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SHORT COMMUNICATION

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Rearrangement of cationic surfactants in magadiite

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Abstract Partly loaded magadiite samples have been prepared from a synthetic sodium magadiite, 0.9 $Na_2O \cdot 13.9\ SiO_2 \cdot 9.3\ H_2O$, by a two-step intercalation process using *n*-cetylpyridinium (CP) chloride as a model surfactant. Usually, partly loading with long-chain organic cations yields a non-uniform distribution of the surfactant molecules in the interlamellar space of the layered silicates. The resulting samples contain fully expanded crystals or zones within the crystals besides unreacted crystals or domains. After equilibration in water the partly loaded samples transform into products with a uniform expansion of all interlayer spaces due to rearrangement of the CP cations within and between the interlayer spaces.

Key words Layered silicates – Magadiite – Surfactants – Intercalation – Ion exchange

Introduction

Eugster [1] was the first to report on the metal silicate hydrates magadiite and kenyaite found in alkaline sediments of Lake Magadi in Kenya. Until now, five natural sodium silicate hydrates from different origins, kanemite, makatite, magadiite, kenyaite and anhydrous natrosilite, have been discovered and described [2–6]. In addition, more than ten different layered silicates have been synthesized [3, 5, 7–10]. The synthesis of sodium silicate hydrates is carried out hydrothermally in an alkaline region of the ternary system $Na_2O/SiO_2/H_2O$ [9, 11]. Because single crystals large enough for crystal structure analysis have not been obtained either in natural or in synthetic products, the exact structures of most of these materials are still unknown. Only the structures of makatite and ilerite could be solved by single crystal investigation and direct powder methods [12, 13]. However, the layered character of all the metal silicate hydrates is well established, and has been proven by intercalation reactions and by their swelling behavior.

Similar to zeolitic molecular sieves, aluminum-free layered silicates are able to adsorb and to undergo ion-exchange reactions. Thus, a synthetic aluminum-free layered silicate of kanemite has been applied as a detergent builder because of its excellent ability for ion exchange [9, 14].

The increasing interest in aluminum-free layered silicates is based on their structural stability in the presence of acidic solvents [5, 15]. Furthermore, layered silicates are endowed with the properties for intercalation and swelling [6, 11, 16, 17]. The modification of these materials through the insertion of pillars, to vary the pore size and pore volume, would be an interesting alternative for the development of three-dimensional cross-linked silicates [18]. Successful intercalation of cations or neutral molecules inside the interlayer space always leads to expansion of the layers [19].

Interestingly, the synthesis of highly ordered mesoporous materials derived from layered silicates has been successful using kanemite intercalated with surfactants as starting materials [20, 21]. However, the interaction of layered metal silicate hydrates with long-chain organic substances has not been deeply investigated.

Lagaly [22] has summarized the intercalation chemistry of aluminum-free layered silicates. Most investigations have focussed on the behavior of the intercalated surfactant arrangement in the fully loaded state using magadiite and its crystalline silicid acid. In general, a linear correlation between the chain length of intercalated organic cations and the observed basal spacing of magadiite after intercalation has been obtained. On the basis of these results different models for the interlayer structure related to the type of long-chain cations have been developed.

This paper describes the formation and characterization of partly loaded surfactant-magadiite complexes and presents a method to rearrange the long-chain organic cations in the interlayer space of magadiite, the best-known representative of the metal silicate hydrates.

Materials and methods

Synthesis of magadiite

Magadiite was synthesized in a highly viscous, weak alkaline and SiO_2-rich area of the ternary system $Na_2O/SiO_2/H_2O$. Hydrothermal crystallization [17, 23–25] was carried out at 423 K using a reaction mixture with the following molar ratios: 5–9 SiO_2/1 Na_2O/75–150 H_2O.

The composition of the well-crystallized sodium magadiite in the as-synthesized form used for the subsequent studies was $0.9\ Na_2O \cdot 13.9\ SiO_2 \cdot 9.3\ H_2O$.

