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Synthesis and Properties of Nanoparticle Forms Saponite Clay, Cancrinite Zeolite and Phase Mixtures Thereof

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Abstract

The low-temperature synthesis (90°C) of nanoparticle forms of a pure phase smectic clay (saponite) and zeolite (cancrinite) is reported, along with phase mixtures thereof. A synthesis gel corresponding to the Si:Al:Mg unit cell composition of saponite (3.6:0.40:3.0) and a NaOH/Si ratio of 1.39 affords the pure phase clay with disordered nanolayer stacking. Progressive increases in the NaOH/Si ratio up to a value of 8.33 results in the co-crystallization of first garronite and then cancrinite zeolites with nanolath morphology. The resulting phase mixtures exhibit a compound particulate structure of intertwined saponite nanolayers and cancrinite nanolaths that cannot be formed through physical mixing of the pure phase end members. Under magnesium-free conditions, pure phase cancrinite nanocrystals are formed. The Si/Al ratio of the reaction mixture affects the particle morphology as well as the chemical composition of the cancrinite zeolite. Ordinarily, cancrinite crystallizes with a Si/Al ratio of 1.0, but a silicon-rich form of the zeolite (Si/Al=1.25) is crystallized at low temperature from a silica rich synthesis gel, as evidenced by ²⁹Si NMR spectroscopy and XEDS-TEM. Owing to the exceptionally high external surface areas of the pure phase clay (875 m²/g) and zeolite end members (8.9 - 40 m²/g), as well as their unique mixed phase composites (124 - 329 m²/g), these synthetic derivatives are promising model nanoparticles for studies of the bioavailability of poly-aromatic hydrocarbons immobilized in silicate bearing sediments and soils.

Keywords

Saponite; cancrinite; phase mixtures; synthesis

1. Introduction

Most sediments and soils contain an inorganic component rich in crystalline and amorphous silicate minerals, including clays and zeolites. The adsorption and transport of poly-aromatic hydrocarbons (e.g., dioxins) on silicate mineral surfaces can play an important role in determining the fate of these toxic molecules in the environment [1,2], as well as their bioavailability to microorganisms and mammals. However, understanding the bioavailability of poly-aromatics in the adsorbed state is complicated by their low solubility in water and, also, by the variability in the composition and purity of the sorptive silicate medium in its native state. Most synthetic clays and zeolites do not have external surface areas sufficiently

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high to achieve the poly-aromatic dosages needed for quantitative bioavailability studies. In an effort to provide synthetic derivatives of silicate minerals potentially suitable for such studies, we investigate here the synthesis of a representative smectite clay (saponite), a representative zeolite mineral (cancrinite) and their phase mixtures under low temperature (mild hydrothermal) reaction conditions with the intent of forming these aluminosilicates in high surface area form for future use in modeling the bioavailability of adsorbed poly-aromatic molecules.

Saponite is a naturally occurring 2:1 trioctahedral layered silicate wherein the anionic layer charge originates from the isomorphous substitution of Al(III) for Si(IV) in the tetrahedral sheet. The gallery cations can be readily replaced by a variety of functional cations for potential applications in catalysis and adsorption. Synthetic analogs of saponite and related smectite clay minerals have attracted attention in recent years because of their high purity and adjustable compositions [3-8]. Vogels and co-workers [8] first reported the low temperature (90°C) synthesis of saponite derivatives from a gel prepared from sodium silicate as the silicon source, aluminum nitrate as the aluminum source, and M^{2+} -nitrates (M^{2+} =Mg, Zn, Ni, Co) as the source of the divalent ion in the octahedral sheet. A key step in the synthesis was the controlled release of ammonia as a base through the thermal decomposition of urea.

Cancrinite (CAN) is found in nature with the composition $Na_6Ca[AlSiO_4]_6CO_3(H_2O)_2$ [9]. The cancrinite framework is built by ABAB stacking of hexagonal arrays of 6-membered rings of SiO_4 and AlO_4 tetrahedra along the *c*-axis [10,11]. Small 11-hedral cages (ϵ -cages) and a larger 12-ring channel along the [001] direction are the result of this arrangement of sheets. Isomorphous positioning of aluminum in tetrahedral coordination results in negative charges on the framework counterbalanced by cations held within the cavities and channels. The large open channels also host M^+ and M^{2+} cation – anion pairs, such as CO_3^{2-} and other anions, while the ϵ -cages contain chains of alternating framework-balancing cations and water molecules [12,13].

