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Role of alkali-metal cations and seeds in the synthesis of silica-rich heulandite-type zeolites

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Clinoptilolite, the silica-rich member ($Si/Al>4$) of the heulandite family of zeolites, crystallizes from pure Li, Na, K, and Rb ion-containing gel systems as well as mixed Li,K, Na,K and K,Rb gels. Crystallization occurs at temperatures between 140 and 190 °C and is relatively insensitive to the nature of the silica or alumina source. Members of this family are formed over a narrow range of gel Si/Al ratio (2.5–6) and OH/SiO_2 ratio (0.3–0.4 in the Na,K system and 0.6–0.9 in the Li,K system). The nature of the alkali-metal cation does not have a critical structure determining role in the synthesis but does contribute to other properties of the material including the rate of crystallization, the Si/Al ratio of the resulting crystals, the crystal size and the morphology. Potassium ions greatly increase the rate of crystallization and decrease the nucleation time. The addition of other cations to the potassium ion-containing gels slows the rate of crystallization but increases the stability of the resulting clinoptilolite crystals in the mother liquor. Sodium ions increase the Si/Al ratio of the crystals while lithium ions increase their aluminium content. Seeds (1–10 mass%) promote crystallization in the Li-, Na-, Rb- and Rb,K- containing systems, but are not necessary in gels containing K, Na,K or Li,K. In the absence of seeds, other phases co-exist or are preferred, including mordenite, phillipsite, and analcime depending on the Si/Al ratio of the gel. Crystallization time is the key parameter in preparing high purity clinoptilolite materials.

The heulandite (HEU) family of zeolites, including heulandite ($Si/Al<4$) and the silica-rich heulandite, clinoptilolite ($Si/Al>4$), is the most abundant of the natural zeolites.[1] The HEU framework contains a two-dimensional pore structure of intersecting 8- and 10-ring channels making it of interest for use in adsorption, ion exchange and catalytic applications.[2] Natural clinoptilolite exhibits an excellent selectivity for ammonium cations and is used extensively in fish farming and agriculture.[3–5] A more recent application for this zeolite has been in the area of radioactive and metal ion waste removal.[6] Clinoptilolite is highly selective towards cobalt, strontium, and caesium cations which are common radioactive components of nuclear reactor effluent.[7,8] Woo *et al.* have suggested that pure clinoptilolite is a potential catalyst for the isomerization of but-1-ene to 2-ethylpropene[9] and Kallo *et al.* investigated natural clinoptilolites for xylene and *n*-butene isomerization, methanol dehydration and acetylene hydration.[10] Impurities such as iron are commonly found in natural samples and limit the application of natural clinoptilolite as a catalyst. Overall however, clinoptilolite represents a non-renewable natural resource. With the myriad of useful as well as potential applications, it is therefore valuable to have high purity crystalline synthetic clinoptilolite that can be prepared *via* environmentally benign methods.

A number of researchers have reported the synthesis of clinoptilolite-type zeolites under various conditions. Hawkins *et al.* synthesized impure Na,K-clinoptilolite from volcanic glass with seeds at 130–150 °C under the high pressure of 1 kbar.[11] Goto also synthesized Na,K-clinoptilolite from chemical reactants at 200 °C and autogenous pressure (*ca.* 15 atm), but obtained mixtures of clinoptilolite and mordenite.[12] Chi and Sand synthesized end-members Na-clinoptilolite and K-clinoptilolite from chemical reactants with 10 mass% natural clinoptilolite seed crystals at 120–200 °C and autogenous pressure.[13] In one synthesis without seed crystals they obtained only 75% clinoptilolite and 25% other zeolites, mainly mordenite, which cannot be transformed to clinoptilolite. Satokawa and Habashi recently reported the synthesis of a K,Na-clinoptilolite-type phase in the absence of seeds[14(a)] and we have reported similar results for several alkali-metal clinoptilolites in a recent communication.[14(b)] Alkaline-earth clinoptilolite-type zeolites and lithium clinoptilolite-type zeolites were also reported but only under conditions of high temperature and pressure.[15–18] Recently, Khodabandeh and Davis reported that the aluminium-rich variant, heulandite can be synthesized by hydrothermal conversion of zeolite P1 with 3–30 mass% clinoptilolite seeds,[19a] and we have also reported on the synthesis of heulandites.[19b] Despite the diverse conditions and variety of alkali-metal cations used to prepare zeolites with HEU topology, to date no comprehensive study has been undertaken to provide insight into the range over which crystallization occurs and the role the alkali-metal cations play in the crystallization of this phase.

Here we report results of our detailed study of the hydrothermal synthesis of alkali-metal clinoptilolite-type zeolites including the Li, Na, K and Rb forms as well as the mixed Na,K-, K,Li-and Rb,K-clinoptilolite-type phases produced with and without the use of seed crystals from different silica and alumina sources. The synergy between the type of inorganic cations and cation mixtures, and the effect of the OH/SiO_2, SiO_2/Al_2O_3 and cation ratios on the formation and nature of the phases produced is discussed.