Modification of magadiite

The modification of magadiite was carried out in two steps. In the first step *n*-cetylpyridinium (CP) chloride (concentration of the surfactant $c = 5.59 \times 10^{-2}$ mol/l) was intercalated into the layered material. Magadiite samples with different loadings of CP chloride were prepared using different solid/liquid ratios between 1 g/10 ml and 1 g/30 ml (samples denoted as CP-Mag1, CP-Mag2, etc.). The experiments were carried out in batches at room temperature. The time chosen for the first intercalation step was 4 h for all samples. A completely exchanged CP magadiite was prepared for comparison with the partly exchanged CP magadiite samples (sample CP-Mag7). This completely exchanged CP magadiite was obtained by intercalation of CP chloride using a solid/liquid ratio of 1 g/100 ml at room temperature for a period of 3 days.

For the rearrangement of the CP ions the ion-exchanged products were suspended in deionized water with a solid/liquid ratio of 1 g/100 ml (samples CP-Mag1re, etc.). These suspensions were stirred constantly for 4 h at 333 K. All products were filtrated and air-dried at room temperature.

Characterization

Phase analysis of all air-dried products was performed by X-ray diffraction spectroscopy (XRD) in the range 1.8–30° 2Θ using a URD 63 vertical goniometer (Seifert FPT) with Cu Kα radiation. We determined the loading of CP cations by measurement of the remaining content of CP chloride in the filtrates by means of UV/VIS spectrometry at a wavelength of 259 nm. The chemical composition of all products was determined by the ICP technique (Plasma 400 spectrometer, Perkin Elmer). The water content and the total ignition loss were obtained through DTA-TG measurements (derivatograph SDT 2960, TA Instruments).

Results

X-ray powder diffraction patterns of the CP magadiites (samples CP-Mag1–CP-Mag7) are shown in Fig. 1. All reflections in the diffraction pattern of the as-synthesized sodium magadiite can be assigned to the typical pattern of magadiite [26], proving that the sample is free of impurities. The basal spacing of the as-synthesized sodium magadiite and the intercalation products with different CP contents are 15.5 Å and 38.8–40.2 Å, respectively (Table 1). These large shifts demonstrate the successful incorporation of the long-chain organic cations into the interlayer space of the magadiite. Even at a very low CP loading (sample CP-Mag1 with 27% of

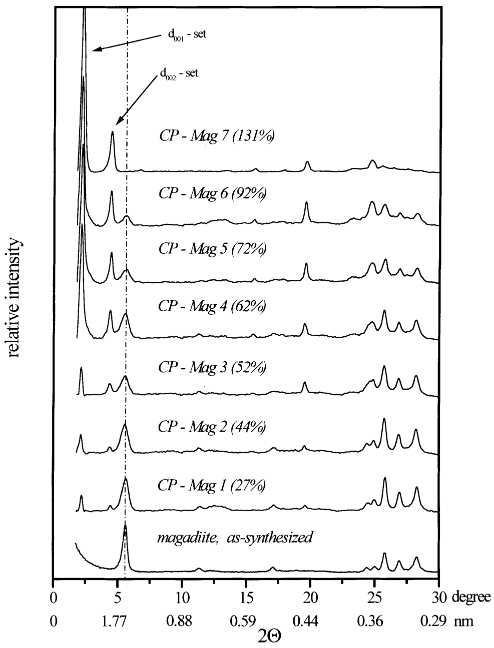

Fig. 1 X-ray powder diffraction patterns of partly loaded cetylpyridinium (*CP*) magadiites in comparison to the as-synthesized form and a totally loaded form

Table 1 Basal spacing of intercalated magadiites

Sample	CP^+ loading %	Layer distances *d* (Å)		
		d_{001}	d_{002}	$d_{\text{as-synthesized form}}$
As-synthesized form		–	–	15.7
CP-Mag1	27	40.2	19.9	15.8
CP-Mag2	44	41.1	20.1	15.8
CP-Mag3	52	41.1	20.3	15.9
CP-Mag4	62	41.1	20.3	15.9
CP-Mag5	72	40.2	20.3	15.8
CP-Mag6	92	40.2	20.1	15.8
CP-Mag7	131	39.3	19.6	–

the theoretical total ion-exchange capacity of magadiite) the quantity of CP is enough to expand at least some of the interlayer packages by 24.5 Å compared with the as-synthesized form. The interlayer expansion is about the same for all loadings. However, the patterns of all partly expanded products also show the original 001 reflection of the as-synthesized sodium magadiite at 15.5 Å with different intensities. Thus, the long-chain surfactant cations are not evenly distributed between the interlayer spaces. Every partly loaded CP silicate still has unaffected zones corresponding to the as-synthesized sodium magadiite. The proportion of unreacted layers decreases with increasing CP loading rate.

