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Direct synthesis and catalytic evaluation of AlSBA-1

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The direct synthesis of the new mesoporous molecular sieve AlSBA-1 containing exclusively tetrahedrally coordinated aluminium and the catalytic activity of the novel material in the isomerization of *n*-decane are reported.

The discovery of mesoporous molecular sieves using the supramolecular templating approach with surfactants or polymers has stimulated extensive research in the synthesis and application of these materials. Huo *et al.*[1] reported the synthesis of the novel mesoporous molecular sieve SBA-1 having a three-dimensional cage type structure with open windows.[2] Incorporation of aluminium into mesoporous molecular sieves is of tremendous interest in order to embed a catalytic function. The synthesis of aluminium-containing mesoporous materials such as MCM-41 and MCM-48 has been studied extensively.[3,4] However, due to the strongly acidic synthesis conditions, the preparation of AlSBA-15 and AlSBA-1 is difficult. For the hexagonal phase AlSBA-15, post-synthesis alumination[5] and direct synthesis[6,7] have been reported, while for AlSBA-1 only a post synthesis method has been developed.[8] In this communication, we report the direct synthesis of AlSBA-1 containing exclusively tetrahedrally coordinated aluminium and the catalytic activity of this material in the isomerization of *n*-decane.

Aluminium-containing SBA-1 was synthesized under acidic conditions using cetyltriethylammonium bromide (CTEABr) as the surfactant, tetraethylorthosilicate (TEOS) as the silica source and aluminium isopropoxide as the aluminium source. The surfactant CTEABr was synthesized by reaction of 1-bromohexadecane with an equimolar amount of triethylamine in ethanol under reflux conditions for two days. The resulting solid CTEABr was purified by recrystallization from a chloroform/ethylacetate mixture. A typical synthesis procedure for AlSBA-1 was as follows: Solution A was prepared by adding 0.812 g of CTEABr to an aqueous solution of HCl. The obtained solution was cooled to 0 °C and homogenized for 30 min. TEOS and $Al(i\text{-}C_3H_7O)_3$ were precooled to 0 °C and then added to solution A under vigorous stirring. Stirring was continued for another 5 h at 0 °C. Thereafter, the reaction mixture was heated to 100 °C for 1 h. The solid product was recovered by filtration and dried in an oven at 100 °C overnight. The molar composition of the gel was 1 TEOS : 0.05–0.25 Al_2O_3 : 0.2 CTEABr : 10 HCl : 125 H_2O. Pure siliceous SBA-1 was synthesized with the same procedure (HCl/TEOS = 56 and H_2O/TEOS = 700) in the absence of aluminium. The as-synthesized materials were then calcined in air at 550 °C for 10 h to remove the organic template. The template content was found (by TG analysis) to be around 46 wt% and 29 wt% for the aluminium-containing and pure siliceous samples, respectively.

The powder XRD patterns of SBA-1 and AlSBA-1 with different n_{Si}/n_{Al} ratios are displayed in Fig. 1 showing the characteristic pattern of the cubic phase (space group *Pm*3*n*). The textural properties of AlSBA-1 were assessed by nitrogen adsorption at 77 K and are also summarized in Table 1. Only minor differences in surface area (A_{BET}), pore diameter (d_p) and pore volume (V_p) were found for the aluminium-containing materials in comparison to all-silica SBA-1. It is noteworthy that despite the high aluminium concentration in the gel the n_{Si}/n_{Al} concentration in the final product is significantly lower (Table 1).

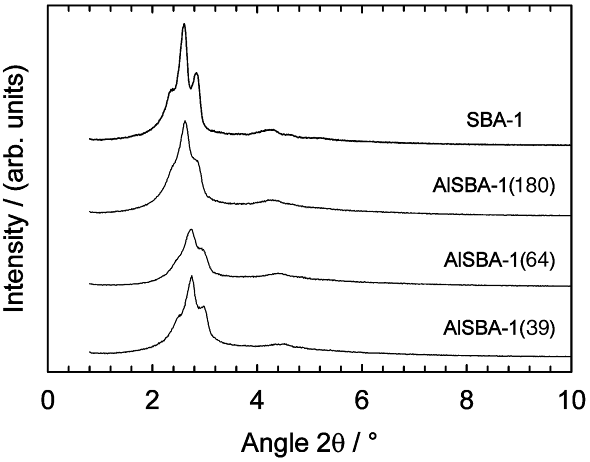

Fig. 1 Powder X-ray diffraction patterns of calcined AlSBA-1 materials.

The ^{27}Al NMR spectrum at a resonance frequency $\omega_0/2\pi$ = 130.32 MHz of the AlSBA-1(39) catalyst is shown in Fig. 2. The peak at 51.8 ppm is assigned to tetrahedrally coordinated aluminium. The absence of a signal at *ca*. 0 ppm (indicative of octahedrally coordinated aluminium) confirms that aluminium is exclusively in tetrahedral coordination. Similar NMR spectra are obtained for the AlSBA-1 materials with lower aluminium content.