Experimental

Materials

Silica sources were Ludox LS colloidal silica, 30 mass% silica, Aldrich Chemical Corp.; fumed silica, 99.8 mass% silica, Sigma; sodium silicate, N-brand, 27 mass% silica, 14 mass% NaOH, Aldrich; and potassium silicate, 8.3 mass% K_2O, 20.8 mass% silica, Pfaltz and Bauer, Inc. Alumina sources were aluminium hydroxide, USP, Pfaltz and Bauer, Inc.; Catapal B alumina (boehmite), Vista Chem. Corp; and sodium aluminate ($NaAlO_2 \cdot 1.95H_2O$) MCB Manufacturing Chemists Inc. Rubidium hydroxide, 99 mass%, 50 mass% solution in water, Aldrich; lithium hydroxide monohydrate, 98 mass%, Aldrich; potassium hydroxide, J. T. Baker Inc.; sodium hydroxide, 97 mass%, GR, a division of EM Industries, Inc.; potassium carbonate, 98% GR, a division of EM Industries Inc.; sodium carbonate, 99% anhydrous, J. T. Baker Inc. were also used. All chemicals were used as received. Natural clinoptilolite is from the Ash Meadows deposit in California. The natural material was heated in deionized water to remove soluble salts and dispersed in deionized water to remove heavy impurities by settling. The purified natural clinoptilolite was used as seed crystals and as the powder X-ray diffraction (XRD) measurement standard.

Synthesis

Crystallization was carried out in stainless steel autoclaves lined with a Teflon container under autogenous pressure from a gel. Excellent crystals of clinoptilolite were prepared as follows. In a typical synthesis, 0.78 g dried aluminium hydroxide $Al(OH)_3$ was added to 0.59 g of 6 M NaOH and 2.80 g of 6 M KOH solution with stirring. After stirring for 0.5 h, 10 g of colloidal silica solution were added with vigorous stirring for 1 h and 10 mass% natural clinoptilolite as seed crystals was added to this gel with stirring. This gel mixture was placed in a static autoclave at 180 °C for 60 h. The pH of the mother liquor at the end of the synthesis period was in the range 9.5–11.7. After cooling to room temperature the resulting solid product was recovered by filtration on a Buchner funnel, washed with water, and dried in air at 70 °C. The products were calcined in an oven in air at 300–600 °C overnight.

Instrumentation

X-Ray powder diffraction patterns were obtained on a Siemens D5000 diffractometer using Cu-Kα radiation. A scan speed of 1.0° min^{-1} was used. Quantitative information was obtained using natural clinoptilolite as a reference and the crystallization percentage of the synthesized samples was calculated from the sum of the integral intensities of the seven strongest lines ($2\theta = 5–40°$) of the investigated sample and the reference, using the technique described previously.[20,21] Scanning electron microscopy (SEM) was performed on a Cambridge 2500 MK3 microscope. Metal ion concentrations were determined by electron microprobe analysis with a JEOL JXA 8600 Superprobe. Electron paramagnetic resonance (EPR) spectra were taken on a Bruker ESP 300 spectrometer.

Results and Discussion

Typical reactant molar compositions, reaction conditions and pH values of the mother liquor at the end of the synthesis period for alkali-metal clinoptilolite-type zeolite syntheses are summarized in Table 1. The X-ray powder diffraction patterns of synthetic alkali-metal clinoptilolites are shown in Fig. 1.

Role of inorganic cations

We have systematically examined the role of inorganic cations in the production of the clinoptilolite-type phase. Although clinoptilolite can be prepared using most alkali-metal cations and several combinations of cations, this phase is preferably prepared in the presence of potassium ions. Table 2 summarizes the cations studied and their ability to crystallize clinoptilolite in the presence and absence of seed crystals. Pure Li-, Na-, K- and Rb-clinoptilolite-type zeolites form easily in the presence of seeds but only the potassium-containing endmember is successfully prepared with 100% crystallinity in the absence of seeds. Of the mixed cation systems, only those containing potassium result in high purity clinoptilolite in the absence of seeds. Both the Li- and Na-end-members crystallize the heulandite structure in the presence of seeds, but the mixed Na,Li cation system does not produce this phase. Ba,Na-containing gels were also explored but they do not produce the clinoptilolite phase even in the presence of seeds.

Although the end-member K-clinoptilolite can be synthesized with 1–10 mass% seeds or without seeds, this phase has a short lifetime in the gel, generally about 26 h in a seeded system (10 mass% seeds) and about 14 h in an unseeded system. At longer times the clinoptilolite-type phase is replaced with analcime. In mixed Na,K gel systems the time over which the clinoptilolite-type phase is stable at 100% crystallinity is doubled. The clinoptilolite crystals are stable in the mother liquor for two days in seeded systems and for one day in unseeded systems. This is illustrated in Fig. 2. The retention time for clinoptilolite crystallization is more than three days for the Li,K-cation system without seeds ($Li/Li+K = 0.8$ at 170–200 °C, $OH/Si = 0.63–0.90$). Like pure Na- and K-containing gels, at longer times analcime is observed as a final product in the mixed cation-containing systems. In an unseeded mixed Na,K-system at high $Na/Na+K$ ratios (>0.5), the primary phase is mordenite. This is not surprising since mordenite crystallizes from a Na-containing gel in the absence of clinoptilolite seeds. Seeds have a very strong influence on clinoptilolite formation in the Na,K mixed cation gel as shown in Fig. 3. In the presence of seeds clinoptilolite can be formed over the entire range of $Na/Na+K$. Slightly lower crystallinity is noted only at low $Na/Na+K$ ratios, but this is due to the very rapid crystallization of clinoptilolite in a potassium-rich system and the subsequent rapid conversion to analcime before the crystals are isolated.

