Synthesis of an iron silicate with the ferrierite structure

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The synthesis of an iron silicate molecular sieve with a ferrierite type structure and possessing significant quantities of iron (Si/Fe ≈ 11) in the zeolite framework positions is reported.

ZSM-35 is a medium-pore zeolite with FER (ferrierite) topology.[1] It is described as an excellent catalyst for the isomerization of butenes and pentenes.[1,2] ZSM-35 is not only selective but also a very stable isomerization catalyst. Ferrierite has an orthorhombic framework with a two-dimensional channel system of 10-membered rings (4.2 × 5.4 Å) and 8-membered rings (3.5 × 4.8 Å). These two channel systems are perpendicularly intersected. The high butene isomerization activity of ZSM-35 has been attributed to the spatial constraints at the intersection of 10-MR and 8-MR channel systems which restrict bimolecular reaction intermediates involved in the side-product formation.[4] It has been suggested that side reactions of butene isomerization are mainly controlled by two factors, *i.e.* acidity and channel dimensions. During butene isomerization, it is observed that the strong structural Brønsted-acid sites are poisoned by coke deposition (due to side reactions) thus lowering the activity of the catalyst.[5] Therefore it is desirable to modify the acidity of this material without changing the framework structure.

One way of modifying the activity and selectivity of a catalyst is isomorphous substitution of Si and Al by other elements such as Ge, Ga, B, Fe and Ti. Isomorphous substitution of Ga and Fe in β, ZSM-5 and ZSM-22 zeolite frameworks resulted in lowering the strength of Brønsted-acid sites when compared with their corresponding Al analogues.[6–10] There is only one report in the literature that describes isomorphous substitution of Ga for Al, in the ferrierite framework.[11] Isomorphous substitution of iron in the ferrierite structure has not been reported so far. Ferrierite type compounds have been synthesized using hexamethylenediamine,[12] trimethylcetylammonium hydroxide,[13] trimethylamine hydrochloride,[14] cyclohexylamine,[15] ethylenediamine[16] or pyrrolidine,[17] as structure-directing agents. Here, we report for the first time the synthesis of iron-substituted ZSM-35 zeolite using hexamethyleneimine, a new template for this class of materials.

Our initial attempts to synthesize iron-substituted ZSM-35 using pyrrolidine as a structure-directing template with a chemical composition 10–30 SiO_2 : 1 Fe_2O_3 : 11.7 Na_2O : 7.5 pyrrolidine : 900 H_2O were unsuccessful. This composition is very similar to one used for the preparation of Al-ZSM-35 in which the Al source is replaced by $Fe_2(SO_4)_3 \cdot 5H_2O$. In the present work, Fe-ZSM-35 was synthesized as follows. Solution A was obtained by adding appropriate quantities of water and hexamethyleneimine to a sodium silicate solution (27% SiO_2, 14% NaOH, 63% water; Aldrich). Solution B was obtained by dissolving iron(III) sulfate [$Fe_2(SO_4)_3 \cdot 5H_2O$; Fluka] in water. Solution B was then added to A and the mixture stirred for another 20 min. Finally, conc. H_2SO_4 (98%; Aldrich) was added to adjust the final pH of the mixture. The final mixture was a lemon-coloured turbid solution. This solution was then transferred into stainless-steel autoclaves of 300 ml capacity, after which the autoclaves were heated at 150 °C for 15–20 days without stirring. The resultant solid product was recovered by filtration and washed with demineralized hot water. Using this procedure, highly crystalline Fe-ZSM-35 samples with Si/Fe ratios of 10–30 were obtained. When the Si/Fe ratio of the starting reaction mixture was >50, the final product was a mixture of ZSM-35 and α-quartz.

The X-ray powder diffraction pattern was obtained on a Rigaku Ru200 automated powder diffractometer using Cu-Kα radiation (λ = 1.5418 Å). The XRD pattern is very similar to those of its aluminosilicate analogues except that the relative peak intensities are somewhat different. Unit-cell dimensions of Al- and Fe-ZSM-35 samples were determined by a least-squares method using 20 reflections in the 2θ range 5–50°. In Table 1 we have compared unit-cell parameters of the as-synthesized orthorhombic Fe-ZSM-35 sample of the present study with Ga-ZSM-35 and Al-ZSM-35 zeolites. The data shows that there is a significant increase in the unit-cell volume of Fe-ZSM-35 when compared with the Al-ZSM-35 zeolite. The increase in the unit-cell volume of Fe-ZSM-35 is a clear indication of substitution of Fe in the zeolite framework positions. A scanning electron micrograph of the Fe-ZSM-35 (Si/Fe = 11) sample (Fig. 1) shows roughly spherical particles 1–1.5 μm in diameter. Each particle appears to be composed of much smaller crystallites. When the Si/Fe ratio of Fe-ZSM-35 was increased to 30, the shape and size of the particles changed significantly. The particles were 8 μm in length and 6 μm in width, composed of well defined elongated rectangular crystals. However, the size of the individual crystals was variable. The largest crystal was *ca.* 8 μm in length, 1.4 μm in width and 0.4 μm in height and the smallest crystal was *ca.* 3 μm in length, 0.6 μm in width and <0.1 μm in height. The shape of Fe-ZSM-35 (Si/Fe = 30) crystals is somewhat similar to that of the Al-ZSM-35 crystals (Si/Al = 11) synthesized using pyrrolidine as a template.[17]