When an excess of CP cations in the exchange solution (twice the amount related to the theoretical exchange capacity) is used and intercalation is carried out for a considerably longer period (3 days), the X-ray pattern (sample CP-Mag7) only shows expanded layers, and reflections of the original magadiite are absent. The 001 series is seen up to the third order with a basal spacing of 39.3 Å. This implies that the fully loaded product is well ordered.

X-ray powder diffraction patterns of the products after rearrangement of the surfactant cations are shown in Fig. 2. The 001 and 002 reflections vary between 33.4 and 36.1 Å, and between 15.5 and 17.2 Å, respectively (Table 2). The basal layer spacing is smaller by 2-6 Å compared with the expansion of the products after the first intercalation step.

Table 2 Basal spacing of intercalated magadiites after rearrangement

Sample	Basal spacing d (Å)		Expansion Δd (Å)
	d_{001}	d_{002}	
As-synthesized form	15.5	–	–
CP-Mag1re	34.0	15.5	18.3
CP-Mag2re	33.4	16.5	17.7
CP-Mag3re	35.4	17.0	19.7
CP-Mag4re	36.1	17.2	20.4
CP-Mag5re	33.4	16.7	17.7
CP-Mag6re	34.7	17.0	19.0
CP-Mag7re	37.6	19.2	21.9

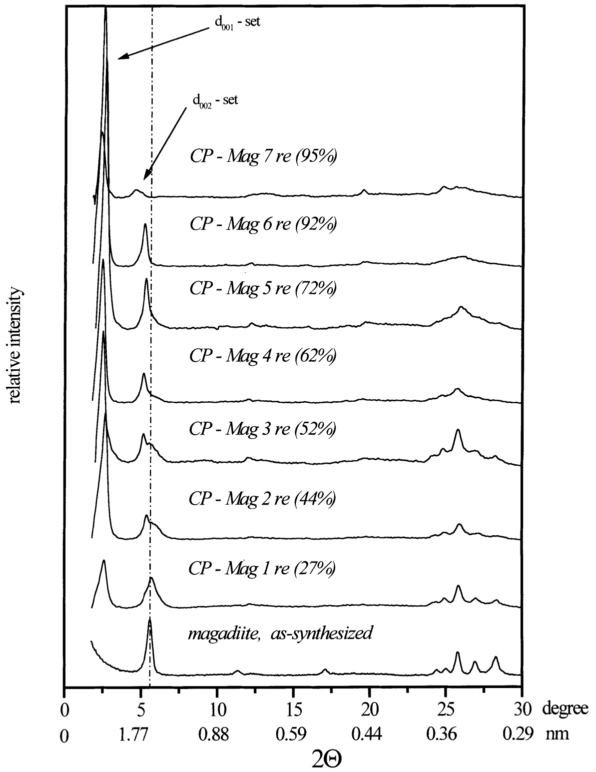

Fig. 2 X-ray powder diffraction patterns of the partly loaded CP magadiites after rearrangement

The position of second reflection of the sample CP-Mag1re with 27% CP loading lies at 15.5 Å. This value coincides exactly with the basal spacing of the as-synthesized magadiite. The reflections of the other partly loaded samples in the range 16.5–17.2 Å clearly represent the second order of reflections of the largely expanded layers (basal spacing >33 Å). The center of the 002 line positions of samples CP-Mag2re and CP-Mag3re are slightly shifted because of a little shoulder due to the reflection of as-synthesized magadiite. However, the X-ray pattern of samples CP-Mag4re, CP-Mag5re and CP-Mag6re show a 002 line position at 17.3 Å without a shoulder or any indication of packets of unreacted magadiite. The X-ray pattern of the rearranged, fully loaded magadiite CP-Mag7re shows only a small shift of the basal spacing from 39.3 to 37.6 Å. This is due to the fact that the chosen number of CP cations in the exchange solution causes a higher number of surfactant molecules in addition to fixed cations to penetrate into the interlayer, upon swelling.

