Creation of Acid Sites on SBA-15 Mesoporous Silica by Alumination

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The new mesoporous silica with large pore size, SBA-15, was aluminated through the reaction with aluminum chloride. The present alumination method showed a good control of aluminum content but little influence on the pore structure. Aluminum atoms were incorporated into the framework of SBA-15, which resulted in a new kind of mesoporous acid catalyst.

The discovery of M41S using a supramolecular templating method with surfactants has stimulated a world-wide exploring in the syntheses and applications of mesoporous molecular sieves.[1] Al-containing mesoporous molecular sieves show a mild cracking activity and have potential usage in petroleum hydrotreating processes.[2,3] However, the practical applications of MCM-41 and MCM-41-like mesoporous materials are greatly limited by their low hydrothermal stability. It has been found that MCM-41 lost its mesoporous structure after boiling in water.[4] MCM-41 and MCM-41-like materials slowly deteriorated even at room temperature in the presence of moisture.[5,6] Though the stability of MCM-41 can be improved by the modified synthesis methods[4] or the post-synthetic silylation,[7] the low hydrothermal stability of MCM-41 and MCM-41-like materials is still the serious problem for their applications. The best way to overcome this problem would be to synthesize mesoporous molecular sieves with thick pore walls. Recently, a new kind of mesoporous silica, SBA-15, has been synthesized with poly(alkylene oxide) triblock copolymers such as poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO).[8] Beside its uniform and large pore size channels (4.6-30 nm), SBA-15 possesses thick pore walls (3.1-6.4 nm). Therefore, it has much higher hydrothermal stability than MCM-41.[8] However, aluminum could not be incorporated into SBA-15 during synthesis in the strongly acidic aqueous system. In this letter, we report the alumination of SBA-15 with $AlCl_3$ in chloroform solution and the catalytic activity of aluminated SBA-15.

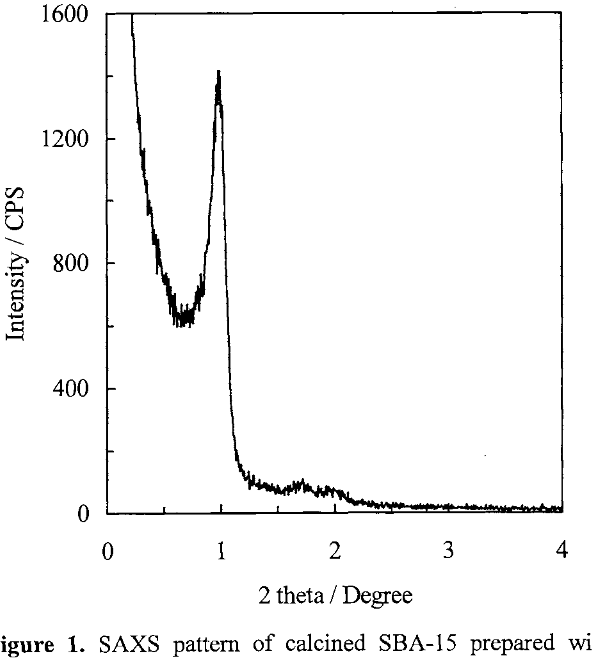

Figure 1. SAXS pattern of calcined SBA-15 prepared with $EO_{20}PO_{70}EO_{20}$.

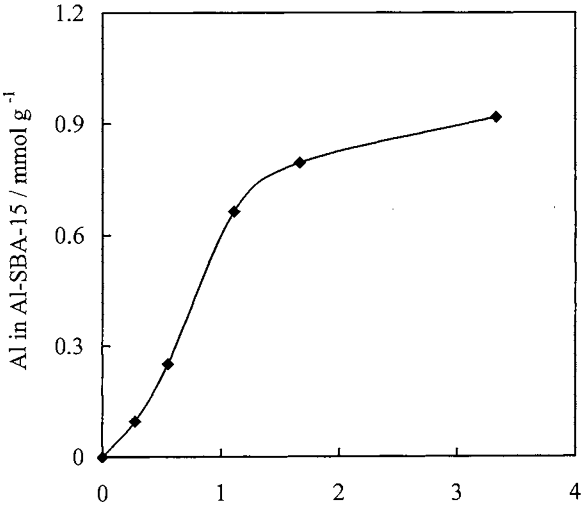

Figure 2. Relation between the aluminum content in Al-SBA-15 and the aluminum content in reactant.

SBA-15 was synthesized with $EO_{20}PO_{70}EO_{20}$ triblock copolymer.[8] The compositions of the reaction mixture were 16 g $EO_{20}PO_{70}EO_{20}$: 34.1 g tetraethyl orthosilicate : 96 ml hydrochloric acid (35-37%) : 420 g H_2O. The syntheses were carried out at 35 °C for 20 h. SBA-15 having large pore size was synthesized with the addition of trimethylbenzene (TMB) and a post-synthetic heating treatment of the reaction mixture at 97 °C for 24 h. As-synthesized SBA-15 was calcined at 550 °C in air for 8 h to remove organics. The calcined SBA-15 synthesized without TMB gave a SAXS pattern as shown in Figure 1 and a pore size of 4.6 nm (calculated from $4V_{meso}/S_{meso}$). SBA-15 with a pore size of 12 nm was obtained with a $TMB/EO_{20}PO_{70}EO_{20}$ weight ratio of 0.5.