TGA analyses were carried out using a DuPont (Model 951) thermal analyser. The sample, *ca.* 20 mg, was placed in a quartz bucket and heated in a mixture of oxygen and nitrogen at a heating rate of 10 °C min^{-1}. The TGA curve clearly shows three mass loss steps. The first step (<250 °C) is due to the desorption of water. The second (250–450 °C) and third (450–650 °C) steps correspond to the desorption and decomposition of the organic template used for the Fe-ZSM-35 synthesis, respectively. The amounts of water and organics

Table 1 Unit-cell parameters of M-ZSM-35 samples in their as-synthesized form

Sample	Si/M[a]	*a*/Å	*b*/Å	*c*/Å	*U*/Å^3	Ref.
Al-ZSM-35	12.5	18.92(1)	14.132(8)	7.462(0)	1995(1)	This work
Ga-ZSM-35	6.6	19.01(1)	14.15(1)	7.461(4)	2007	11
Fe-ZSM-35	11.0	19.336(5)	14.263(4)	7.528(4)	2076(1)	This work

[a] M = Al, Ga or Fe.

desorbed were *ca.* 1.7 and 11.8 mass%, respectively. As-synthesized ferrisilicate was converted into its sodium form by calcination in air at 540 °C for 5 h. The sodium form of ferrisilicate was ammonium exchanged with 5 mol dm^{-3} ammonium chloride solution and the acid or protonated form was obtained by calcination of the ammonium form in air at 400 °C for 2 h. The bulk and the surface compositions determined by conventional and X-ray photoelectron spectroscopic methods for the as-made and protonated form of Fe-ZSM-35 are given in Table 2. The constancy in the Si/Fe ratio before and after ion exchange indicates that Fe^{3+} ions are present in non-exchangeable positions of the ferrierite framework.

Gravimetric adsorption capacities for Al-ZSM-35 and Fe-ZSM-35 in their Na-form are presented in Table 3. Pellet *et al.*[18] studied the adsorption of pentane and carbon dioxide in Al-ZSM-35 zeolite. They found *ca.* 0.091 ml of pentane and 0.104 ml of CO_2 were adsorbed per gram of zeolite. The adsorption capacities determined using water and hexane as adsorbates in the present work are very close to the reported values.[18] The cyclohexane adsorption capacity for Fe-ZSM-35 was found to be somewhat higher than that of Al-ZSM-35 zeolite. This data, along with XRD, TGA and SEM results, confirms the structure identity and the phase purity of the sample. The adsorption study also suggests that the Fe species are in zeolite framework positions and not as an occluded iron oxidic species. The presence of iron oxidic species in the zeolitic channels would lower the adsorption capacity of the sample.

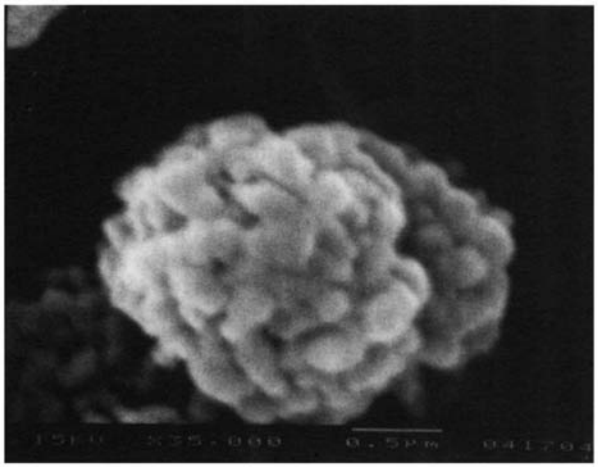

Fig. 1 Scanning electron micrographs of Fe-ZSM-35 (Si/Fe = 11)

Table 2 Bulk and surface compositions of as-made and H-form Fe-ZSM-35 samples

Fe-ZSM-35	Na/Fe (bulk)	Si/Fe Bulk	Si/Fe Surface
As-made	0.40	12.5	14.8
H-form	0.03	12.4	14.2
As-made	0.38	11.2	11.5
H-form	0.04	11.0	11.4

Table 3 Gravimetric adsorption capacities for ZSM-35 zeolites in their Na-form

Sample	Si/M[a]	Adsorption/ml g^{-1} Water	Hexane	Cyclohexane
Fe-ZSM-35	11.0	0.090	0.062	0.030
Al-ZSM-35	12.0	0.095	0.046	0.015

[a] M = Al or Fe.

The presence of extraframework iron oxidic species is well characterized by examining the O 1s XPS peak of Fe-ZSM-35. The O 1s spectrum of the Fe-ZSM-35 sample showed peaks at 532.3 and 531.5 eV (not shown). The main peak at 532.3 eV corresponds to the oxygen species associated with the zeolite lattice and the shoulder at 531.5 eV is due to extraframework iron oxidic species.[19] The area contribution due to extraframework iron oxidic species is < 10% compared to the main O 1s peak. Since most of the extraframework species are present on the surface of the crystallites, this 10% value may still be <2% of the bulk iron content.[20] It reflects that the extraframework iron oxidic species are formed during the course of Fe-ZSM-35 synthesis. The presence of such small amounts of iron oxidic species have been observed by us and others for other iron-containing zeolitic materials.[21–24] This indicates that most of the iron is situated at the zeolite lattice positions.

To summarize, a synthesis of an iron silicate molecular sieve possessing the ferrierite structure using hexamethyleneimine as an organic template, is reported.

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