Synthesis of pure clinoptilolite without the use of seed crystals

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The present work re-examines the work of Chi and Sand together with that of Satokawa and Itabashi and reports the modifications required to obtain a pure clinoptilolite using conventional reagents, in the absence of seed crystals, at temperatures between 150 and 175 °C under autogeneous pressure.

The natural zeolite clinoptilolite is widely distributed in nature, being the most abundant of natural zeolites.[1] However it has proved quite difficult to synthesise clinoptilolite under laboratory conditions. This has been ascribed to the rather narrow ranges of gel Si/Al and OH/Si ratios found to produced an acceptable final product. There have been three principal contributions to the synthesis of clinoptilolite in the laboratory. Hawkins *et al.*[2] produced Na,K-clinoptilolite, with the aid of seeds, at temperatures between 130 and 150 °C using volcanic glass as a reagent and high pressures, the final product was impure. Goto[3] produced Na,K-clinoptilolite from more standard chemical reactants at temperatures of 200 °C and autogeneous pressure, however the products were contaminated with mordenite. Chi and Sand[4] produced both Na,Na,K and K-clinoptilolite from standard laboratory reagents at temperatures between 120 and 200 °C and autogeneous pressure, using seed crystals. Recently Satokawa and Itabashi[5] reported the formation of Na,K-clinoptilolite, without the addition of seeds, using conventional chemical reagents.

The materials used in this work were as follows: Silica sources were fumed silica, 99.8 mass% [Cab-o-sil M5 (Carbot Corp; supplied by BDH)], colloidal silica, 40 mass% [Ludox AS40 and HS40 (Du Pont, supplied by Aldrich)]. Alumina sources were aluminium wire, 99.9 mass% (BDH), Versal 900 alumina, 72 mass% [pseudoboehmite (La Roche)], reagent-grade sodium and potassium hydroxide, 98+ mass% (Scientific & Chemical Supplies) and deionised water. The seed crystals (if used) were natural Anaconda 1010A clinoptilolite. Syntheses were carried out in 250 or 500 ml stainless steel autoclaves, stirred at 100 rpm at temperatures between 150 and 175 °C under autogeneous pressure. The reaction gels were prepared as follows; the alkali hydroxide was weighed out into a Teflon beaker and the required mass of aluminium wire or Versal 900 was added together with water (50 ml). This solution was stirred by hand and allowed to cool for 15 min. After this time the silica source was added, together with the outstanding water and the resultant gel was stirred electrically for 5 min until a fluid homogenised gel was obtained. If seed crystals were to be added they were added at this stage. The gel was then transferred to the autoclave and allowed to react for the required time. Both autoclaves were fitted with sampling devices to allow the degree of crystallization to be monitored. Once the gel had fully crystallized the products were recovered by filtration on a Buchner funnel and washed with water (3 × 50 ml), they were then dried in air at 40 °C for 16 h. The synthesised samples were analysed by powder X-ray diffraction using a Philips PW1710 diffractometer utilizing Cu-Kα radiation. The scan was run between 2θ 3.5 and 50°, using a scan speed of 1° min^{-1}. The diffractometer is linked to a DEC 3100 MicroVAX using Sandman Search and Match routines to search the ICDD database. The purity of the natural and synthesised clinoptilolite was determined using Philips computerised quantitative software in conjunction with the ICDD database. Scanning electron microscopy (SEM) was performed on the samples using a Philips SEM 515 microscope.

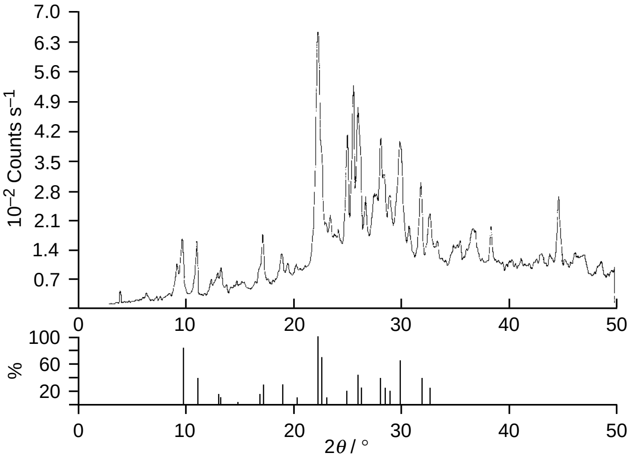

Fig. 1 Powder X-ray diffractogram for pure clinoptilolite $(NaKCa)_6(SiAl)_{36}O_{72}\cdot 20H_2O$ (JCPDF 25–1349)