Table 1 Structural properties of AlSBA-1 samples

Sample	n_{Si}/n_{Al} (in gel)	n_{Si}/n_{Al} (AAS)	A_{BET}/ $m^2\ g^{-1}$	d_p/nm	V_p/ $cm^3\ g^{-1}$
SBA-1	—	—	1430	2.0	0.68
AlSBA-1 (180)	10	180	1341	2.1	0.69
AlSBA-1 (64)	3.3	64	1350	2.0	0.67
AlSBA-1 (39)	2	39	1324	1.9	0.64

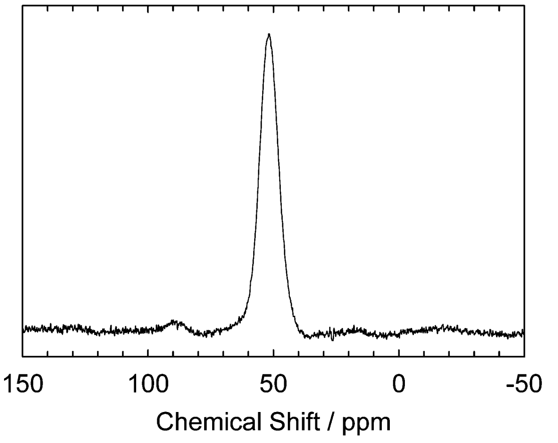

Fig. 2 ^{27}Al MAS NMR spectrum of AlSBA-1(39) after calcination.

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The catalytic activity of the novel material was tested with the isomerization of *n*-decane, which needs a bifunctional catalyst (metal sites and Brønsted acid sites). The bifunctional catalyst was prepared by adding a solution of $Pt(NH_3)_4Cl_2$ to an aqueous slurry of AlSBA-1 and subsequently the water was removed in an rotary evaporator at 70 °C. The reaction was performed in a fixed-bed flow type reactor with on-line gas chromatographic analysis of the reaction products. Prior to the catalytic experiments, the catalyst was dehydrated at 260 °C for 2 h in a flow of argon, activated in oxygen at 310 °C for 4 h and flushed with argon at 410 °C for 4 h. Finally, the platinum clusters were obtained by hydrogen reduction at 310 °C for 4 h. As shown in Fig. 3, 0.5Pt/AlSBA-1(39) is active in the isomerization and hydrocracking of *n*-decane. Conversion of *n*-decane starts around 230 °C. With increasing conversion, hydrocracking of C_{10} isomers occurs as a consecutive reaction. The yield of feed isomers passes through a maximum around 25% and then declines again. The activity of the bifunctional catalyst 0.5Pt/AlSBA-1(39) is significantly higher compared to the monofunctional catalysts 0.5Pt/SBA-1 which exhibits a *n*-decane conversion of 55% at a reaction temperature of 380 °C.[9] These results are in complete agreement with the well known reaction mechanism for isomerization and hydrocracking of *n*-alkanes[10] and confirm the presence of Brønsted acid sites in our samples.

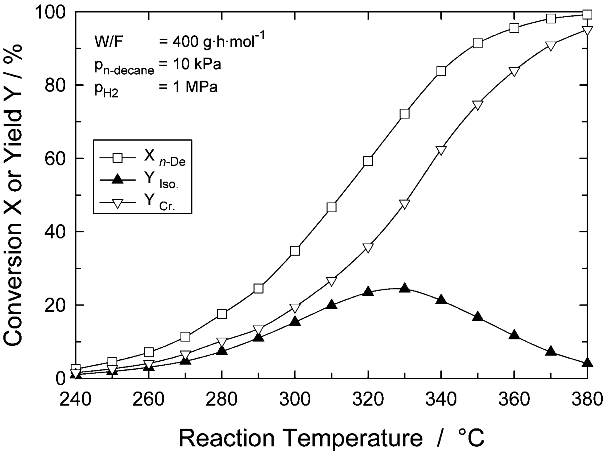

Fig. 3 Conversion of *n*-decane ($X_{n\text{-De}}$) and yield of isomerization ($Y_{Iso.}$) and cracking products ($Y_{Cr.}$) over 0.5Pt/AlSBA-1(39).

In conclusion, we have developed a method for the preparation of the aluminium-containing mesoporous cubic phase AlSBA-1 with aluminium exclusively in tetrahedral coordination. The derived bifunctional catalyst 0.5Pt/AlSBA-1(39) has shown activity in the isomerization of *n*-decane, which requires the presence of Brønsted acid sites. Temperature programmed desorption of pyridine is being used to quantify the density and the strength of these acid sites.

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