The alumination of SBA-15 was performed by the reaction of calcined SBA-15 with aluminum chloride in refluxing chloroform. The compositions of reaction mixtures were 1.8 g SBA-15 : 0.0665-0.800 g $AlCl_3$: 100 g $CHCl_3$. To avoid the influence of water, dehydrated chloroform and SBA-15 just after

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calcination were used. After 6 h reaction, aluminated SBA-15 (Al-SBA-15) was filtrated out and washed with 20 ml chloroform and then with 200 ml water. The sample was dried at 130 °C overnight and calcined in air at 500 °C for 5 h. The aluminum content in Al-SBA-15 was analyzed with ICP after dissolving it in an HF aqueous solution. Figure 2 shows the relation between the aluminum contents in Al-SBA-15 and the reactant. The aluminum content in Al-SBA-15 increased almost linearly with the aluminum content in reactant up to 1 mmol g-SBA-15^{-1}, which suggests that the aluminum content in Al-SBA-15 can be controlled by the composition of reactant. However, the slope was less than one, indicating that a little fraction of aluminum charged was not incorporated into Al-SBA-15. A high $AlCl_3$ concentration in reactant, the aluminum content in Al-SBA-15 reached a saturated value of 0.9 mmol g-Al-SBA-15^{-1} which corresponds to ca. 0.9 Al-atoms nm^{-2}. We also observed the same behavior on the alumination of MCM-41 with $AlCl_3$, where the same saturated aluminum concentration was obtained. It is far below the concentration of surface silanol groups of 3.0 nm^{-2}.[9]

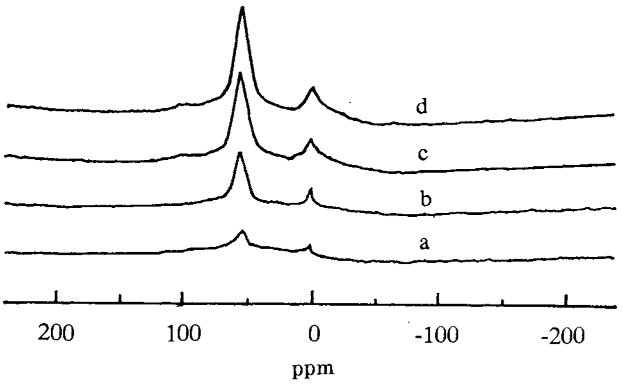

Figure 3. ^{27}Al NMR spectra of Al-SBA-15 catalysts with Si/Al molar ratio of 242(a), 66(b), 24(c) and 17(d).

The ^{27}Al NMR spectra of the Al-SBA-15 catalysts are shown in Figure 3. The appearance of a peak at 53 ppm due to tetrahedrally coordinated aluminum species[10] means that aluminum atoms have been incorporated into the framework of SBA-15 through the reaction with $AlCl_3$. The peak at 0 ppm is due to octahedrally coordinated aluminum species. Both tetrahedral and octahedral aluminum species increased with aluminum content keeping the tetrahedral species the main species.

The alumination by the reaction with $AlCl_3$ generated little influence on the mesoporous structure of SBA-15. The pore diameters of Al-SBA-15 catalysts were the same as those before the alumination.

Table 1. Cracking activities of Al-SBA-15, HAlMCM-41 and HZSM-5 catalysts

Catalyst	Si/Al molar ratio	Conversion of Cumene / %[a]
Al-SBA-15	17	81
Al-SBA-15	24	77
Al-SBA-15	66	52
Al-SBA-15	242	38
HAlMCM-41	51	21
HZSM-5	33	89

[a] Reaction conditions: Catalyst, 0.200 g; He, 42 ml min^{-1}; cumene, 8.2 ml min^{-1} (gas); temperature, 450 °C; time on stream, 30 min.

The catalytic activities of these Al-SBA-15 catalysts were tested with the cracking of cumene and compared with those of HZSM-5 and HAlMCM-41 (hydrothermally synthesized). As shown in Table 1, Al-SBA-15 catalysts exhibited much higher activities than HAlMCM-41 with a similar Si/Al ratio. Al-SBA-15 with the low Si/Al ratio showed a cumene conversion close to that of HZSM-5. The high cracking activity of Al-SBA-15 may be due to the effect of octahedral aluminum and residual chloride. The high cracking activity indicates that Al-SBA-15 has potential usage in the acid-catalyzed reactions of large molecules such as hydrotreating of residual oil.

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