

Direct synthesis of AISBA mesoporous molecular sieves: characterization and catalytic activities

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Aluminium-incorporated SBA mesoporous materials have been obtained for the first time by direct synthesis; the resulting materials retain the hexagonal order and physical properties of purely siliceous SBA-15 and present higher catalytic activities in the cumene cracking reaction than AIMCM-41 materials.

Mesoporous molecular sieves, MCM-41, have attracted much interest because of their potential application in reactions or separations involving bulky molecules.^{1,2} The synthesis and catalytic applications of AIMCM-41 have been reported by various authors.^{3–8} The crucial problem is that AIMCM-41 has poor hydrothermal stability, either in steam or in hot water.^{7,9} This becomes a serious limitation to the application of these new materials. Recently, Zhao *et al.*¹⁰ reported the synthesis of a novel mesoporous silica denoted SBA-15 using an organic copolymer to organize the structure of a polymerizing silica precursor template. This material has a more regular structure and thicker walls than MCM-41, resulting in much higher stability. The aluminium-containing SBA-15 was also obtained by post-synthesis.^{11,12} Here, we report a direct synthesis of aluminium-incorporated SBA mesoporous molecular sieves using a triblock copolymer as template. The physical properties and catalytic activities of the resulting materials were also studied.

The aluminium-containing SBA mesoporous solid was prepared as follows: 9 mL of tetraethyl orthosilicate (TEOS) and a calculated amount of aluminium tri-*tert*-butoxide, to obtain a given Si/Al ratio (10 or 20), were added to 10 mL of aqueous HCl at pH 1.5. This solution was stirred for > 3 h and then added to a second solution containing 4 g triblock poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (EO₂₀PO₇₀EO₂₀, Aldrich) in 150 mL of aqueous HCl at pH 1.5 at 313 K. The mixture was stirred for another 1 h and allowed to react at 313 or 373 K for 48 h. The solid obtained was filtered off, dried at 373 K, and finally calcined in air flow (9 L h⁻¹) at a heating rate of 24 K h⁻¹ up to 823 K and then maintained at this temperature for 4 h. The sample of SBA-15 was prepared according to the literature.¹⁰ The samples studied are denoted AISBAX(*T*_s) where X and *T*_s represent the Si/Al ratio and the synthesis temperature, respectively.

Table 1 gives the preparation conditions and textural properties of the resulting aluminium-incorporated mesoporous

Table 1 Preparation and properties of AISBA samples

Sample	Si/Al (in gel)	<i>T</i> _s /K	Synthesis pH	<i>S</i> _{BET} / m ² g ⁻¹	Pore diameter/ nm	<i>V</i> _p /cm ³ g ⁻¹
AISBA10(373)	10	373	1.5	1004	7.4	1.53
AISBA20(373)	20	373	1.5	1022	7.4	1.40
AISBA10(313)	10	313	1.5	689	4.0	0.64
AISBA20(313)	20	313	1.5	788	3.6	0.63
SBA-15(373)	—	373	<0	901	6.5	1.20
SBA-15(313)	—	313	<0	762	4.4	0.67

molecular sieves, together with the data of SBA-15 for comparison. The textural properties of AISBA are similar to those of SBA-15. Fig. 1 shows the N₂ adsorption–desorption isotherm and pore size distribution of the AISBA10(373) sample. The isotherm shows a clear H1-type hysteresis loop at high relative pressure, suggesting that AISBA has very regular mesoporous channels despite their large pore size, which was also proved by its narrow gaussian pore size distribution. The BET surface areas and mesopore volumes of AISBA determined by nitrogen adsorption–desorption at 77 K are in the range 689–1022 m² g⁻¹ and 0.63–1.53 cm³ g⁻¹, respectively. The calculated pore diameters by the BJH method are in the range of 3.6–7.4 nm, depending on the preparation temperature (*T*_s).

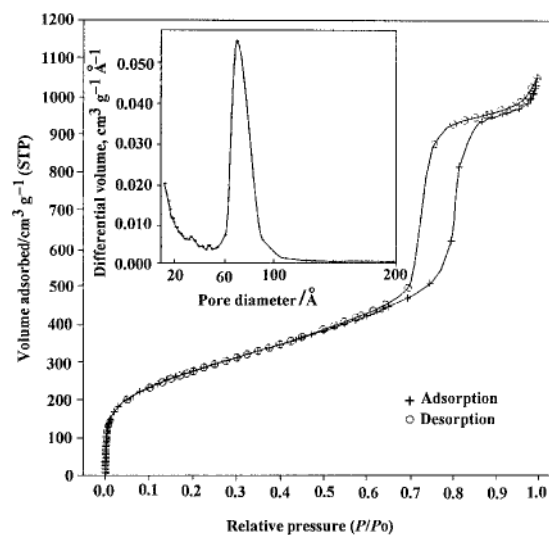


Fig. 1 N₂ adsorption–desorption isotherms of AISBA10(373) at 77 K. The insert shows the BJH pore size distribution calculated from the desorption branch of the isotherm.

Transmission electron microscopy images show well ordered hexagonal arrays of 1D mesoporous channels and confirm that the AISBA samples have a 2D *P6mm* hexagonal structure as does SBA-15.¹¹ Fig. 2 shows the TEM images of the AISBA10(373) sample. The distance between two consecutive centres of hexagonal pores estimated from the TEM image is *ca.* 10 nm. The average thickness of the wall is *ca.* 3 nm, which is much larger than for MCM-41, and the pore diameter is around 7 nm, in agreement with the N₂ adsorption measurements.

