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LAYERED SODIUM DISILICATES AS PRECURSORS
OF MESOPOROUS SILICAS.
PART II: HYDRATION OF δ -Na₂Si₂O₅ AND α -Na₂Si₂O₅

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Abstract. Reaction of δ -Na₂Si₂O₅ and α -Na₂Si₂O₅ with water at ambient conditions has been studied. The first substrate produced kanemite, the other a crystalline solid, assumed to be the layered hydrated α phase of yet unknown structure. Important differences have been observed in the kinetics of δ -Na₂Si₂O₅ and α -Na₂Si₂O₅ reactions with water, the phase transformation of the latter being distinctly slower. The observed different rates of hydration were associated with the different structural properties of the disilicates investigated. Hydrated δ -Na₂Si₂O₅ and α -Na₂Si₂O₅ possess, respectively, the platy and the needle-like morphology. Hydrated α -Na₂Si₂O₅ contains less interlayer water, which is considered the reason for basal spacing being lower than that of kanemite. The interlayer water trapped between the layers of hydrated α -Na₂Si₂O₅ is more strongly bound than that in kanemite.

Key-words: Na₂Si₂O₅, layered silicates, kanemite, hydration

INTRODUCTION

There are several crystalline polymorphs of layered anhydrous Na₂Si₂O₅, of which α (with subgroups like α_I , α_{II} , α_{III}), β , γ and δ are best known. Among them of particular significance is δ -Na₂Si₂O₅, which can react with water to yield a hydrated layered silicate known as kanemite NaHSi₂O₅·3H₂O (Beneke, Lagaly 1977). The characteristic feature of this compound, common with other hydrous silicates, is its innercrystalline reactivity, associated with a high capacity for ion exchange. The ease, with which sodium ions can be replaced by organic moieties such as long chain alkylammonium

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cations, makes kanemite an attractive precursor of unique porous silica phases, such as FSM-16 (Folded Sheet Mesoporous materials) and others (Yanigasawa et al. 1990; Inagaki et al. 1993, 1996; Kimura et al. 2000a,b, 2002, 2004). FSM-16 solids represent a class of porous silicas particularly useful in sorption and catalysis applications due to the fact that the dimensions of their uniform channels can be adjusted by the choice of the alkylammonium cation with an appropriate length of the alkyl chain. Recently, for instance, we have demonstrated that the use of FSM-16 solids as supports for catalytically active organometallic compounds offers means for controlling the spectrum of reaction products (Zimowska et al. 2007).

Till recent years no other sodium disilicate polymorph was reported to undergo a transformation similar to that observed for δ - $\text{Na}_2\text{Si}_2\text{O}_5$ upon reaction with water. However, in the study of α - $\text{Na}_2\text{Si}_2\text{O}_5$ stability upon exposure to humid air, Ai et al. (2002) reported that the α phase, allowed to stand over the period of 6 months in the atmosphere of 35–50% humidity, gradually transformed to a new phase of unknown structure. Kato et al. (2004, 2005) used the solid resulting from the reaction of α - $\text{Na}_2\text{Si}_2\text{O}_5$ with water to synthesize novel mesoporous silicas named SSW-1 and SSW-2 and published for the first time the XRD pattern of the hydrated α phase. However, the work reported the d value for one peak only – the reflection at $d = 0.96$ nm ($2\theta = 9.2^\circ$), which, when compared with the half the cell parameter b of α - $\text{Na}_2\text{Si}_2\text{O}_5$ (0.772 nm), was taken as an indication of expansion of the lattice in the direction perpendicular to the layers.

The aim of the present work was to get more insight into the structural transformation accompanying the hydration of α - $\text{Na}_2\text{Si}_2\text{O}_5$ phase and to compare it with the hydration of δ - $\text{Na}_2\text{Si}_2\text{O}_5$.

EXPERIMENTAL

α - $\text{Na}_2\text{Si}_2\text{O}_5$ and δ - $\text{Na}_2\text{Si}_2\text{O}_5$ disilicates were obtained according to the optimized procedures described in Part I (Michalik-Zym et al. 2008). In brief, α - $\text{Na}_2\text{Si}_2\text{O}_5$ was synthesized by mixing the suspension of 0.05 M SiO_2 (Merck, Silica gel 60) in 10 ml methanol with 0.05 M NaOH (POCH Gliwice, p.a) dissolved in 13.5 ml distilled water. The slurry was dried at 100°C for 24 h and calcined at 825°C for 24 h. δ - $\text{Na}_2\text{Si}_2\text{O}_5$ was prepared from water glass (Aldrich, reagent grade, molecular formula $\text{Na}_2\text{Si}_3\text{O}_7$), with Na/Si ratio adjusted to 1 by addition of an appropriate amount of 2 M NaOH solution. The liquid was dried at 100°C for 24 h and the remaining solid calcined for 15 min at 700°C. Hydrated materials were obtained at room temperature by mixing 1g of the powdered disilicate with 10 ml distilled water for various periods of time ranging from 5 min to 8 h. The hydrated solids were recovered by filtering, washed briefly with water and dried at room temperature.