The solution pH, a measure of the free hydroxide content, of unseeded systems was generally 1.5 units higher than that of the seeded systems. It seems likely that the higher pH decreases the product stability in unseeded systems. However, this is difficult to test rigorously since the pH is not easily controlled in a crystallizing system.

K,Li-clinoptilolite crystallizes from a narrow $Li/Li+K$ ratio (*ca.* 0.8) in an unseeded system. At lower $Li/Li+K$ ratios (<0.8), analcime and mordenite coexisting with clinoptilolite or analcime and mordenite are the exclusive products. With higher $Li/Li+K$ ratio (>0.8), an unknown phase coexists with clinoptilolite. With 10 mass% seed crystals, Li-heulandite is formed while without seeds only 50% Li-heulandite is obtained. With 10 mass% seed crystals clinoptilolite is also crystallized in the presence of Rb and K cations at $Rb/Rb+K = 0.25$. With 10 mass% seed crystals end-member Rb-clinoptilolite can be produced in high purity. However, in the absence of seed crystals, only 80% Rb,K-clinoptilolite and 70% Rb-clinoptilolite result. One of the best bases found for this synthesis system is potassium carbonate. With potassium hydroxide, analcime often coexists with clinoptilolite.

The nature of the inorganic cation influences the nucleation time and the crystallization rate of clinoptilolite. The crystallization rate of clinoptilolite is slower in the Na-system than in the K- and Rb-systems. With Li^+ cations, the crystallization time is significantly suppressed and the synthesis of heulandite/clinoptilolite requires seven days at 190 °C. The addition of sodium to the potassium-containing gels increases the stability of clinoptilolite in the mother liquor and decreases the rate of clinoptilolite crystallization. The addition of clinoptilolite seeds also increases the clinoptilolite crystallization rate (see Fig. 2), allows clinoptilolite to more rapidly reach 100% crystallinity and suppresses mordenite formation at high sodium contents.

The nature of the cations in the gel influences the resulting Si/Al ratio of the clinoptilolite crystals produced. Table 3 shows a comparison of the Si/Al ratios in the gel used for the various cations and the final Si/Al ratios of the clinoptilolite produced. In all cases seeds were present except for the one noted. The presence of lithium ions in the gel produces the heulandite-type phase with an Si/Al ratio of 4.0, while the use of sodium produces clinoptilolite with a significantly higher Si/Al ratio ($Si/Al = 6.4$). This is not surprising since sodium-containing gels tend to crystallize the more silica-rich mordenite phase. The pure potassium end-member is also more silica-rich than the starting gel, as is the mixed Na,K-containing clinoptilolite, and both are lower in Si/Al ratio than the sodium end-member. Both the Rb- and the Li,K- systems produce lower silica

Table 1 Synthesis conditions for heulandite/clinoptilolite zeolites

run no.	reaction composition	seed (mass%)	temperature/ °C	time/ h	final pH[f]	product(s)
142	$LiOH/Al(OH)_3/SiO_2{}^a/H_2O$ 36 10 45 2868	10	190	194	10.1	heulandite (100%)
143	$LiOH/Al(OH)_3/SiO_2{}^a/H_2O$ 36 10 45 2868	0	190	194	10.3	clinoptilolite (50%)
169	$Na_2O^b/Al_2O_3{}^b/SiO_2{}^a/H_2O$ 5 5 45 511	10	160	98	9.6	clinoptilolite (100%)
170	$NaOH/Al(OH)_3/SiO_2{}^a/H_2O$ 16 10 45 497	1	140	144	11.7	clinoptilolite (100%)
181	$Na_2O^b/Na_2O^c/Al_2O_3{}^b/SiO_2{}^c/H_2SO_4/H_2O$ 5 17.5 5 45 15.4 625	10	160	98	9.6	clinoptilolite (100%)
178	$KOH/Al(OH)_3/SiO_2{}^a/H_2O$ 16 10 45 550	10	180	60	9.9	clinoptilolite (100%)
179	$KOH/Al(OH)_3/SiO_2{}^a/H_2O$ 16 10 45 550	0	180	84	11.5	clinoptilolite (100%)
117	$K_2CO_3/Al(OH)_3/SiO_2{}^a/H_2O$ 11 10 45 646	1	190	106	9.8	clinoptilolite (100%)
180	$RbOH/Al(OH)_3/SiO_2{}^a/H_2O$ 16 10 45 606	10	180	95	10.3	clinoptilolite (100%)
184	$RbOH/Al(OH)_3/SiO_2{}^a/H_2O$ 16 10 45 606	0	180	125	11.5	clinoptilolite (70%) analcime (20%)
107	$LiOH/KOH/Al(OH)_3/SiO_2{}^a/H_2O$ 327 6.8 10 45 1135	0	190	165	10.1	clinoptilolite (100%)
84	$NaOH/KOH/Al(OH)_3/SiO_2{}^a/H_2O$ 3 13 10 45 542	10	180	60	10.2	clinoptilolite (100%)
94	$NaOH/KOH/Al(OH)_3/SiO_2{}^a/H_2O$ 3 13 10 45 542	1	180	92	11.4	clinoptilolite (100%)
91	$NaOH/KOH/Al(OH)_3/SiO_2{}^a/H_2O$ 3 13 10 45 542	0	180	112	11.5	clinoptilolite (100%)
88	$Na_2O^b/K_2CO_3/Al_2O_3{}^b/Al(OH)_3/SiO_2{}^a/H_2O$ 2.4 7.1 2.4 5.2 45 579	10	190	91	10.2	clinoptilolite (100%)
124	$Na_2O^b/K_2CO_3/Al_2O_3{}^b/Al(OH)_3/SiO_2{}^a/H_2O$ 2.4 7.1 2.4 5.2 45 579	0	190	118	9.8	clinoptilolite (100%)
85	$Na_2CO_3/K_2CO_3/Al(OH)_3/SiO_2{}^a/H_2O$ 14.8 7.1 10 45 627	10	190	109	9.5	clinoptilolite (100%)
130	$RbOH/K_2CO_3/Al(OH)_3/SiO_2{}^a/H_2O$ 4.8 7.1 10 45 627	5	190	71	9.9	clinoptilolite (100%)
141	$RbOH/K_2CO_3/Al(OH)_3/SiO_2{}^a/H_2O$ 14.8 7.1 10 45 627	0	190	95	10.5	clinoptilolite (80%) analcime (16%)
134	$RbOH/Al(OH)_3/SiO_2{}^a/H_2O$ 2.4 10 45 1006	10	180	94	9.5	clinoptilolite (100%)
133	$Na_2O^b/K_2CO_3/Al_2O_3{}^b/Al(OH)_3/SiO_2{}^d/H_2O$ 2.3 7.1 2.3 5.3 45 643	10	180	100	10.0	clinoptilolite (100%)
175	$NaOH/KOH/Al_2O_3{}^e/SiO_2{}^a/H_2O$ 3 13 10 45 524	10	180	68	9.8	clinoptilolite (100%)
183	$NaOH/KOH/Al(OH)_3/SiO_2{}^a/H_2O$ 2.3 10 10 25 350	10	185	84	9.6	heulandite (100%)