Few studies have been reported on the synthesis of cancrinite under mild hydrothermal conditions. Pure-phase cancrinite synthesis can be difficult due in part to the disordering of the cancrinite structure and the co-crystallization of sodalite [10,14-20]. Pure nitrate-containing cancrinite crystals less than 100 nm in length were prepared by Liu et al. [21] based on a synthetic route at 90°C, without the formation of an intermediate phase or sodalite. The successful low temperature synthesis of the pure phase zeolite by Liu et al. may be due in part to the absence of crystalline precursors in the reaction mixture. Most previously reported cancrinite syntheses [10,14-18] used crystalline reagents (e.g., kaolinite, zeolite A) as the silica and alumina sources and this contributed to the co-crystallization of sodalite.

The present study demonstrates that increasing the alkalinity of a saponite synthesis gel results in the co-crystallization of first zeolitic garronite and then cancrinite. Completely eliminating the magnesium from the synthesis gel affords pure phase cancrinite with nanometric morphology. In addition we synthesize for the first time a silica-rich form of this zeolite. The large external surface areas associated with the nanometric dimensions of the particles indicate that these synthetic analogs of crystalline silicate minerals may indeed serve as model systems for the studies of the adsorption and bioavailability of poly-aromatic hydrocarbons in mineral sediments and soils.

2. Experimental

2.1. Materials

Sodium silicate containing 27 wt.% SiO_2 and 14 wt.% NaOH and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were purchased from Aldrich Chemical Co. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was purchased from Columbus Chemical Industries, Inc. The reagents were used as received without further purification.

2.2. Synthesis of Pure Phase Saponite

Synthetic saponite clay was prepared at 90°C following the general procedure of Vogels et al. [8] using water glass solution (27 wt.% silica, 14 wt.% NaOH), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NaOH as the source of base. For a typical synthesis in which the molar ratio of Si : Al : Mg : NaOH (not including the NaOH in water glass solution) was 3.6 : 0.4 : 3.0 : 5 per 400 moles of water, 5.50 g of sodium silicate solution and 1.031 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were mixed in 49.5 g of deionized water at room temperature for 1.5 h. Then 1.37 g of NaOH was introduced to the white suspension, followed by another 1.5 h of stirring at room temperature. The mixture was then brought to 90°C and heated under stirred condition for 30 min, followed by the introduction of 5.28 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The resulting mixture was refluxed under stirring at 90°C for 24 h in a 250 mL flask. The product was centrifuged, triple washed with deionized water, and dried at 80°C under N_2 flow.

2.3. Synthesis of Saponite/Cancrinite Phase Mixtures

The synthesis conditions are similar to those for saponite synthesis, except that the amounts of sodium hydroxide and magnesium nitrate are varied in order to investigate the influence of concentration on the saponite to cancrinite product ratio. The reactions were carried out for different time periods ranging from 24 h to 168 h.

2.4. Pure Phase Cancrinite Synthesis

Synthetic cancrinite was prepared at 90°C using water glass solution (27 wt.% silica, 14 wt.% NaOH), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and NaOH. The molar ratio of Si : Al : NaOH (not including the NaOH in the water glass solution) is $x : 0.4 : 30$ per 400 moles of water for $x = 3.6, 2.4, 1.6, 0.8, 0.4$. The mixture was refluxed under stirring at 90°C for 72 or 168 h, and the resulting product was centrifuged, triple washed with deionized water, and dried at 80°C under N_2 flow.

2.5. Characterization

Powder samples for X-ray diffraction analysis were pressed onto a glass sample holder. X-ray diffraction (XRD) patterns were obtained on a Rigaku Rotaflex 200B diffractometer equipped with Cu $\text{K}\alpha$ X-ray radiation and a curved crystal graphite monochromator, operating at 45 kV and 100 mA.

N_2 adsorption-desorption isotherms were recorded at -196°C on a Micrometrics Tristar 3000 sorptometer. Prior to analysis samples were out-gassed at 150°C and 1.33×10^{-4} Pa for a minimum of 12 h. BET surface areas were calculated from the linear part of the BET plot and BJH pore sizes were obtained from adsorption isotherms.

