literature,[11] which was designated as CMSM.

In Figure 1A, the peaks attributed to d_{100} of the two-dimensional hexagonal structure are observed in low-angle range. Wide-angle XRD patterns show the presence of crystallized zirconia (Figure S1[14]). It can be seen from XRD patterns that the synthesized samples with different methods both exhibit a relatively high ordered hexagonal mesostructure. The difference is, after the steam treatment, that the diffraction peak of the sample CMSM has an obviously upward shift in the 2θ value. It is probably due to shrinkage in the pore walls of SBA-15 with the high-temperature steam treatment, indicating partial collapse of the pore structure. The position of the diffraction peak of the sample NMSM displayed little change after the steam treatment. This implies the NMSM sample has good hydrothermal stability. Adoption of the high-temperature synthesis increased

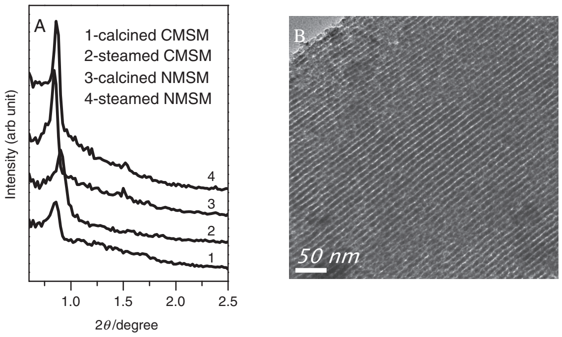

Figure 1. Low-angle XRD patterns (A) of the samples and TEM image (B) of NMSM-800.

Table 1. Texture properties of NMSM and CMSM samples

Sample	S_{BET} /$m^2\,g^{-1}$	Pore volume /$cm^3\,g^{-1}$	d_{100} /nm	Pore diameter /nm	S_{BET} Retaine d /%
NMSM	302	0.78	10.6	8.3	—
Steaming 5 h	264	0.75	10.4	8.5	87.4
CMSM	314	0.36	10.5	5.5	—
Steaming 5 h	191	0.30	9.7	5.4	60

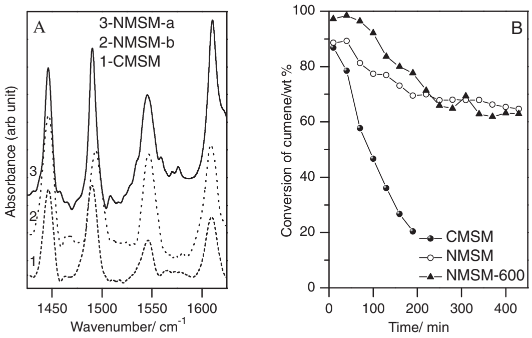

Figure 2. In situ FTIR spectra of adsorbed pyridine (A) and the time dependence of catalytic activity (B) of the samples.

the silica condensation degree in the mesoporous walls.[12] It may be the main reason for enhancing stability. A transmission electron micrograph (TEM) of the material after being steamed at 800 °C for 5 h is shown in Figure 1B, illustrating clearly well-ordered mesostructure.

All samples exhibit clearly larger hysteresis loops adsorption isotherms in the interval of P/P_0 ranging from 0.45 to 0.9 (shown in Figure S2[14]), suggesting highly ordered framework with cylindrical mesoporous channels. The pore size distribution of NMSM shows a wide distribution with diameter around 8 nm. These results indicate NMSM has high pore volume and large pore size compared with CMSM due to the formation of disordered mesotunnels on the silica walls during the high-temperature hydrothermal treatment.[13]

The pore properties are displayed in Table 1. The decrease in BET surface area and total pore volume after the steam treatment at 800 °C for 5 h are 12.6% and 3.9%, respectively. For comparison, CMSM exhibits greater decrease of BET surface area, which are 40% and 15%, respectively. The result is that the hydrothermal stability of the mesoporous sulfated zirconia–silica materials has been enhanced extremely.

Figure 2A shows the FTIR spectra of adsorbed pyridine. It can be seen that Brønsted (1545 cm^{-1}) and Lewis (1446 cm^{-1}) acid sites coexist on the surface of materials. NMSM exhibits a strong dominance of Brønsted sites. There is no change about the acid sites of NMSM even after being steamed at 600 °C.

The catalytic activities of these materials were studied for cumene cracking at 300 °C. Both NMSM and CMSM exhibit relatively high initial activity (Figure 2B). With prolonged reaction time, the activity of CMSM decreased quickly. The conversion of cumene was decreased to 20 wt % when the reaction time was 190 min. However, NMSM was nearly 3.5 times more active than CMSM. According to the above results, the formation of larger mesotunnels facilicates diffusion and transport of molecules.[7] In the industrial process, a temperature of 600 °C is proper for the steam treatment to evaluate usually the hydrothermal stability of catalysts. NMSM was steamed at 600 or 800 °C for 2 h and then used as the catalyst of cumene cracking. It was obvious that NMSM and NMSM-600 still kept relatively high activity and stability even after the reaction time of 430 min because of their similar acid properties (Figure S3[14]). The higher initial activity of the NMSM-600 has been assigned to its relatively strong acid sites. The coke level on the surface of the catalysts potentially results in the catalytic deactivation, but after being calcined at 600 °C, the deactivated catalysts could revert to the original catalytic activity. It demonstrates NMSM has high structural and reactive stability. These results are beneficial to acid-catalytic reactions of industrial application. But the activity of NMSM-800 in the reaction was decreased rapidly, due to the leaching of sulfur grafted on the surface of the sulfated zirconia–silica material.

In summary, NMSM with high hydrothermal stability and relatively steady catalytic activity was synthesized by a facile method. The precrystallization of Zr precursor and high-temperature hydrothermal synthesis at lower pH are the key factors in the process. Besides, NMSM displays much better catalytic activity in cumene cracking before and after steam treatment at 600 °C.

Financial support of this work by the National Science Foundation of China (NSFC, No. 50772070) is greatly acknowledged.

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