A Layered Microporous Aluminosilicate Precursor of FER-type Zeolite

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A two-dimensional aluminosilicate microporous compound, synthesized from fluoride-containing aqueous media at 170 °C in the presence of 4-amino-2,2,6,6-tetramethylpiperidine as the template, transforms upon calcination above 500 °C into a FER-type zeolite.

The structure of the mineral ferrierite (structure code FER[1]) is based on five-membered rings. Four such five-membered rings are linked to give [5^4] polyhedral units from which the three-dimensional framework can be constructed.[2] There are two types of perpendicularly intersecting channels. The main channels delimited by ten-membered rings run along the orthorhombic *c*-axis, whereas the other channels parallel to the *b*-axis are outlined by eight-membered rings. The high bond density 'layers' parallel to the *bc* plane are interconnected by T–O–T bonds, the resulting interlayer bond density being much lower; this situation is responsible for the usual plate-like morphology of the ferrierite crystals.

Many synthetic FER-type aluminosilicate materials were prepared hydrothermally using mainly various quaternary ammonium cations or amines generally associated with an alkali cation at temperatures ranging from 100 °C up to 300 °C.[3] Thus, FER-type materials with a Si : Al molar ratio in the framework up to 35 : 1 were obtained. The siliceous form was finally prepared by Gies and Gunawardane[4] from an aqueous medium and was more recently synthesized through a non-aqueous route in the presence of fluoride ions by Kuperman *et al.*[5] In the latter case, crystals with millimetre dimensions and a plate-like morphology were obtained.

Usually the synthesis reaction leads to a crystalline solid ('precursor') that already possesses a three-dimensional framework of TO_4 tetrahedra and the subsequent elimination of the template by calcination occurs without significant structural variations. Surprisingly this is not the case for the 'precursor' reported in this work. Indeed, our investigations seem to show that it is a layered compound, whose calcination leads to a FER-type material. A similar behaviour was very recently reported for the layered microporous borosilicate ERB-1.[6]

The precursor was synthesized from a fluoride-containing aqueous mixture in the presence of 4-amino-2,2,6,6-tetramethylpiperidine as the template (R). Typically, the molar composition of the used gels was 1 $SiO_2 : x\ Al_2O_3 : 1\ R : 1.5\ NH_4F : 0.5\ HF : 10–30\ H_2O$ with x being either 0 or 0.1. After ageing for about 1 hour at room temperature, the gel was transferred into a PTFE-lined stainless-steel autoclave and heated statically at 170 °C for 15 days. After reaction (pH $\approx$ 9) the solids were recovered by filtration, washed with distilled water and dried at 60 °C overnight.

The plate-like morphology of the crystals changes only slightly according to the Al and/or water contents in the reaction mixture. Fig. 1 shows a micrograph of a sample prepared from an Al-containing medium. The aggregates are made of very thin stacked crystals (about 60 × 20 × 0.5 μm).

Variable-temperature X-ray diffraction (Philips PW 1140 diffractometer equipped with a Huber model 631 photographic chamber, Cu-Kα radiation) was performed under air from 30 to 670 °C in steps of 30 °C. The structure of the precursor is only stable up to about 150 °C. Intermediate structures of apparently lower crystallinity occur between about 150 and 500 °C, the observed pattern over 500 °C being characteristic of a well crystallized FER-type zeolite. As an illustration, Fig. 2 displays the powder XRD patterns (STOE STADI-P diffractometer, Cu-Kα_1 radiation) corresponding to the precursor (*a*) and to the compound calcined at 330 °C (*b*) and at 550 °C (*c*). The pattern of the intermediate phase shows both broad and sharp peaks, which could be indicative of a structural disorder. For the precursor and the final FER-type zeolite, all the observed reflections could be indexed with orthorhombic symmetry. The values of the *b* and *c* unit-cell parameters are practically unchanged, whereas the value of the *a* parameter drastically decreases during the transformation into the FER-type structure (Table 1). The values found for this FER-type material are usual.

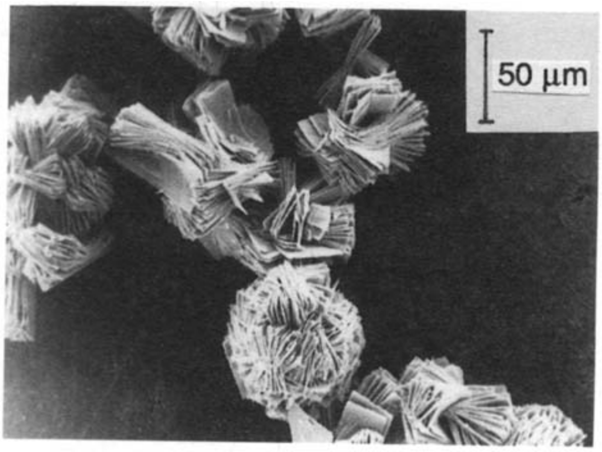

Fig. 1 Micrographs of the layered 'precursor' (molar composition of the reaction mixture 1 $SiO_2 : 0.1\ Al_2O_3 : 1.5\ NH_4F : 0.5\ HF : 10\ H_2O$)