All changes in the X-ray patterns in the range $2\Theta = 2$–$7.5°$ for the sample CP-Mag5 for the different preparation steps are shown in Fig. 3. In addition, the XRD patterns of the as-synthesized and the fully loaded forms are given. After rearrangement the 001 reflection of the as-synthesized magadiite disappear and the basal spacing shifts from 40.2 to 33.4 Å. The basal spacing of CP-Mag5 (40.2 Å) is nearly the same as that of the fully loaded CP-Mag7 (39.3 Å).

The chemical compositions of all samples are summarized in Table 3. The numbers of CP cations of the partly loaded products do not change on rearrangement. However, in case of the fully loaded, better "overloaded", sample CP-Mag7 some of the intercalated surfactant (CP cations + counterions) is washed out during treatment with water at 333 K, accompanied by a basal spacing decrease from 39.3 to 37.6 Å. Analysis of all products showed a decrease in the number of Na cations with increasing CP content. The total number of cations (sum of CP and Na cations) is close to the cation-exchange capacity of the original magadiite (about 2.40 mEq/g SiO_2). This indicates that the intercalation of the surfactant at this stage is a Na^+/CP^+ ion-exchange process. After equilibration in water the number of sodium ions is reduced and the sum of the CP and Na cations is distinctly below the expected total exchange capacity. In order to maintain charge neutrality protons exchange inside the interlayer of these rearranged products.

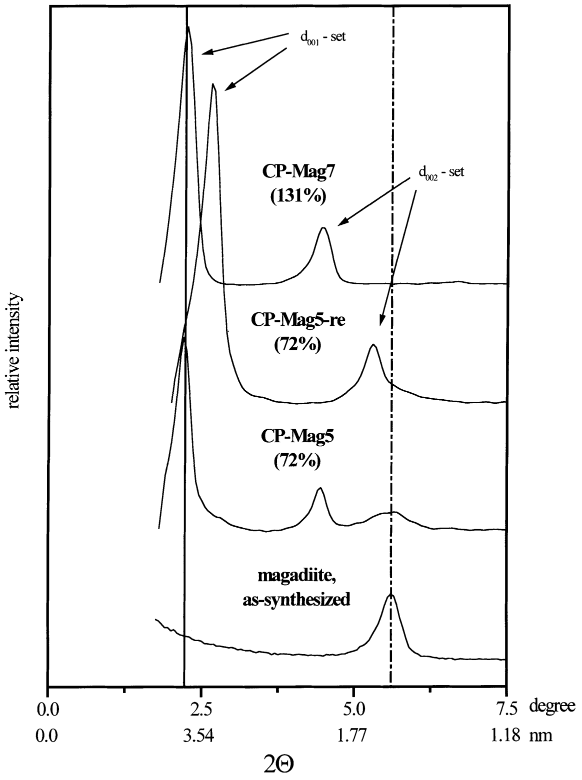

Fig. 3 X-ray powder diffraction patterns of CP-Mag5 after different reaction stages

Also, the water content of the products decreases from between 7–9% to between 4–5%, due to the reduced Na content. The basal spacings of all products after intercalation and rearrangement are summarized in Tables 1 and 2.

The observed interlayer separation of the fully expanded samples of about 40–41 Å is explained by a bilayer arrangement of the surfactant as proposed by Lagaly et al. [19]. The decrease in the spacing of about 4–6 Å after rearrangement can be elucidated from the conformational changes of the intercalated cations or by interdigitation. This was reported previously for other layered silicates [27, 28].