Transmission electron microscopy (TEM) images were obtained on a JEOL 2200FS field emission microscope with a ZrO/W Schottky electron gun and an accelerating voltage of 200 kV. The powdered samples were sonified in ethanol, and dripped onto 300 mesh copper grids for imaging analysis. X-ray energy dispersive spectra (XEDS) for elemental analysis were collected by converging the electron beam on the area of interest.

^{29}Si and ^{27}Al MAS NMR spectra were obtained at 79 MHz on a Varian VXR-400S solid-state NMR spectrometer equipped with a magic angle-spinning probe. Samples were spun at 4 kHz for each measurement. The pulse delay for ^{29}Si MAS NMR was 400 s. Talc with a chemical shift of -98 ppm was used as internal reference. The pulse delay for ^{27}Al MAS NMR was 0.50 s, and a 0.10 M aqueous $\text{Al}(\text{NO}_3)_3$ solution was used as the chemical shift reference. FTIR spectra of samples dispersed in KBr disks were recorded at ambient temperature on a Mattson Galaxy 3000 FTIR spectrometer over the range 400-4000 cm^{-1} .

3. Results and Discussion

The digestion at 90°C of a synthesis gel corresponding to the unit cell composition of saponite ($\text{Si}:\text{Al}:\text{Mg}:\text{NaOH} = 3.6:0.40:3.0:5.0$) affords pure phase saponite in quantitative yield. Doubling the NaOH content of the gel results in the co-crystallization of the zeolite garronite (GIS) and saponite (SAP), and further increasing the NaOH content four-fold results in the co-crystallization of a third phase, namely the zeolite cancrinite (CAN). A six-fold increase in the NaOH content of the gel results in a two-phase mixture of SAP and CAN. Thus, although SAP does not undergo a phase transformation over the $\text{Si}:\text{NaOH}$ range from 3.6:5.0 to 3.6:30, the phase purity of the products formed over this is kinetically determined by the co-nucleation of the two zeolite phases (GIS and CAN) that also are stable over the same $\text{Si}:\text{NaOH}$ range.

The assignment of SAP, GIS, and CAN as reaction products is based on the X-ray powder diffraction patterns shown in Fig. 1. Owing to the nanometric dimensions of the SAP layers (see below), the hkl reflections are generally broadened. Applying the Scherrer equation to the line width of the 060 reflection, we estimate the scattering domain size of the silicate layers to be 21.4 nm. This result is consistent with the 5-50 nm lateral dimensions of the layers estimated from TEM image (cf., Fig. 2). Also, there is little or no ordered stacking of the nanolayers, as evidenced by the absence of a 001 reflection in the diffraction pattern. These textural features also were found for the saponite made in the presence of urea as the source of base [8]. However, as discussed in greater detail below, the presence of urea is not essential for the formation of poorly stacked aggregates of saponite nanolayers.

The diffraction lines for the GIS and CAN phases are much narrower in comparison to those for SAP due primarily to the well-expressed crystal morphology of these zeolite phases. Fig. 3 provides TEM images of the mixed CAN and SAP products formed from synthesis gel with a $\text{Si}:\text{NaOH}$ molar ratio of 3.6:30. The CAN phase forms nanolaths approximately 50-100 nm in width and 100-600 nm in length. The co-crystallized SAP phase maintains the same unstacked nanolayer morphology observed for the pure phase product made at a $\text{Si}:\text{NaOH}$ molar composition of 3.6:5.0. Particularly noteworthy is the compound composite structure of the particles. The intricate union of the nanolaths and nanolayers leading to the formation of the aggregates could not be duplicated through the physical mixing the pure phase end members, suggesting that the two phases nucleate together in forming the compound structures.

Saponite is a smectite clay with a 2:1 layer lattice structure with silicon and aluminum in tetrahedral interstices and magnesium in octahedral positions within the layer. Conversely, cancrinite and garronite are tectosilicates formed by linking SiO_4 and AlO_4 tetrahedra through bridging oxygen atoms. In the presence of magnesium, cancrinite formation competes favorably with saponite crystallization, provided the synthesis gel is sufficiently basic, e.g., $\text{Si}:\text{NaOH} = 3.6:30$ (cf., Fig. 1). As expected on the basis of composition, reducing the magnesium content of the synthesis gel reduces the yield of saponite in favor of cancrinite. As shown by the X-ray diffraction patterns in Fig. 4, the SAP content of the products decreases and the CAN fraction increases with diminishing magnesium content.

