Hydrothermal synthesis of an iron silicate with layered structure

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A method is provided for the synthesis of a crystalline layered iron silicate using a particular reaction gel composition containing an organic directing agent and possessing significant quantities of iron (Si/Fe = 38.6) in trivalent oxidation state; the present layered iron silicate has a structure related to kenyaite and/or silica-X.

Kenyaite is a hydrous sodium silicate mineral first found in the lake beds of Lake Magadi in Kenya.[1] Synthetic forms of similar silicates using potassium instead of sodium ions, with layered structures, were subsequently prepared.[2–5] Synthetic kenyaite has the chemical formula $K_2Si_{20}O_{41}\cdot xH_2O$. The intercalation behaviour of this material was used to establish its layered structure. The crystal structure of kenyaite remains unknown at present. The layered silicate, identified as silica-X, was first reported by Heidemann.[6] Silica-X was synthesized hydrothermally using silicic acid and KOH solution at 175 °C for 3–10 days,[6,7] Attempts made by Greenwood,[8] to synthesize silica-X using silicic acid and Na^+, Mg^{2+} and NH_4^+ cations instead of K^+, were unsuccessful. However, the synthesis of silica-X using diaquat-4 halide[9] and of kenyaite using poly(diethyldiallylammonium chloride)[5] as a structure-directing template is reported in the literature. Incorporation of Al in kenyaite or silica-X by synthetic routes was also achieved.[5,9] Comparison of X-ray powder diffraction patterns of silica-X with kenyaite suggests that these materials are closely related to each other. Here, we report the synthesis of an iron silicate with a kenyaite/silica-X type structure using hexamethyleneimine (HMI) as template.

A typical procedure to synthesize the iron containing layered silicate is as follows. Solution A was obtained by adding appropriate quantities of water and the nitrogen-containing template to a sodium silicate solution (27% SiO_2, 14% NaOH and 69% water, Aldrich). Solution B was prepared by dissolving iron(iii) sulfate [$Fe_2(SO_4)_3\cdot 5H_2O$, Fluka] in water. Then, solution B was added (dropwise addition) to A. The addition of the $Fe_2(SO_4)_3\cdot 5H_2O$ solution is a crucial step. Slow addition produces a lemon-coloured solution and fast addition produced a red–brown mixture. When addition was complete, the mixture was stirred for another 20 min. Finally, conc. H_2SO_4 (98%, EM Science) was added to adjust the final pH of the mixture. The final mixture was a lemon-coloured turbid solution with the chemical formula: 20–40 $SiO_2 : 1\ Fe_2O_3 : 9.8\ Na_2O : 13.7\ HMI : 1360\ H_2O : 9.8\ H_2SO_4$. This solution was then transferred into stainless-steel autoclaves of 300 ml capacity, which were heated at 150 °C for 15 days without stirring. The resultant solid product was recovered by filtration and washed with demineralized hot water. This product is denoted as as-made kenyaite. The Na-form of the sample was prepared by air calcination of the as-made sample at 540 °C for 4 h. This material was repeatedly ion-exchanged with 5 m ammonium chloride solution at 80 °C to obtain the NH_4-form of kenyaite. The H-form was obtained by calcination of the NH_4-form in air at 400 °C for 2 h. Using this procedure, highly crystalline iron silicate samples with input SiO_2/Fe_2O_3 ratios of 20–40 were obtained.

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, presented in Fig. 1, is similar to kenyaite and or silica-X type materials. Scanning electron micrographs of the iron silicate (Fig. 2) show spherical

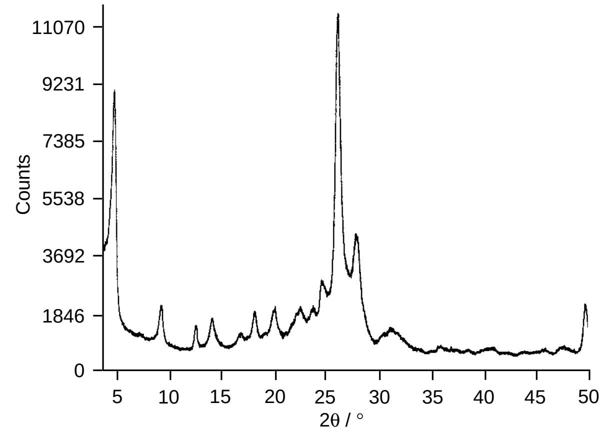

Fig. 1 X-Ray powder diffraction pattern of iron-containing kenyaite (as-made)