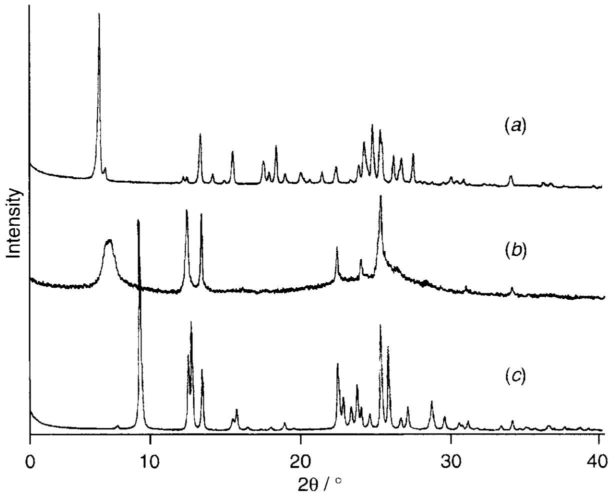

Fig. 2 XRD patterns of (*a*) the layered precursor, (*b*) the intermediate phase (calcined at 330 °C) and (*c*) the final FER-type zeolite (after calcination at 550 °C) (Si : Al molar ratio of the products *ca.* 60 : 1)

Table 1 Unit-cell parameters (Å) of the precursor and of the resulting FER-type zeolite (Si : Al molar ratio of the products *ca.* 60 : 1)

	a	*b*	*c*
'Precursor'	26.25	14.05	7.44
FER-type zeolite	18.78	14.05	7.42

Whatever the x value in the reaction mixture the recovered crystalline solids are essentially siliceous (when x = 0.1, the Si : Al molar ratio in the precursor is *ca.* 60). According to the ^{13}C MAS NMR spectrum of the precursor (not shown) the only occluded organic is the amine initially present in the reaction mixture. The content of organic material is close to 21 mass%; this is much higher than the usual value for FER-type materials, *i.e. ca.* 12%. If one assumes that the unit cell of the precursor contains the same number of TO_4 tetrahedra as the unit cell of the FER-type zeolite, *i.e.* 36, each unit cell of the precursor would contain 4 molecules of template. According to the ^{19}F MAS NMR spectrum, fluoride ions are probably present in the precursor as (Al,F) impurities.

The DTA curve of the precursor recorded under air exhibits one endotherm between *ca.* 100 and 280 °C and a large exotherm between *ca.* 280 and 600 °C. The mass loss on the TG curve occurs in two steps, *i.e. ca.* 10% between 20 and 300 °C and *ca.* 20% between about 300 and 600 °C. This latter mass loss fits well the content of organic material determined by chemical analysis.

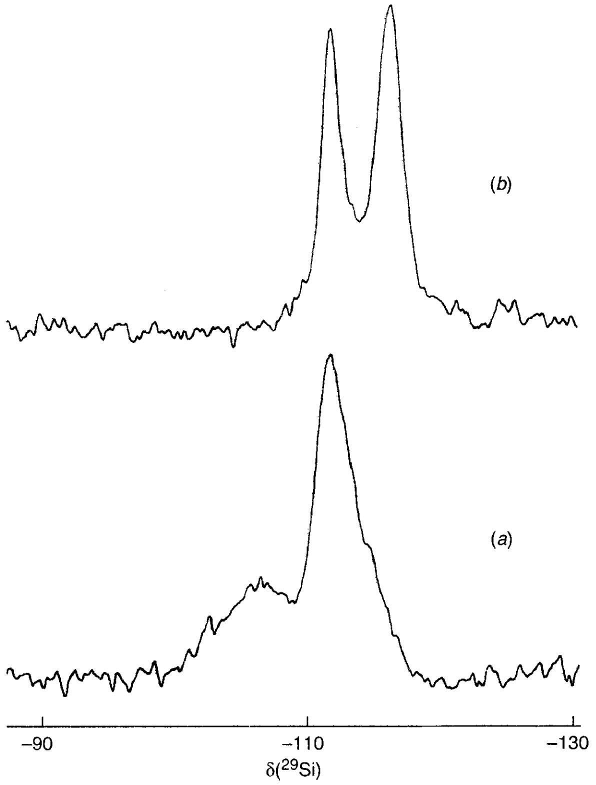

Fig. 3 ^{29}Si MAS NMR spectra of (*a*) the layered precursor and (*b*) the final FER-type zeolite (after calcination at 550 °C) (Si : Al molar ratio of the products *ca.* 60 : 1)

Both structures of the precursor and of the FER-type zeolite are obviously closely related. The observations made above suggest that the structure of the precursor is probably made of the (100) ferrierite layers which are not interconnected and thus display dangling ≡Si–OH (or ≡Si–O$^-$) groups in the [100] direction, these groups condensing upon heating. Indeed the FER-type structure can hardly accommodate the large template used here. The previous assumption is confirmed by ^{29}Si MAS NMR spectroscopy. The spectrum [Fig. 3(*a*)] of the precursor (Si : Al molar ratio ≈ 60 : 1) shows in fact, beside the two peaks at δ −112.0 and −114.7 corresponding to Q4-type silicon atoms, a third peak at δ −106.5 which is probably mainly attributable to Q3-type silicon atoms[7,8] [the Si (3Si,1Al) atoms present in the structure account for a small part of this signal]. The proportion of Q3-type silicon atoms is slightly lower than one third. After calcination the FER-type material displays only the usual peaks corresponding to Q4-type silicon atoms [Fig. 3(*b*)].[9]

The whole of these results suggest that this 'precursor' may consist of two-dimensional sheets, stacked along the *a*-axis of the structure, the bulky organic template being intercalated in the space between the sheets. During calcination the condensation of the silanol groups and the elimination of the organic template occur; this is accompanied by a decrease of the interlayer spacing. Finally the three-dimensional FER-type structure is obtained above 500 °C. Additional experiments are still necessary for a better understanding of the transition mechanism and work is in progress in order to determine the structure of the precursor.

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