The complete elimination of magnesium from the synthesis gel results in the formation of pure phase CAN after reaction times of 3 days, as evidenced by TEM images as well as XRD. Increasing the reaction time to 7 days improves the aspect ratio of the laths, as indicated by the TEM images in Fig. 5. The lath-like nanoparticle morphology is in agreement with morphology observed previously for cancrinite formed under analogous reaction conditions [21].

The lattice structure of saponite and cancrinite were further characterized using solids state NMR. The ^{29}Si MAS NMR spectrum of saponite (c.f., Fig. 6) exhibits the presence of two resonances. In accord with previous ^{29}Si chemical shift assignments for saponite [22], the -85.4 ppm line is assigned to Si centers linked through bridging oxygen atoms to three neighboring SiO_4 and one AlO_4 units (i.e., $\text{Q}^4(1\text{Al})$ sites in the Engelhardt notation). The -92.7 ppm resonance is ascribed to SiO_4 centers with four SiO_4 neighbors. The ^{27}Al MAS NMR spectrum of SAP contains two signals at chemical shifts of 61.6 ppm and 10.5 ppm, indicating that Al substitution occurs in both the tetrahedral and octahedral sheets of the 2:1 layered silicate structure.

In the case of the CAN/SAP phase mixture in Fig. 6, the sharp ^{29}Si signal at -87.3 ppm agrees well with the value expected for a 1:1 ratio of alternating SiO_4 and AlO_4 centers in the framework. The line at -92.7 ppm arises primarily from the co-crystallized saponite phase. Pure phase CAN made in the absence of magnesium from a 3.6:0.4 Si:Al synthesis gel ($\text{Si}/\text{Al}=9.0$) also exhibits a -92.7 ppm line due to SiO_4 centers linked to one SiO_4 and three AlO_4 neighbors (i.e., $\text{Q}^4(3\text{Al})$ sites). However, the silicon concentration in the framework is not sufficiently high to observe resolved resonances for $\text{Q}^4(2\text{Al})$ and $\text{Q}^4(1\text{Al})$ sites. X-ray energy dispersive analysis indicated the Si/Al ratio of the CAN crystals to be 1.25, verifying that the Si/Al ratio exceeds 1.0. Also, the ^{27}Al MAS NMR spectrum of pure phase CAN exhibits a single line at 57.1 ppm, as expected for aluminum in tetrahedral coordination. Clearly, the reaction stoichiometry $\text{Si}:\text{Al}:\text{NaOH} = 3.6:0.4:30$ facilitates the formation of a Si-rich cancrinite at 90°C . To our knowledge, this is the first example of a synthetic cancrinite derivative in which the Si/Al ratio substantially exceeds the conventional ratio of 1.0. Cancrinite, a cancrinite-group zeolite, is found in nature with $\text{Si}/\text{Al}=1.40$ [23], but a high silica analog has not been reported previously.

The occlusion of nitrate anions in the channels of cancrinite is verified by FTIR. Fig. 7 compares the FTIR spectrum of pure CAN, along with the spectrum of SAP. In addition to a weak bending mode near 820 cm^{-1} , the presence of nitrate groups in the zeolite channels is confirmed by the strong ν_{as} vibration at 1425 cm^{-1} and 1444 cm^{-1} . The weak absorption at 1383 cm^{-1} has been attributed to small amounts of precipitated sodium nitrate on the outer surface of the crystals [24]. These nitrate bands are absent in the spectrum of SAP. Another potential occluded anion for the cancrinite is CO_3^{2-} . This ion may form through the reaction of atmospheric CO_2 with the concentrated NaOH in the reaction mixture. However, carbonate was not incorporated to a detectable extent because the two CO_3^{2-} stretching bands [10] at 1410 and 1455 cm^{-1} are not observed here, indicating that NO_3^- is the major anion in the channels of the cancrinite structure.