[a]Ludox LS colloidal silica. [b]Sodium aluminate. [c]Sodium silicate. [d]Fumed silica. [e]Catapal B alumina. [f]pH of the mother liquor at the end of the synthesis period.

clinoptilolite phases; neither, however, are in the heulandite composition range. The use of seeds has little influence on the Si/Al ratio of the product as seen in the comparison of two Na,K-containing gel systems which crystallize with the same Si/Al ratio. The Na,K-containing gel system does accomodate the synthesis of both clinoptilolite as well as heulandite-type phases. Lowering the Si/Al ratio of the Na,K-containing gel from 4.5 to 2.5 produces high quality heulandite crystals with an Si/Al ratio of 3.2 as shown in Table 1.

The type of inorganic cation present in the crystallizing gel influences the morphology and crystal size of the clinoptilolite product. The results from scanning electron photomicrographs are summarized in Table 4 and some typical photomicrographs are shown in Fig. 4. Na,K-Clinoptilolite and K-clinoptilolite synthesized in an unseeded system show a platy morphology. The crystal sizes are typically 5–10 µm. Na,K-Clinoptilolite, Na-clinoptilolite and K-clinoptilolite synthesized in a seeded system have a similar platy morphology but the crystal sizes are typically 1–5 µm which are smaller than those in an unseeded system. Li-heulandite synthesized in a seeded system shows radical aggregate morphology. Unlike Na,K-clinoptilolite, which shows crystal twins, Li, K-clinoptilolite synthesized in an unseeded system shows excellent lath crystal morphology and the crystal sizes are typically 30–40 µm, which are much bigger than that of Na,K-clinoptilolite.

Role of base

Clinoptilolite can be synthesized from different bases, including weak bases such as K_2CO_3 and Na_2CO_3. With these weaker bases, higher temperatures or longer times are required. As shown in Table 1, a mixture of potassium carbonate and sodium hydroxide is probably the best selection of base for the formation of clinoptilolite.

In a seeded system (10 mass%), increasing the OH/Si ratio initially increases the percentage crystallinity of the clinoptilolite, and then greatly decreases it indicating a very narrow window over which clinoptilolite-type zeolites can crystallize. The effects of the OH concentration in the gel as well as the free OH content on the crystallinity of clinoptilolite are illustrated in Fig. 5. The optimum OH/Si ratio is 0.36 for the synthesis of clinoptilolite with solution pH between 11.0 and