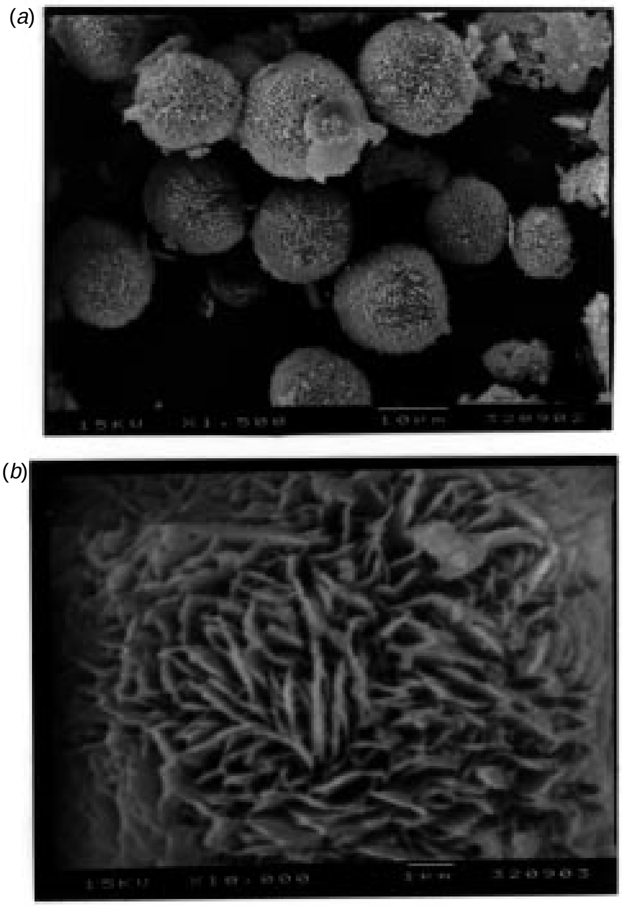

Fig. 2 Scanning electron micrographs of iron-containing kenyaite at different magnifications

particles 5–15 μm in diameter. The spherical aggregates are made up of a variety of thin stacked crystals in rosette form. This platelet morphology is very similar to those of kenyaite[5] and ferrierite type materials.[10,11] After calcination at 540 °C for 4 h, the peak at 3.25 Å disappeared completely and all peaks were shifted towards lower *d* values. The relative shift in *d* values was significant for the first two peaks. For kenyaite, Eugster[1] indexed these two peaks as 001 and 002 reflections, assuming tetragonal symmetry. In as-synthesized iron silicate these 00*l* reflections appear at 20.2 and 10.1 Å and in the calcined sample at 17.6 and 8.8 Å. Similar observations have been made by Schwieger *et al.*[5] for kenyaite. TGA experiments were carried out using a DuPont (Model 951) thermal analyser. About 20 mg of the sample was placed in a quartz bucket and heated in a nitrogen–oxygen atmosphere at a heating rate of 10 °C min^{-1}. The TGA curve clearly showed three mass losses. The first step (25–200 °C) is due the desorption of water and the second (200–600 °C) and third steps (600–950 °C) are due to desorption/decomposition of the organic template and dehydroxylation of iron silicate, respectively. The (Na + organic)/(Si + Fe) ratio in as-made kenyaite is 0.073/1. The mass loss associated with each step was 4.7, 6.6 and 4.0%, respectively. That the third step is indeed due to dehydroxylation and not due to the residual carbon was confirmed by carrying out additional TGA experiments with Na^+ and H^+ forms of kenyaite containing no template. The chemical composition and sorption capacity of iron silicate are reported in Table 1. The constancy in the Si/Fe ratio before and after ion exchange indicates that Fe is not present in occluded form or in ion-exchangeable sites. Sorption data presented in Table 1 suggest that the iron silicate of the present study sorbs water as well as *n*-hexane in amounts 3–4 times greater than silica-X.[9] The measured N_2 BET surface area of the iron silicate was 170 $\mathrm{m}^2\ \mathrm{g}^{-1}$.