It is very interesting to note that no CP chloride was found in the aqueous solution after rearrangement. The surfactant cations of partly loaded samples are not desorbed because all CP cations are bound by the negative charges at the silicate layers. The observed rearrangement during the second step can only be realized if one assumes a movement of surfactant in and between the interlayer spaces. In addition Na^+/H^+ ion-exchange takes place. Whereas the sum of the CP^+ and the Na^+ content of the samples after the first treatment step is equal to or a little higher than the total ion-exchange capacity, the sum of the CP and Na cations of the rearranged samples is always smaller than about 2.4 mEq/g SiO_2. The intensity of the 001

Table 3 Interlayer composition of intercalated and rearranged samples

Sample[a]	CP^+ loading		Ignition loss % (due to H_2O desorption)		Na^+ content	Sum of cations (CP^+ + Na^+)
	mEq/g SiO_2	%	Total	H_2O	mEq/g SiO_2	mEq/g SiO_2
As-synthesized form	–	–	15.2	15.2	2.40	2.40
CP-Mag1	0.64	27	27.8	8.8	1.76	2.40
CP-Mag2	1.05	44	32.8	8.2	1.28	2.33
CP-Mag3	1.24	52	35.4	8.6	1.38	2.62
CP-Mag4	1.48	62	37.5	8.8	0.99	2.47
CP-Mag5	1.73	72	40.1	7.3	0.91	2.64
CP-Mag6	2.20	92	45.0	6.8	0.61	2.81
CP-Mag7	3.15	131	52.0	4.2	0.12	3.27
CP-Mag1re	0.64	27	23.2	4.8	1.07	1.71
CP-Mag2re	1.05	44	29.5	4.9	0.55	1.60
CP-Mag3re	1.24	52	31.1	4.7	0.45	1.69
CP-Mag4re	1.48	62	34.1	4.1	0.23	1.71
CP-Mag5re	1.73	72	39.1	4.9	0.22	1.95
CP-Mag6re	2.19	92	41.9	4.5	0.02	2.21
CP-Mag7re	2.28	95	45.5	3.9	0.02	2.30

[a] "re" indicates samples with rearrangement treatment

reflection of the as-synthesized magadiite decreases with Na^+ content. However, at this stage of the investigation it is not possible to decide whether the CP^+/Na^+ or the Na^+/H^+ ion-exchange process takes place first, or if Na^+/H^+ ion-exchange is a precondition for the observed rearrangement of the surfactant molecules inside the interlayer space.

Further ion-exchange investigations of the fully loaded sample CP-Mag7 showed that a displacement of the incorporated CP cations by Na cations was not possible, even on treatment with sodium hydroxide solution (0.1 N). The X-ray diffraction patterns of samples after these exchange experiments did not show any changes. However, the reaction with hydrochloric acid led to an X-ray pattern equivalent to a proton form of magadiite [10]. Via this route, sodium magadiite with a typical X-ray pattern was obtained by additional H^+/Na^+ ion exchange, which proves that the bulk phase of the magadiite, that is the structure of the silicate layers, remains unaltered by the different reaction steps.

Discussion

Our investigations confirm earlier results [20] that the intercalation of long-chain CP cations into the layered silicate magadiite proceeds easily at room temperature by an ion-exchange process. The number of surfactant molecules finally intercalated indicates that the ion-exchange reaction Na^+/CP^+ is equivalent. As proven by an indirect proton-ion exchange process, the intercalation of CP cations is reversible. It is possible to prepare "overexchanged" materials (cf. CP-Mag7) in which the "overloaded" surfactant (cations + counterions) is physically intercalated between the fixed surfactant cations. The physically absorbed surfactant can be removed by washing the sample with water and adjusting the equivalent ion-exchange state again. Previous publications have mainly focused on the preparation of completely exchanged samples to study the structural behavior of alkyl chains in the interlayer space. We suppose that an intermediate proton-ion exchange occurs during the surfactant exchange as the Na^+/H^+ ion-exchange process is much faster.

The two-step procedure is the only way to prepare partly loaded samples with a nearly uniform distribution of the surfactant inside the interlayer space.