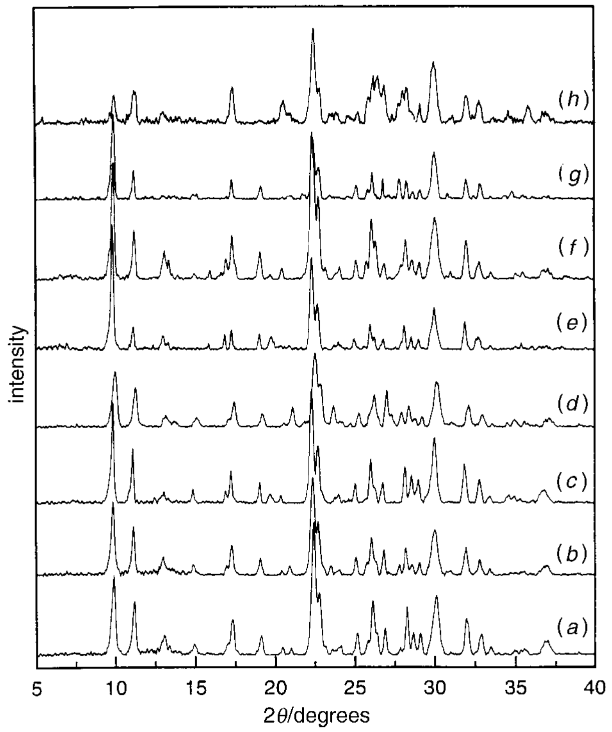

Fig. 1 X-Ray powder diffraction patterns of as-synthesized alkali heulandite-clinoptilolites: (*a*) Na,K-clinoptilolite synthesized in an unseeded system; (*b*) Na,K-clinoptilolite in a seeded system (10 mass%); (*c*) K,Li-clinoptilolite in an unseeded system; (*d*) K-clinoptilolite in an unseeded system; (*e*) Li-heulandite in a seeded system (10 mass%); (*f*) Na-clinoptilolite in a seeded system (1 mass%); (*g*) K-clinoptilolite in a seeded system (10 mass%) and (*h*) Rh-clinoptilolite in a seeded system (10 mass%)

Table 2 Correlation between inorganic cations in the gel and the presence or absence of seed crystals on the formation of high purity clinoptilolite-type zeolite

	formation of clinoptilolite	
cations	seeds	no seeds
Li	yes	no
Na	yes	no
K	yes	yes
Rb	yes	no
Na,K	yes	yes
Li,K	yes	yes
Rb,K	yes	no
Na,Li	no	no
Ba,Na	no	no

11.5. With lower OH/Si ratio (0.28–0.36), clinoptilolite can be crystallized at longer times or at higher temperatures. At higher OH/Si ratio (>0.45), crystallization occurs at shorter times and lower temperatures, but clinoptilolite coexists with analcime or only the analcime phase is formed.

The final pH value (free hydroxide content) of the mother liquor in an unseeded system compared with that in a seeded system is much higher as shown in Fig. 2 and Table 1. The presence of higher concentrations of free base in an unseeded system may be one of the reasons for the instability of this phase over time and why pure clinoptilolite is difficult to synthesize in an unseeded system as other phases tend to predominate at high pH.

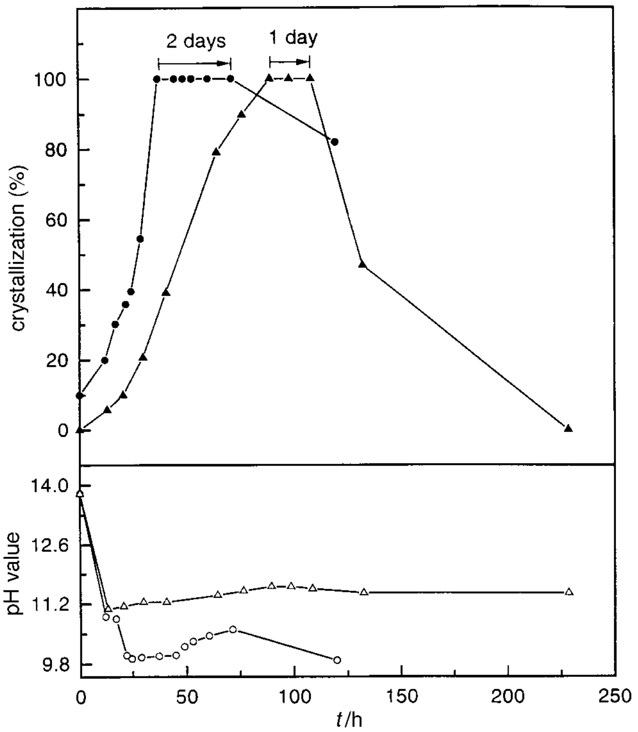

Fig. 2 Comparison of crystallization percent (solid symbols) and final pH values (open symbols) for the crystallization of Na,K-clinoptilolite from 2.92 NaOH : 13.3 KOH : 10 $Al(OH)_3$: 45 SiO_2 : 542 H_2O at 180 °C with 10 mass% seed crystals (circles) and without seeds (triangles)

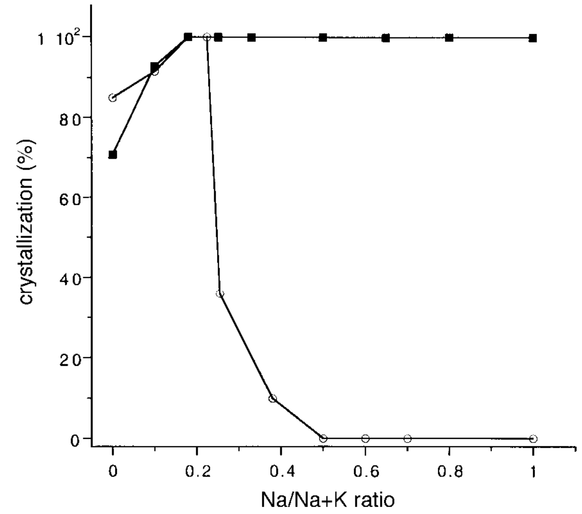

Fig. 3 Change of crystallization percentage with the Na/Na+K ratio in the gel with 10 mass% seed crystals (solid squares) and without seed crystals (open circles). The gel composition was $SiO_2/Al_2O_3=9$, $OH/SiO_2=0.36$, $H_2O/SiO_2=12$ and the hydrothermal conditions were 180 °C for 72 h for the seeded system and 180 °C for 110 h for the unseeded system.