The water bending mode near 1630 cm^{-1} and a broad OH stretching band between 3100 and 3600 cm^{-1} are found in both CAN and SAP. The IR spectrum of pure saponite shows absorption bands at 1020 and 653 cm^{-1} indicative of asymmetric and symmetric T-O-T vibrations. For silica-rich CAN the absorbance for the $\nu_{\text{Al-O}}$ asymmetric stretch of the Al-O-Si linkages is split into four peaks at 1125 , 1044 , 1010 and 963 cm^{-1} . These vibrations appear at 1120 , 1040 , 998 , and 963 cm^{-1} for the pure CAN phase with $\text{Si}/\text{Al} = 1.0$, but the relative intensities of the bands remain unchanged. In addition, characteristic fingerprint peaks for CAN occur at approximately 575 , 622 , 683 , and 770 cm^{-1} .

Nitrogen isotherms and for single-phase saponite and cancrinite, and CAN/SAP phase mixtures are provided in Fig. 8. Table 1 summarizes the BET surface areas and pore volumes derived from the nitrogen isotherms. The exceptionally large BET surface area and pore volume for the pure saponite ($875 \text{ m}^2/\text{g}$ and $1.54 \text{ cm}^3/\text{g}$, respectively) is in accord with the poor stacking order and small in-plane dimensions of the clay platelets. Well stacked smectite clays afford surface areas typically in the range $20 - 150 \text{ m}^2/\text{g}$. It is noteworthy that the disordered layer stacking and textural properties for the pure phase saponite product reported here are comparable to those observed previously for saponite made through the use of urea as the source of base [8]. At 90°C urea decomposes slowly to ammonia and carbon dioxide, allowing the pH of the reaction mixture to increase gradually. However, the slow increase in pH through the thermal hydrolysis of urea is not a prerequisite for the nucleation and growth of pure phase saponite nanolayers. As indicated by the present results, an equivalent nanoparticle form of the clay is formed when NaOH is used as the source of base in the initial reaction mixture.

The pore aperture in the cancrinite framework structure is $5.9 \times 5.9 \text{ \AA}$, which is large enough for N_2 molecules to access. But the presence of intercalated nitrate in pure phase CAN blocks the big channels and restricts nitrogen adsorption to the external surfaces of the silicate. The observed surface areas of $10.2 \text{ m}^2/\text{g}$ is consistent with the nanometric dimensions of the CAN laths. As expected, CAN/SAP phase mixtures exhibit surface areas in proportion to the relative abundance of the two phases.

The crystallization of phase pure CAN at 90°C does not require a Si:Al reaction stoichiometry beyond the theoretical 1:1 value typical of the framework composition. This is in agreement with the findings of Liu et al [21]. For instance, as shown by the diffraction patterns in Fig. 9, varying the silicon Si:Al:NaOH composition of the synthesis gel over the range 3.6:0.40:30 (Si/Al = 9.0) to 0.40:0.40:30 (Si/Al = 1.0) results reliably in the formation of phase pure CAN. Although a large excess of silica in the synthesis gel (Si/Al = 9.0) facilitates the formation of Si-rich cancrinite with a Si/Al composition of 1.25, a gel composition of Si/Al = 4.0 returns the Si/Al ratio for the crystals to 1.02, as determined by XEDS-TEM and ^{29}Si NMR. However, the Si/Al ratio of the synthesis gel substantially influences the textural properties of cancrinite products, as evidenced by the up to four-fold differences in surface areas for the reaction products (c.f., Table 1). TEM investigations of the product made at a reaction composition Si/Al=4 show a large fraction of small lathlike crystals less than 100 nm in length, admixed with larger crystals (c.f., Fig. 10). The increased fraction of small crystallites explains the comparatively high surface area of $40.0 \text{ m}^2/\text{g}$.

4. Conclusions

The reaction systems described herein afford nanometric forms of a smectite clay (saponite) and a zeolitic aluminosilicate (cancrinite) and their phase mixtures under exceptionally mild hydrothermal reaction conditions (90°C). A synthesis gel composition corresponding to the unit cell formula of saponite, namely $[\text{SiO}_2]_{3.6}[\text{Al}_2\text{O}_3]_{0.20}[\text{MgO}]_{3.0}$, yields this silicate in pure phase form. An increase in the alkalinity of the reaction mixture results in the co-crystallization of first garronite and then cancrinite along with saponite. Reducing the magnesium content of the synthesis gel leads to a progressive greater fraction of cancrinite in CAN-SAP phase mixtures. The mixed phase particles are compound composites of lamellar and lath-like nanocrystals that cannot be duplicated by physical mixing of the pure phase end members. Completely eliminating the magnesium from the reaction mixture produces pure phase cancrinite. Also, increasing the Si/Al ratio of the synthesis gel to 9.0 provides for the first time a high silica derivative of this zeolite with Si/Al = 1.25.