Table 1 Reaction compositions and conditions used for clinopltilolite synthesis

Attempt	Reaction gel compostion	Seeds (%)	*T*/°C	*t*/h	Silica source	Alumina source	Ref.
1	$2.1K_2O:0Na_2O:Al_2O_3:10SiO_2:105H_2O$	0	175	20	Ludox HS40	Versal 900	4[a]
1a	$2.1K_2O:0Na_2O:Al_2O_3:10SiO_2:105H_2O$	0	175	20	Ludox HS40	Al wire	4[a]
2	$2.1K_2O:0Na_2O:Al_2O_3:10SiO_2:105H_2O$	1	175	96	Ludox HS40	Versal 900	4[a]
2a	$2.1K_2O:0Na_2O:Al_2O_3:10SiO_2:105H_2O$	1	175	96	Ludox HS40	Al wire	4[a]
3	$2.1K_2O:0Na_2O:Al_2O_3:10SiO_2:105H_2O$	10	175	96	Ludox HS40	Versal 900	4[a]
3a	$2.1K_2O:0Na_2O:Al_2O_3:10SiO_2:105H_2O$	10	175	96	Ludox HS40	Al wire	4[a]
4	$0.72K_2O:0.27Na_2O:Al_2O_3:8.4SiO_2:210H_2O$	0	150	360	Ludox HS40	Versal 900	5[b]
4a	$0.72K_2O:0.27Na_2O:Al_2O_3:8.4SiO_2:210H_2O$	0	150	360	Ludox HS40	Al wire	5[b]
5	$0.72K_2O:0.27Na_2O:Al_2O_3:8.4SiO_2:210H_2O$	0	150	336	Ludox AS40	Versal 900	5[b]
5a	$0.72K_2O:0.27Na_2O:Al_2O_3:8.4SiO_2:210H_2O$	0	150	336	Ludox AS40	Al wire	5[b]

[a] Run 211. [b] Example 1.

Table 2 Phase compositions of the final products obtained

Attempt	Phase composition mass%[a]	t_b/h
1	100% Merlinoite	20
1a	90% Merlinoite–10% philipsite	20
2	37% Merlinoite–63% potassium feldspar	96
2a	21% Merlinoite–60% potassium feldspar–19% quartz	96
3	100% Sanidine	96
3a	91% Sanidine–9% quartz	96
4	69% Clinoptilolite–31% potassium feldspar	360
4a	20% Clinoptilolite–75% potassium feldspar–5% quartz	360
5	100% Clinoptilolite	336
5a	88% Clinoptilolite–12% mordenite	336

[a] Derived by quantitative XRD analysis. [b] Reaction time.

The molar compositions used in this work and their original reference are detailed in Table 1. All experimental synthesis procedures were repeated three times to check for reproducibility. The powder X-ray diffractogram for the pure clinoptilolite sample is shown in Fig. 1. The mass% of the various phases formed are given in Table 2. Chemical analysis was carried out on the pure clinoptilolite sample using X-ray fluorescence analysis and thermal analysis, the results are shown in Table 3.

As can be seen, several attempts were made to repeat the work outlined by Chi and Sand, however, for each attempt the required phase, clinoptilolite, appeared elusive. It would appear that the substitution of Ludox AS40 for Ludox HS40 can lead to the successful synthesis of a pure clinoptilolite without the need to use seed crystals. It is well known that clinoptilolite has a high affinity for the ammonium ion and Ludox AS40 is stabilised by the ammonium ion, as opposed to Ludox HS40 which is sodium stabilised. It can also be seen that the fast dissolution characteristics of aluminium wire favour the formation of denser phases, with all reaction runs producing mixed final products. Therefore it would seem expedient to use an alumina source which dissolves into solution more slowly, such as the Versal 900 or similar hydrated aluminium oxides. Finally it can be concluded that it is difficult to synthesise clinoptilolite in the laboratory free from impurities and that pure clinoptilolite is transitory in nature. This observation may explain why so few reports of a successful pure clinoptilolite synthesis method can be found in the literature.

Table 3 Elemental compositions fo the pure clinoptilolite obtained

Elemental oxide[a]	Conc. (%)
SiO_2	61.0
Al_2O_3	11.8
K_2O	8.13
Na_2O	1.78
Fe_2O_3	0.066
ZrO_2	0.030
H_2O (LOI)	17.3

[a] Determined by XRF and TG.

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Footnote and References

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