Role of Si/Al ratio

The nature of the other zeolite phases which can crystallize with or subsequent to clinoptilolite is dependent on the Si/Al ratio of the gel. Clinoptilolite crystallizes between Si/Al ratios of 2.5 and 5.0. As shown in Fig. 6, for an Si/Al ratio of 5.0–6.0, mordenite coexists with clinoptilolite. Only mordenite is formed for Si/Al > 6.0. An amorphous phase is obtained for Si/Al below 2.5. Phillipsite coexists with clinoptilolite for an Si/Al ratio of 3.0–4.0 while analcime commonly appears between Si/Al ratios of 4.0–5.0.

Effect of silica and alumina sources

Clinoptilolite can be synthesized from different silica and alumina sources, including sodium silicate, fumed silica, sodium aluminate, dried aluminium hydroxide, and Capatal alumina (pseudoboehmite). With a higher degree of prepolymerization

Table 3 Comparison of the Si/Al ratio of the gel with the final Si/Al ratio for the crystalline clinoptilolite-type phase as a function of the inorganic cation

cations in gel[a]	Si/Al ratio in gel	Si/Al ratio in crystal
Li	4.5	4.0
Na	4.5	6.4
K	4.5	5.3
Rb	4.5	4.4
Na,K	4.5	5.0
Na,K	2.5	3.2
Na,K (no seeds)	4.5	5.0
Li,K	4.5	4.3

[a] All with seeds except the one noted.

Table 4 Comparison of the morphology of the resulting clinoptilolite crystals as a function of the cation present in the gel

cations in the gel	crystal morphology
Li (seeds)	radial aggregates
Na (seeds)	platy 1–5 μm
K (no seeds)	platy 5–10 μm
K (seeds)	platy 1–5 μm
Rb (seeds)	platy 1–4 μm
Na,K (no seeds)	platy 5–10 μm
Na,K (seeds)	platy 1–5 μm
Li,K (no seeds)	lath crystals 30–40 μm

in the silica and alumina sources such as fumed silica and pseudoboehmite, clinoptilolite requires a longer crystallization time (94 or 68 h) at 180 °C in comparison with Ludox and dried aluminium hydroxide (60 h). Considering the effect of cations on the crystallization time, aqueous colloidal silica and dried aluminium hydroxide represent one of the best selections of silica and alumina for the preparation of clinoptilolite.

Role of seeds

It has been known that addition of seed crystals to synthesis batches can promote crystallization of certain zeolite phases as well as increase the rate of crystallization.[22,23] As shown in Table 1, Na,K-clinoptilolite (100%) can be synthesized with 10 mass% seeds after 60 h at 180 °C, with 1 mass% seeds after 92 h and without seeds after 112 h. The more seeds, the faster the rate. Clinoptilolite can also be crystallized using synthetic clinoptilolite as the seed. The rate is faster since these synthetic crystals are purer than the natural clinoptilolite crystals.

The effect of seed crystal addition on the crystallization mechanisms of clinoptilolite has not been thoroughly assessed or understood. The seed crystals used in the synthesis of clinoptilolite-type phases described here are natural clinoptilolite which contain paramagnetic iron (Fe^{3+}) impurity. In order to gain information about the growth mechanisms of clinoptilolite and the effect of seed crystals on the synthesis, the EPR spectra of the products were measured during the course of the syntheses. As shown in Fig. 7(*a*), natural clinoptilolite exhibits an EPR signal at $g=4.28$ which has been attributed to Fe^{3+} located in a framework tetrahedral site of clinoptilolite.[24–26] This signal broadens after 20–30 h at 180 °C during which time the clinoptilolite phase begins to crystallize [Fig. 6(*b*), (*c*)]. When clinoptilolite reaches 100% crystallinity, it exhibits an EPR signal similar to that in the natural clinoptilolite seed. This suggests that the structure of framework Fe^{3+} in the clinoptilolite seeds is destroyed partly during the crystallization process, and with time the Fe^{3+} is introduced into the framework of the newly forming clinoptilolite crystals. We did not investigate the deliberate addition of Fe^{3+} to the system.

