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Synthesis and characterisation of a novel microporous niobium silicate catalyst

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The synthesis and characterisation of a novel microporous niobium silicate (AM-11), an excellent catalysts for the conversion of alcohols, are reported.

Recently, the synthesis of microporous framework titanium silicates, displaying zeolite-type properties and containing Ti(IV) usually in octahedral coordination, has attracted much interest.[1–4] As a natural extension of this work, we have embarked on a systematic study aimed at preparing novel microporous zirconium[5] and niobium[6] silicates. Here we report the synthesis and structural characterisation of a novel microporous niobium silicate denoted AM-11 (Aveiro-Manchester microporous solid no. 11).

AM-11 was prepared in Teflon-lined autoclaves under static hydrothermal conditions. An alkaline solution was made by mixing 1.27 g tetraethylorthosilicate (Aldrich), 2.40 g ethanol, 6.40 g H_2O, 1.68 g NaOH (Merck) and 0.53 g NaF (Aldrich). A second solution was made by mixing 20.0 g H_2O, 3.00 g oxalic acid (Panreac), 1.00 g niobium oxalate (Niobium Products) and stirred overnight. These two solutions were combined, seeded with 0.1 g ETS-4[1] and stirred thoroughly. The pH (after a 1 : 100 water dilution) was adjusted to 10.2 by adding an ammonia solution (25%, Merck). The gel, with a composition 1.0 Na_2O : 1.0 SiO_2 : 0.15 Nb_2O_5 : 240 H_2O, was autoclaved for 15 days at 200 °C. The crystalline product was filtered off, washed with distilled water and dried at ambient temperature, the final product being an off-white microcrystalline powder.

AM-11 samples were characterised by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), ^{93}Nb, ^{29}Si and ^{23}Na magic-angle spinning nuclear magnetic resonance (MAS NMR), Raman spectroscopy, thermogravimetry (TG), adsorption isotherms and catalytic tests.

SEM (not shown) reveals that AM-11 crystals are needles *ca.* 10 μm in length. Energy dispersive absorption of X-rays yields Si/Nb and Na/Nb molar ratios of *ca.* 4.6 and 0.3, respectively.

The total AM-11 mass loss between 30 and 700 °C is *ca.* 16.5%. Two stages of dehydration are observed (not shown): between 30 and 270 °C the solid loses *ca.* 10.5% while between 270 and 700 °C the mass loss is *ca.* 6%. The adsorption behaviour of AM-11 was investigated in order to assess the porosity of the material. Nitrogen and methanol adsorption isotherms are both type I with maximum uptakes of *ca.* 0.15 and 0.11 g g^{-1}, respectively. Although the material is microporous, the propane uptake was found to be negligible suggesting a very small pore size. However, ethanol, *n*-propanol and 2-methylpropan-1-ol have uptakes of *ca.* 0.6–0.7 g g^{-1} at $P/P^0 = 0.5$. This conflicting behaviour may originate in the polarity of the sorbate.

The powder XRD pattern of AM-11 is shown in Fig. 1, while the *d*-spacings and intensities of the main reflections are collected in Table 1. Peak intensities were altered by changing the method of sample preparation indicating the occurrence of preferred orientation effects. *In situ* powder XRD patterns recorded under vacuum at temperatures up to 650 °C (not shown) are similar to the pattern given by the parent hydrated material. The water in AM-11 is zeolitic and its removal is not permanent. This was confirmed by first heating a sample at 650 °C and then keeping it, for several hours, in contact with air at room temperature. The powder XRD patterns and TG curves of the parent and calcined hydrated materials were found to be identical.

The ^{29}Si MAS NMR spectrum of AM-11 [Fig. 2(*a*)] displays a resonance at δ −95.6, a group of (at least) three overlapping peaks at δ −105.5, *ca.* −106.7 and −108.1 and a sharp signal at δ −111.1. The attribution of these resonances is difficult because, to the best of our knowledge, no systematic study is available on the relationship between the ^{29}Si NMR chemical shift and the number of niobium polyhedra coordinating a given silicon tetrahedron. Our previous study on synthetic analogues of the mineral nenadkevichite, containing framework niobium,[6] suggests that this relationship may be similar to that found for titanium silicates where a systematic downfield chemical shift is observed when increasing numbers of titanium polyhedra coordinate a given silicon tetrahedron.[7] We assign the peak at δ −111.1 to Si(4 Si, 0 Nb) environments. The resonances at δ −105.5, *ca.* −106.7 and −108.1 are tentatively assigned to Si(4 Si, 0 Nb) or Si(3 Si, 1 Nb) environments,[3] while that at δ −95.6 is attributed to Si(3 Si, 1 Nb) or Si(2 Si, 2 Nb) sites.