In the first step the intercalation conditions have to be adjusted carefully to ensure that only the desired number of long-chain cations is taken up. However, this results in non-uniform samples (Fig. 1). In the second step, rearrangement of the surfactant molecules which have already been intercalated is induced by an equilibration process carried out in salt-free aqueous solution. As shown in Fig. 2, a loading of about 60% of the total exchange capacity of magadiite (2.4 mEq/g SiO_2 as

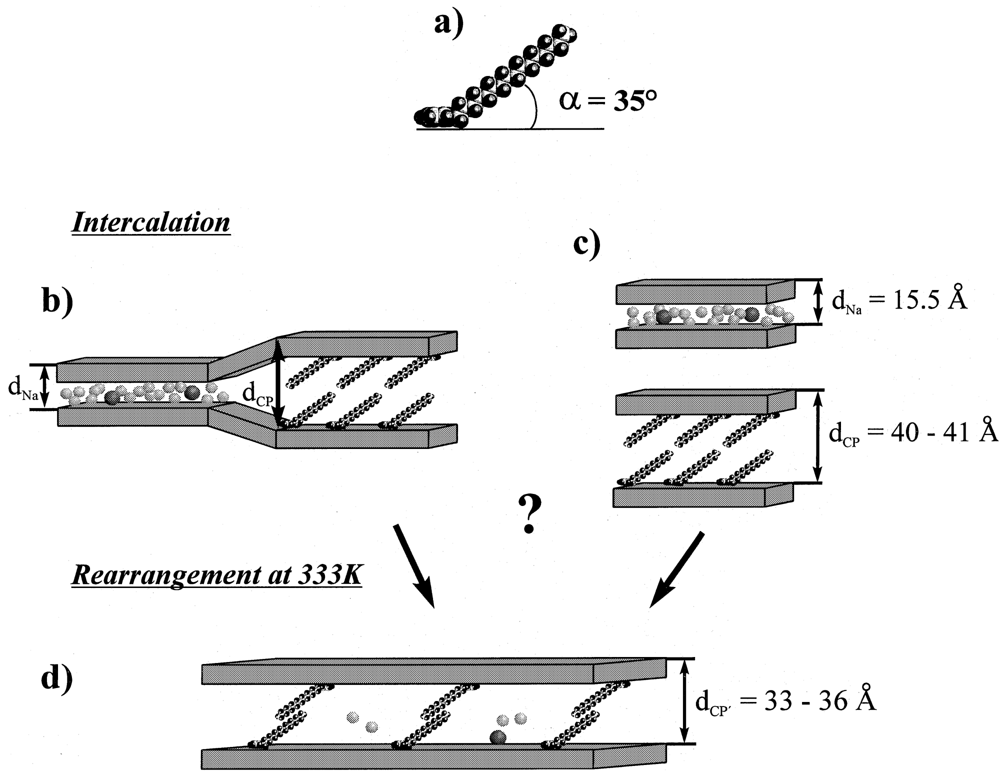

Fig. 4a–d Representation of the arrangement of the surface active cations inside the interlayer spaces. **a** Alkyl chain orientation, **b, c** non-uniform distribution of CP and Na cations after ion exchange (first step of reaction), **d** uniform distribution of CP and Na cations after equilibration in water at 333 K

theoretical value) is sufficient to yield a homogeneous distribution of the intercalated organic cations (see sample CP-Mag4re in Fig. 2). Moreover, it is evident that the organic cations in such "half-loaded" magadiite with a nearly uniform distribution of the CP cations are not closely packed creating a hollow space between the bulk layers.

Lagaly et al. [29] developed a model for the incorporation of the long-chain surfactant in magadiite, shown in Fig. 4. The pyridinium rings lie flat on the silicate layer and the chains take up a tilt angle of 35° (Fig. 4a). This orientation corresponds to the energetically favorable all-trans conformation of long alky1 chains. Figure 4b and c shows two possibilities for arrangement of the CP cations in partly loaded samples which may be attained after the first step. All experimental results, especially the X-ray patterns, could be explained by assuming that the CP cations enter only a certain proportion of the interlayer spaces of all magadiite crystals or only some of the magadiite crystals are totally loaded: we cannot decide between these possibilities. After the rearrangement step, both types of products lead to samples with a nearly homogeneous distribution of the long-chain cations (Fig. 4d). One has to conclude that the long-chain cations are mobile inside the layered materials in order to achieve the final thermodynamic state. The products have a basal spacing between 33 and 36 Å which is somewhat lower than that of the fully loaded state (40.2 Å found by Lagaly [29] and 37.6 Å for the rearranged sample CP-Mag7) because the CP cations are not closely packed, the packing density depends on the loading rate reached in the first step.

The results reveal that for certain intercalating organic cations organized (ordered) and variable voids in the interlayer space are obtained.

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