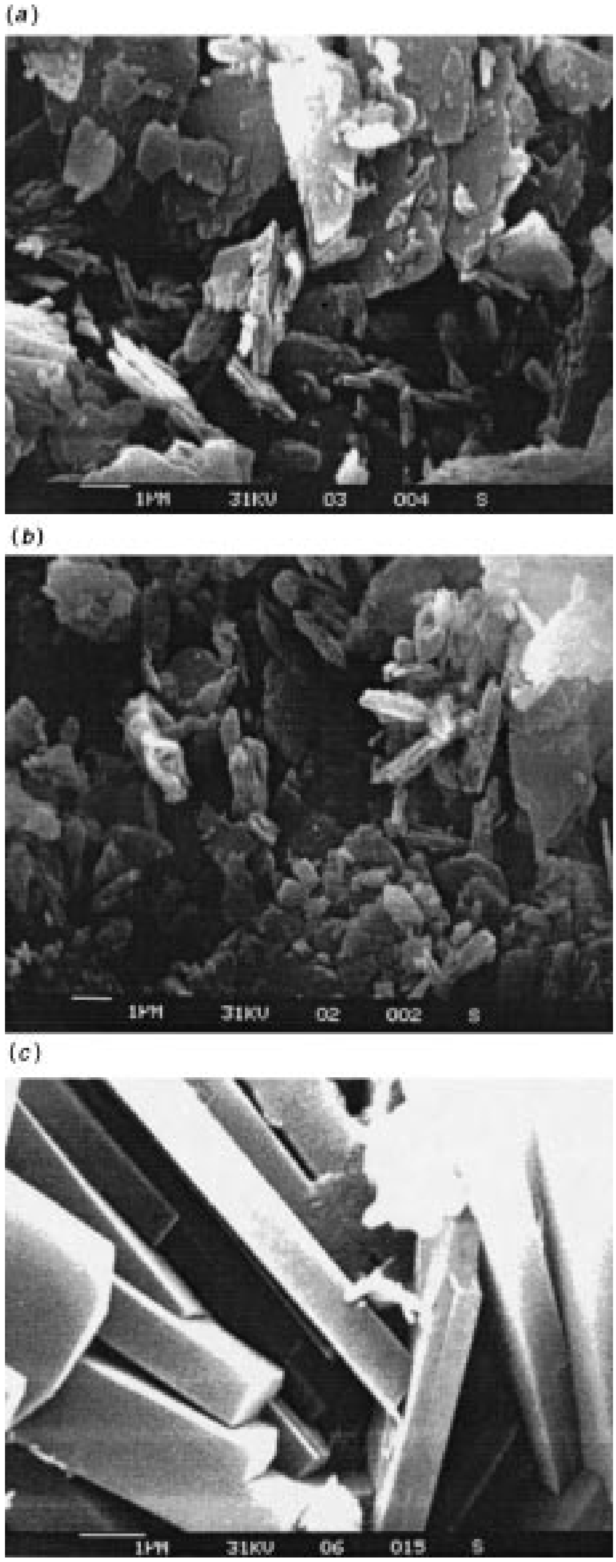

Fig. 4 Scanning electron photomicrographs of (*a*) Na,K-clinoptilolite synthesized without seeds, (*b*) Na,K-clinoptilolite synthesized with 10 mass% seeds, and (*c*) Li,K-clinoptilolite synthesized without seeds

It is important to point out that upon close examination of the synthesis products, two phases are observed. One has a gray color similar to natural clinoptilolite, although the crystals are much bigger in size. The second is a white phase. The gray phase can be assigned to clinoptilolite crystallizing over the natural clinoptilolite seed crystals and the white phase to clinoptilolite nucleated by a source other than the seed crystals.[18]

The two phases were separated using flotation methods so that each could be examined individually. Both have the same

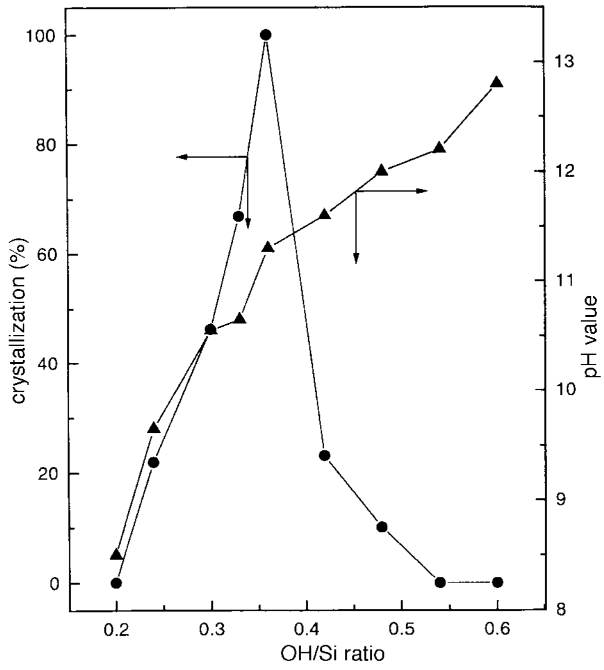

Fig. 5 The change of crystallization percentage (circles) and the final pH values (triangles) *versus* OH/Si ratio in the gel with 10 mass% seed crystals. The gel composition was $SiO_2/Al_2O_3=9$, $OH/SiO_2=0.36$, $H_2O/SiO_2=12$ and the hydrothermal condition was 180 °C for 72 h.

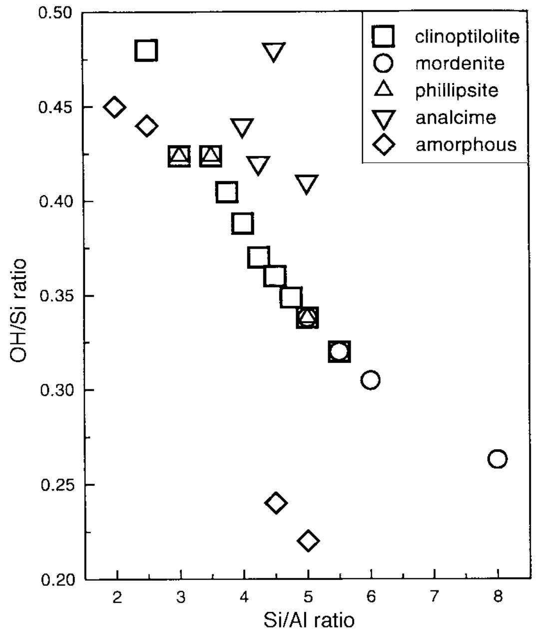

Fig. 6 Crystallization field of the phases grown from the gel NaOH–KOH–$Al(OH)_3$–SiO_2–H_2O with 10 mass% seed crystals. The silica source was colloidal silica. The gel composition was $H_2O/SiO_2=12$, $Na/Na+K=0.18$ and the hydrothermal condition was 180 °C for 72 h.