The central-transition ^{93}Nb MAS NMR spectrum [Fig. 2(*b*)] of AM-11 contains a broad (full-width at half maximum, FWHM, *ca.* 127 ppm) resonance centred at δ −100 relatively to solid Nb_2O_5 (the other peaks are spinning sidebands). Considering the few ^{93}Nb NMR spectra reported for niobium

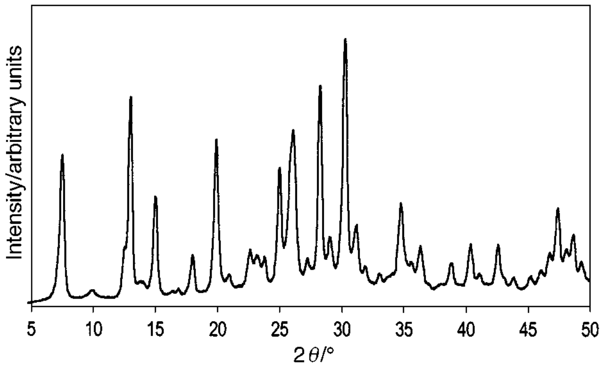

Fig. 1 Powder XRD pattern of AM-11.

Table 1 Powder XRD data of AM-11

d/Å	I/I_0	*d*/Å	I/I_0
11.861	64	3.421	63
8.964	4	3.279	7
7.114	14	3.165	85
6.841	80	3.080	15
6.489	3	2.959	100
6.337	3	2.873	23
5.923	34	2.810	7
4.941	15	2.715	5
4.474	61	2.584	36
4.243	6	2.523	8
3.940	17	2.475	18
3.860	6	2.323	12
3.827	8	2.237	20
3.750	12	2.198	6
3.571	43	2.125	20

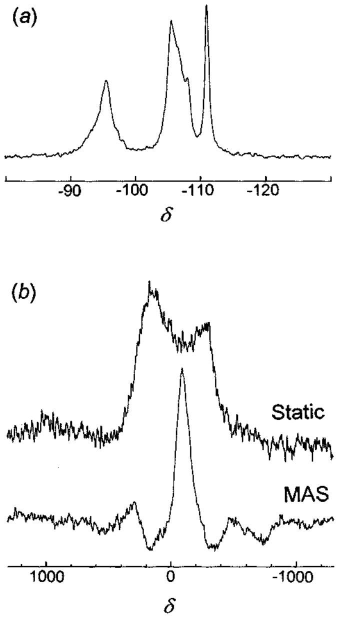

Fig. 2 (*a*) ^{29}Si MAS, (*b*) ^{93}Nb MAS and static NMR spectra of AM-11, recorded at 79.50 and 97.84 MHz on a Bruker MSL 400P spectrometer using spinning rates of 5 and 32 kHz, respectively.

Table 2 Conversions and product distributions (wt%) of isopropanol and *tert*-butanol over AM-11[a]

	Isopropanol[b]	*tert*-butanol[c]
Conversion	99.9	99.9
Propene	85.7	
Acetone	14.2	
Isobutene		98.9
C_5–C_9		1.0

[a] Catalyst activation at $T = 400$ °C and $P = 1$ atm for 3 h. [b,c] $P = 1$ atm, WHSV $= 2$ h^{-1}, TOS $= 60$ min; [b] $T = 350$ °C, Ar carrier gas flow 10 ml min^{-1}; [c] $T = 250$ °C, Ar carrier gas flow 30 ml min^{-1}.

silicates containing hexa-coordinated niobium which give resonances at *ca.* δ 0,[6] this value is slightly shifted to low frequency. This may be due to a large quadrupole coupling constant, (simulation of the static spectrum in Fig. 2(*b*) indicates a rather large value, in excess of 26 MHz) which results in a significant low-frequency shift. The FWHM of the static spectrum is *ca.* 640 ppm. Hence, MAS narrows the NMR resonance by a factor of five. Now, when second-order quadrupole effects dominate, MAS only narrows the peaks by a factor of *ca.* 3.6. We conclude that other line broadening mechanisms, such as chemical shift anisotropy and dipolar interactions are in operation.

The central-transition ^{23}Na MAS NMR spectrum of AM-11 (not shown) contains a broad peak centred at δ −6 with a faint shoulder at *ca.* δ −12 (relatively to aqueous NaCl).

The Raman spectrum of AM-11 (not shown) displays a main, strong and sharp, band at 687 cm^{-1} and several fainter bands in the range 100–300 cm^{-1}. The former peak is typical of NbO_6 octahedra in porous niobium silicates: the synthetic analogues of nenadkevichite give a similar peak at 668 cm^{-1} and weak bands at 100–300 cm^{-1}.[6]

A preliminary charcterisation of the acid–base properties of AM-11 was performed by means of isopropanol conversion, a probe reaction which is tailored for both acidity and basicity.[8] The main products of this catalytic process are propene and acetone resulting from acid dehydration and base-catalysed dehydrogenation respectively. The product distributions are given in Table 2 and indicate that this material exhibits both acidic and basic active sites in its as-synthesised form. Further studies of the catalytic properties of AM-11 were carried out using *tert*-butanol. From the results given in Table 2, it is apparent that AM-11 dehydrates *tert*-butanol to isobutene with remarkably high activity and selectivity. This finding coupled with the large pore volume of this material point to its potential in catalysis. Moreover, conventional ion-exchange experiments may enhance both its basic and acidic properties.

In conclusion, we report the synthesis and characterisation of AM-11, a novel microporous niobium silicate which is a promising catalyst for the dehydration of alcohols. Work is in progress in order to solve the crystal structure of this material.

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