The poor stacking order of the saponite nanolayers and the nanometric dimensions of the lathlike cancrinite crystals, as well as the compound structure of the mixed phase products, provide exceptionally high surface areas in comparison to the conventional forms of these silicate minerals. These morphological features and the accompanying high surface areas make the synthetic clay and zeolite attractive candidates for modeling the bioavailability of poly-aromatic hydrocarbons on silicate nanoparticles similar to those found in mineral sediments and soil.

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Fig. 1. XRD patterns of products formed at 90°C as a function of increasing alkalinity of the reaction mixtures. The specified ratios represent the Si:Al:Mg:NaOH stoichiometries for the starting reaction mixture.

Fig. 2.
TEM image of synthetic saponite formed at 90°C after a reaction time of 1 day.

Fig. 3. TEM images of saponite and cancrinite phase mixtures showing the compound structure of the particles through the uniting of nanoplates and nanolaths. The products were formed by digestion at 90°C of synthesis gels with the Si:Al:Mg:NaOH molar composition of (A) 3.6:0.4:3.0:30 and (B) 3.6:0.4:1.5:30 after reaction times of 4 days and 3 days, respectively.

Fig. 4. Powder XRD patterns of the products formed at 90°C from synthesis gels with different magnesium content. The molar ratios of Si:Al:Mg:NaOH in the reaction mixture are labeled for each product, as well as the reaction time.

Fig. 5. TEM images of pure-phase cancrinite crystallized at 90°C from a magnesium-free synthesis gel with the molar composition Si:Al:NaOH=3.6:0.4:30; reaction time, 7 days.

Fig. 6. ^{29}Si and ^{27}Al MAS NMR spectra of (a) pure phase saponite, (b) a cancrinite/saponite phase mixture and (c) pure phase cancrinite formed from synthesis gels with Si:Al:Mg:NaOH compositions of 3.6:0.40:3.0:5.0, 3.6:0.40:0.75:30, 3.6:0.40:0.00:30 and reaction times of 1.0, 4.0 and 3.0 days, respectively. The asterisks indicate spinning sidebands.

Fig. 7.

FTIR spectra of (a) pure phase saponite after 1 day of aging at 90°C of a synthesis gel with a Si:Al:Mg:NaOH stoichiometry of 3.6:0.40:3.0:5.0, and (b) pure phase cancrinite after 3 days of aging at 90°C of a synthesis gel with a Si:Al:Mg:NaOH stoichiometry of 3.6:0.40:0.00:30.

Fig. 8.

N_2 adsorption-desorption isotherms of pure saponite and cancrinite, and phase mixtures thereof. The stated ratios represent the molar Si:Al:Mg:NaOH compositions of the reaction mixtures. The reaction time for pure saponite is one day and 3 days for all other products.

Fig. 9. XRD patterns of cancrinite products formed as a function of the Si/Al ratio of the synthesis gel after 3 days of reaction time under magnesium-free condition.

Fig. 10. TEM images of cancrinite crystals formed under magnesium-free conditions and a reaction stoichiometry of Si:Al:NaOH=1.6:0.40:30.

Table 1

Textural properties of saponite, cancrinite and their phase mixtures

Product	Si:Al:Mg:NaOH ratio of reaction mixture	Reaction time (days)	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	BJH adsorption pore size (nm)
SAP	3.6:0.4:3:5	1	875	1.54	1.8
CAN/SAP	3.6:0.4:3:30	3	329	0.42	1.4
CAN/SAP	3.6:0.4:1.5:30	6	186	0.35	1.9
CAN/SAP	3.6:0.4:1.5:30	3	227	0.39	1.8
CAN/SAP	3.6:0.4:0.75:30	6	124	0.26	1.9
CAN/SAP	3.6:0.4:0.75:30	3	134	0.31	2.0
CAN	3.6:0.4:0:30	7	10.2	0.068	-
CAN	3.6:0.4:0:30	3	8.9	0.060	-
CAN	2.4:0.4:0:30	3	21.8	0.14	-
CAN	1.6:0.4:0:30	3	40.0	0.17	-
CAN	0.8:0.4:0:30	3	36.6	0.17	-
CAN	0.4:0.4:0:30	3	21.3	0.095	-