XRD patterns (not shown) consistent with clinoptilolite and both have the same Si/Al ratio of 5.0 as determined by the electron microprobe. The amount of Fe^{3+} is greater in the white phase based on EPR measurements. The EPR signals at $g=4.32$ and 3.90 from framework Fe^{3+} are present in both. The white phase also shows a strong EPR signal at $g=\approx 2.56$ as shown in Figure 7(*e*′), which can be assigned to extraframework iron oxide. This suggests that Fe^{3+} from the seed crystals can be transferred into the new crystals but that much of the Fe^{3+} is not located in the framework. An amorphous iron-containing phase may in fact be a site for nucleation of this second population of crystals.[27]

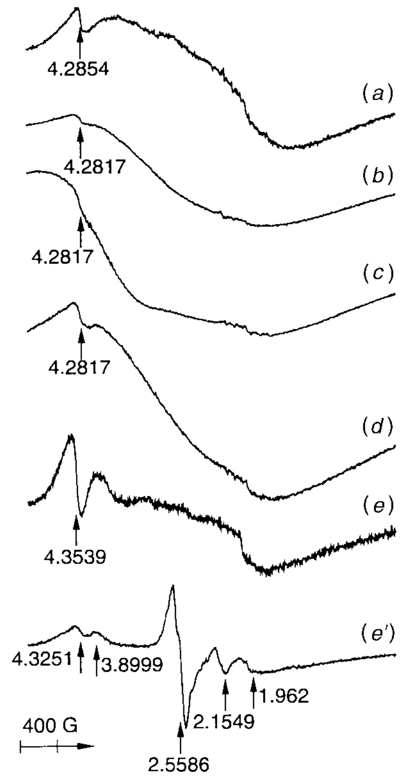

Fig. 7 EPR spectra at 77 K of (*a*) natural clinoptilolite, and Na,K-clinoptilolite synthesized with 10 mass% seed crystals for a crystallization time of (*b*) 20 h; (*c*) 30 h; (*d*) 41 h and (*e*) 65 h at 180 °C. The silica source was Ludox colloidal silica. The gel composition was 2.92 NaOH : 13.3 KOH : 10 $Al(OH)_3$: 45 SiO_2 : 542 H_2O. Spectrum (*e*′) is from the white phase (minor phase) separated from the 65 h product by flotation; see text.

Relation between clinoptilolite, mordenite and analcime

In general, the crystallization of clinoptilolite and mordenite is faster than that of analcime. Analcime nucleates over *ca.* three days at 180 °C in the K cation system. Crystallization of analcime seems to be favored by a higher OH/Si ratio and higher temperature. As shown in Fig. 6, phillipsite also coexists with clinoptilolite. A lower Si/Al ratio favors the formation of phillipsite, which agrees with previous reports.[11,12]

Mordenite and analcime, once formed, persist. Compositionally and structurally, mordenite and clinoptilolite are similar. Only a small free energy difference should exist between the two,[11,12] meaning that once both phases are present above some critical crystallite size, there should be very little driving force for one phase to grow at the expense of the other. Thus, the existence of clinoptilolite as a single phase probably reflects the fact that even though both mordenite and clinoptilolite nucleate, the clinoptilolite crystallites are able to achieve a critical size more quickly than mordenite, subsequently suppressing mordenite growth. In addition, the rate of crystallization at lower OH/Si ratio and lower temperature seems slower for mordenite and thus favors pure clinoptilolite crystallization.

Conclusions

Alkali-metal heulandite/clinoptilolites were synthesized from Na-, K-, Li- and Rb-containing systems as well as from mixtures of Na,K-, K,Li- and Rb,K-cations, with and without seed crystals. The surprising difficulty in synthesizing alkali-metal clinoptilolites is due to the limited range of the crystallization parameters and the limited time that clinoptilolite is stable in the gel. One might assume that clinoptilolite would crystallize for a wide range of conditions in view of its abundant natural occurrence. The experimental data reveal that clinoptilolite is formed at lower temperature and lower pH values, while mordenite and analcime are formed at higher temperature and higher pH values. Thus, controlling these parameters helps achieve the desired phase. A small amount of seed crystals improves both the rate of crystallization and the time range for retention of the clinoptilolite phase; they also induce a lower free hydroxide content in the gel which contributes to the stability of the clinoptilolite phase. The formation of the heulandite topology is not strongly dependent on the nature of the alkali-metal cation since, in the presence of clinoptilolite seeds, this phase can be prepared in high purity regardless of the alkali-metal cation present in the gel. In an unseeded system though, potassium cations favor the formation of clinoptilolite and analcime, and sodium cation favors mordenite. The stability of clinoptilolite in the gel can be improved by the addition of other cations to a potassium cation-containing gel. The mixed cations of Na,K- and K,Li- both increase the time range for retention of the clinoptilolite phase in solution over the parent K-containing gel. The seed crystals partially dissolve in the reactive gels but clinoptilolite crystal growth continues on the seed surfaces since crystals larger than the original seed crystals do result. This may be related to subtle pH changes. Secondary nucleation also appears to be initiated by the presence of other impurities such as insoluble iron-containing species generated by the dissolved seeds. Thus, several crystallization mechanisms may simultaneously occur in this system.

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