

# Acidity and catalytic activity of aluminosilicate mesoporous molecular sieves prepared using primary amines

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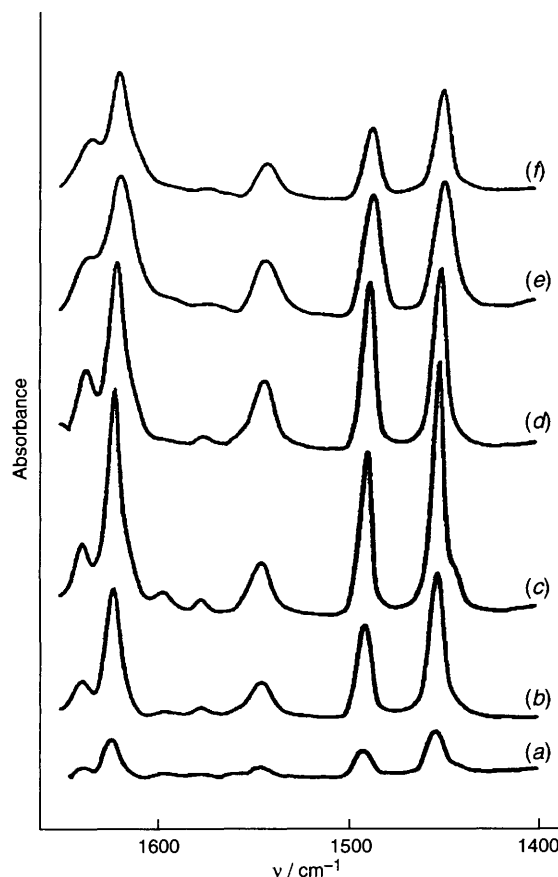
**Mesoporous molecular sieves with enhanced Brønsted acidity and catalytic activity are generated using a primary amine surfactant route; the acidity and catalytic activity of these materials are higher than those of the equivalent aluminosilicate MCM-41.**

The recent discovery of mesoporous molecular sieves<sup>1,2</sup> has attracted considerable interest with MCM-41 being representative of these types of mesoporous solids. A potential application for these materials, as a result of the introduction of active sites in the framework during synthesis, is as solid-acid catalysts. An example of the introduction of Brønsted-acid sites is the incorporation of Al into an electrically neutral siliceous framework followed by ammonium exchange and calcination to generate protons.<sup>3</sup> We have, in the preceding paper<sup>4</sup> reported a synthetic approach in which four-coordinate Al is incorporated into an aluminosilicate mesoporous framework thereby generating materials with Brønsted-acid sites without the need for ammonium exchange and calcination (treatments known to result in the undesirable loss of framework Al).<sup>5,6</sup> Here we report on the acidity and catalytic properties of the materials. We note that whilst the structural features (e.g. powder X-ray diffraction, surface area and chemical composition) for MCM-41 and our materials are similar, catalysts generated through our procedure possess significantly higher Brønsted acidity and catalytic activity (for the conversion of cumene) compared to aluminosilicate MCM-41 materials containing the same amount of aluminium.

The preparation and physical characterisation of the aluminosilicate mesoporous molecular sieves (designated Al-MMSX, where X is the Si : Al ratio used in the synthesis gel) is described in the preceding paper.<sup>4</sup> In order to evaluate the amount and type of acid sites, we used the 'diagnostic' bases pyridine and cyclohexylamine. The IR spectra of adsorbed pyridine were obtained using self-supporting sample wafers on a Nicolet 205 FTIR spectrometer with 2 cm<sup>-1</sup> resolution. The sample wafers, previously calcined at 650 °C for 4 h (in the case of Al-MMS samples) were further calcined *in vacuo* at 500 °C for 2 h prior to exposure to pyridine. The Brønsted- and Lewis-acidity values (per gram of clay) were calculated (using the absorption coefficients of Hughes and White)<sup>7</sup> from the pyridine IR bands following pyridine adsorption and subsequent evacuation at 200, 300 and 400 °C. Cyclohexylamine acidity values (per gram at 240 °C) were obtained using TGA of the (calcined) Al-MMS samples following adsorption of cyclohexylamine (CHA). The mass loss between 240 and 420 °C is used to quantify the acidity in mmol of base desorbed assuming that each base molecule interacts with one Brønsted acid site.