The presence of most of the Fe in the trivalent oxidation state and indeed situated in the layered silicate framework position is confirmed by studying the O 1s XPS and EPR spectra of iron silicate. The surface Si/Fe ratio determined by XPS was 32.8 and by bulk chemical analysis 38.9 for the Na-form of the iron silicate indicating a somewhat inhomogeneous Fe distribution and/or the presence of a small amount of extraframework iron oxidic species on the surface of the sample. In addition, the O 1s XPS spectra (not shown) gave a main peak at 532.4 eV and a shoulder at 530.7 eV corresponding to oxygen species associated with the silicate framework and extraframework iron oxidic species, respectively. The relative area contribution due to the shoulder peak to the main O 1s peak was *ca.* 13%. When the Na-form of the iron silicate was exchanged with $\mathrm{NH_4Cl}$ the relative contribution of the O 1s shoulder peak to the main peak reduced to 7%, indicating that there are some iron oxidic species that can be washed away by $\mathrm{NH_4}^+$ treatment. Since the Na/Fe ratio was close to 1 in the Na-form of the material, the possibility of the presence of Fe in an ion-exchangeable site is less likely. It is obvious that these excess Fe species must be occluded iron oxidic/hydroxidic species. The formation of such small amounts of extraframework iron oxidic species during the synthesis of iron-containing zeolites was previously observed.[12–14] X-Band EPR spectra were obtained at room temperature using a Bruker ER-200 D spectrometer. The spectrum shown in Fig. 3 shows four signals at $g = 2.0$, *ca.* 2.9, 4.3 and 9.6. The signal at $g = 4.3$ in conjunction with the signal at $g = 9.6$ is commonly assigned to incorporation of Fe^{3+} on a strongly distorted rhombic site.[15–18] The signal at $g = 2.8$ has been assigned to Fe as iron oxidic or hydroxidic phases. This is consistent with the O 1s XPS results. The signal at $g = 2.0$ may be due to framework or non-framework Fe^{3+} species.[15] These two species can be distinguished by EPR by conducting dehydration–rehydration studies with the same sample. Thus, an EPR study in combination with XPS clearly shows the presence of most of the Fe^{3+} in framework positions. The FTIR spectra of chemisobed $\mathrm{NH_3}$ revealed the formation of $\mathrm{NH_4}^+$ ions (*ca.* 1460 cm^{-1}) with Brønsted-acid sites indirectly suggesting that Fe is present in the framework position.[19]

To summarize, synthesis of an iron silicate with a kenyaite and/or silica-X type material using a hexamethyleneimine template is reported.

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Table 1 Chemical composition and sorption capacity of iron silicate in various forms

	Tem- plate	Mass%			Mole ratio		Mass%	
Sample	(mass%)	Na	Si	Fe	Na/Fe	Si/Fe	Water	*n*-Hexane
As-made	6.6	0.72	36.88	1.77	0.99	38.6	—	—
Na Form	—	0.80	37.20	1.91	0.98	38.9	5.86	3.90
H Form	—	0.05	37.10	1.85	0.06	40.1	5.67	4.00

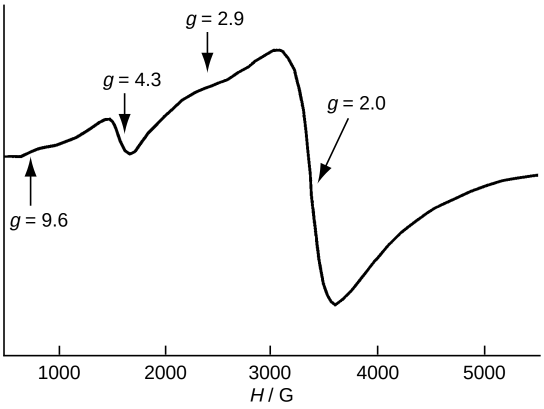

Fig. 3 Room-temperature EPR spectrum of as-made iron-containing kenyaite

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