Fig. 3(a) shows the ²⁷Al MAS NMR spectrum of the AISBA10(373) sample. It exhibits signals at δ 52 from four-coordinate Al, at δ 38 from five-coordinate Al and at δ 0 from six-coordinate Al. This proves that a large amount of aluminium is incorporated in the framework of this sample, though some non-framework aluminium is still present. Such non-framework

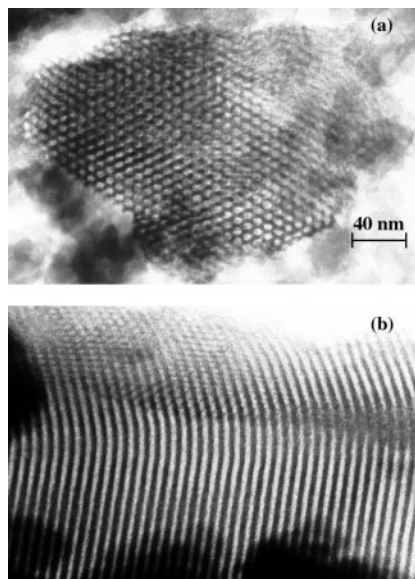


Fig. 2 TEM images of AISBA10(373): (a) in the direction of the pore axis and (b) in the direction perpendicular to the pore axis.

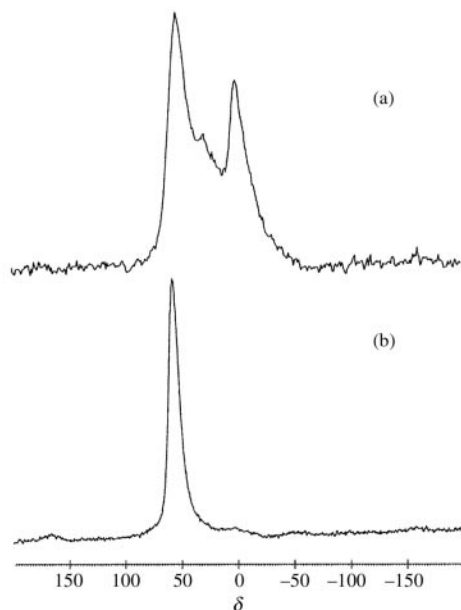


Fig. 3 ^{27}Al MAS NMR spectra of the AISBA10(373) sample before (a) and after NH_4Cl washing (b).

aluminium was eliminated by washing the solid in NH_4Cl solution [Fig. 3(b)].

The stability of AISBA samples following various treatments was also studied. XRD patterns of the AISBA10(373) sample after calcination at 1073 K, steaming at 823 K and treatment in solution at different pH (Fig. 4) exhibit one very intense line and two weak lines, which are similar to those of the parent sample, indicating that the hexagonal structure of the AISBA was not affected by these treatments. Compared with the same treatments on Al-MCM-41,⁹ it can be concluded that the stabilities of AISBA samples are much higher.

The catalytic activities of AISBA samples towards the cumene cracking reaction have been investigated. The reaction was performed in a continuous-flow fixed-bed microreactor system with helium (25 mL min^{-1}) as carrier gas. The catalyst load for the tests was 100 mg and was preheated at 573 K for 3 h before reaction. A stream of cumene vapor in helium (25 mL min^{-1}) was generated using a saturator at room temperature. The steady state activities are given in Table 2. All samples have considerable activity in spite of their different textural properties, and the catalytic activity depends strongly on the Si/Al ratio. The activity towards cumene cracking of AISBA

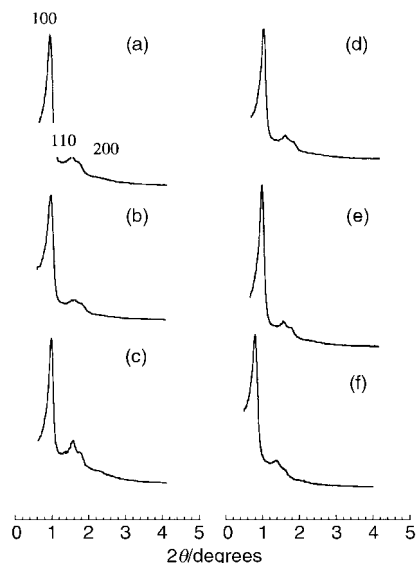


Fig. 4 XRD patterns of the initial AISBA10(373) sample (a) and after a variety of treatments: (b) calcination at 1073 K; (c) steaming at 823 K; (d) in pH = 2 solution; (e) in pH = 7 solution and (f) in pH = 11 solution.

Table 2 Activities for cumene cracking reaction

Catalyst	Conversion (%)		
	473 K	523 K	573 K
AISBA10(373)	12.6	43.2	87.0
AISBA20(373)	2.5	17.1	56.0
AISBA10(313)	12.8	34.8	86.5
AISBA20(313)	9.4	27.7	75.8
SBA-15(373)	0	0	0
AIPSMCM5 (Si/Al = 5) ¹³	—	—	50.0

molecular sieves is much higher than that of AIMCM-41¹³ or AISBA-15 prepared by post synthesis.¹² The only products of the cracking are benzene and propene, indicating that the active sites of this kind of material are of the Brönsted type. Currently we are performing two dimensional ^{27}Al solid state NMR (HETCOR) experiments to identify and establish the framework location of aluminium in these solids. Ammonia chemisorption and temperature-programmed desorption (TPD) and ^1H NMR at 4 K are being used to quantify the strength of the acidic sites.

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