Fig. 1 shows the infrared spectra of pyridine in the region 1650–1400 cm<sup>-1</sup> following its adsorption on protonic zeolite-Y (Laporte, Si : Al 3.65), H<sup>+</sup>-MCM-41-10 (prepared using the method of Luan *et al.*<sup>5,6</sup>) and Al-MMS samples and subsequent thermal treatment at 200 °C. All the samples exhibit the expected bands due to Lewis-acid bound pyridine (1450, 1575 and 1623 cm<sup>-1</sup>), pyridine bound on Brønsted-acid sites (1545 and 1650 cm<sup>-1</sup>) and a band at 1490 cm<sup>-1</sup> attributed to pyridine associated with both Lewis- and Brønsted-acid sites.<sup>8</sup> The acidity data shown in Table 1 indicate that the incorporation of

aluminium into the solid framework generates acid sites with the number of acid sites (both Brønsted and Lewis) generated increasing with the degree of aluminium incorporation. The Brønsted:Lewis (B:L) acid ratio calculated from the band areas is similar to that previously reported for aluminosilicate



**Fig. 1** IR spectra of pyridine adsorbed on (a) Al-MMS40, (b) Al-MMS20, (c) Al-MMS10, (d) Al-MMS5, (e) zeolite-Y and (f) H-MCM-41-10 following thermal treatment at 200 °C under vacuum

**Table 1** Acidity of Al-MMS samples (CHA = cyclohexylamine)

Sample	(mmol CHA) g <sup>-1</sup>	(μmol pyridine) g <sup>-1</sup>					
		Brønsted			Lewis		
		200	300	400	200	300	400
Al-MMS40	0.60	16	9	2	37	40	27
Al-MMS20	0.86	29	13	6	70	73	64
Al-MMS10	1.00	36	16	7	88	82	61
Al-MMS5	1.24	46	19	9	90	82	67
Zeolite-Y	1.49	42	19	4	75	65	54
H-MCM-41-10 <sup>a</sup>	0.66	23	9	1.6	48	54	40

<sup>a</sup> See ref. 10 for analytical data concerning this material.

MCM-41 materials.<sup>3,9,10</sup> Furthermore, as previously observed for MCM-41,<sup>12</sup> the B:L ratio does not change with the bulk Si:Al ratio of the Al-MMS samples. We believe that this indicates that the proportion of framework aluminium removed during calcination of the as-synthesised material does not change with the total amount of framework Al; if the proportion of extra-framework aluminium were to increase with the Si:Al ratio, we would expect to see a decrease in the B:L ratio as the Si:Al ratio increases. The acidity values also indicate that increasing evacuation temperatures reduce the number of Brønsted-acid sites capable of interacting with pyridine and thus the B:L ratio reduces. However, the most significant observation is that the (Brønsted) acidity of Al-MMS materials prepared using our direct method is much higher than that of equivalent MCM-41 materials (see comparison between H-MCM-41-10 and Al-MMS10 in Table 1). We believe that the Brønsted-acid sites in the Al-MMS samples are generated during calcination of the as-synthesised material; the templating amine surfactant decomposes (in a fashion similar to the decomposition of the ammonium ion in NH<sub>4</sub><sup>+</sup>-MCM-41) generating protons which are retained as charge-balancing cations. This gives rise to Brønsted-acid sites in the form of 'bridging' Si(OH)Al hydroxy groups.

We have used the cracking/dehydrogenation of cumene, a reaction often used to characterise the acidity of solid-acid catalysts,<sup>11,12</sup> as a test reaction. The catalysis was performed using a pulse microreactor with a helium flow of 25 ml min<sup>-1</sup>. Prior to reaction the catalyst bed (0.05 g, 30–60 mesh) was first activated for 1.5 h at 500 °C under helium (25 ml min<sup>-1</sup>).

**Table 2** Cumene cracking activity of Al-MMS samples

Sample	% Conversion		
	300	400	500
Al-MMS40	9.2	28.4	52.2
Al-MMS20	35.1	61.7	83.6
Al-MMS10	40.0	72.0	84.0
Al-MMS5	61.1	83.0	92.0
Zeolite-Y	62.5	84.0	90.8
H-MCM-41-10	18.0	39.5	59.4

During the measurements, which were performed at 300, 400 and 500 °C, the volume of a cumene pulse was 0.25 µl (1.8 µmol). The catalytic data in Table 2 indicates that Al-MMS materials possess considerable catalytic activity, with the conversion of cumene increasing with increasing content of framework aluminium. The conversion proceeds almost exclusively *via* catalytic cracking to benzene and propene with only trace amounts of  $\alpha$ -methylstyrene (product of dehydrogenation over Lewis-acid sites) indicating that the active sites are Brønsted-acid sites.<sup>12</sup> In particular we note that the activity of the Al-MMS materials is superior to that of equivalent MCM-41 materials (see comparison between H-MCM-41-10 and Al-MMS10 in Table 2). Our synthetic approach therefore provides new opportunities for the design of mesoporous catalysts with activities comparable to current zeolitic catalysts.

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