Methods

X-ray diffraction patterns were recorded with a Siemens D5005 powder diffractometer using $\text{CuK}\alpha$ radiation. Thermal analysis was carried out with a DSC/TG Netzsch

STA 409 PC LUXX apparatus. Scanning electron microscopic studies were carried out by means of a JEOL JSM – 7500F field emission scanning electron microscope. A K575X Turbo Sputter Coater was used for coating the specimens with chromium (deposited film thickness – 4.3 nm).

RESULTS AND DISCUSSION

The choice of the shortest time of hydration applied to the synthesized disilicates was 5 min, due to the fact that this is the usual procedure when producing an intermediate for further treatment with trimethylammonium cationic surfactant in the synthesis of FSM-16 mesoporous silicas. Figure 1 shows the XRD pattern of the parent δ - $\text{Na}_2\text{Si}_2\text{O}_5$ (containing small amount of an α phase impurity) and the product of its hydration after 5 min contact with water. It may be seen that the product obtained after hydration does not contain reflections assignable to the δ - $\text{Na}_2\text{Si}_2\text{O}_5$, but instead is dominated by the pattern characteristic of hydrated silicate kanemite (basal spacing $d = 1.03$ nm). A minor impurity detected in the XRD diagram of hydrated sample points to the presence of a small amount of the hydrated α phase. In the case of δ - $\text{Na}_2\text{Si}_2\text{O}_5$, the result shows that the reaction hydration, which is described by equation (1), proceeds in these conditions very swiftly and the 5-min treatment is sufficient to complete the exchange of proton for sodium cation required for the phase transformation of δ - $\text{Na}_2\text{Si}_2\text{O}_5$ to kanemite.

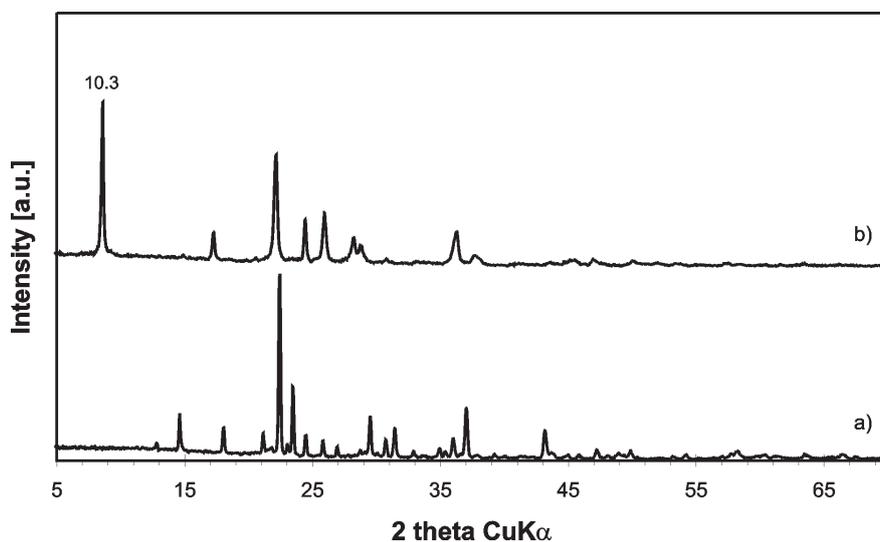
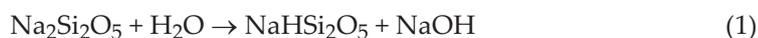


Fig. 1. XRD monitoring of δ - $\text{Na}_2\text{Si}_2\text{O}_5$ hydration: a) parent δ - $\text{Na}_2\text{Si}_2\text{O}_5$, b) after 5 min reaction with water (basal d spacing of kanemite marked)

A different picture was obtained for the hydration of the α - $\text{Na}_2\text{Si}_2\text{O}_5$ phase (Fig. 2). After 5 min of water treatment the XRD pattern revealed a set of new reflections, including the one at $d = 0.96$ nm, but α - $\text{Na}_2\text{Si}_2\text{O}_5$ was still the major phase. Gradual extension of hydration times showed that full transformation could be achieved only after 8 h of treatment in the applied conditions.

The hydration experiment showed clearly that while both modifications of $\text{Na}_2\text{Si}_2\text{O}_5$ react with water to give crystalline hydration products, the reaction is more difficult for α - $\text{Na}_2\text{Si}_2\text{O}_5$. To understand the reasons of such a behaviour it is necessary to recall the crystal structures of both disilicates. The main building units of both α and δ phases are folded layers of corner-connected SiO_4 tetrahedra and sodium cations residing between the silicate sheets for charge compensation. Figure 3 shows the projections along the c

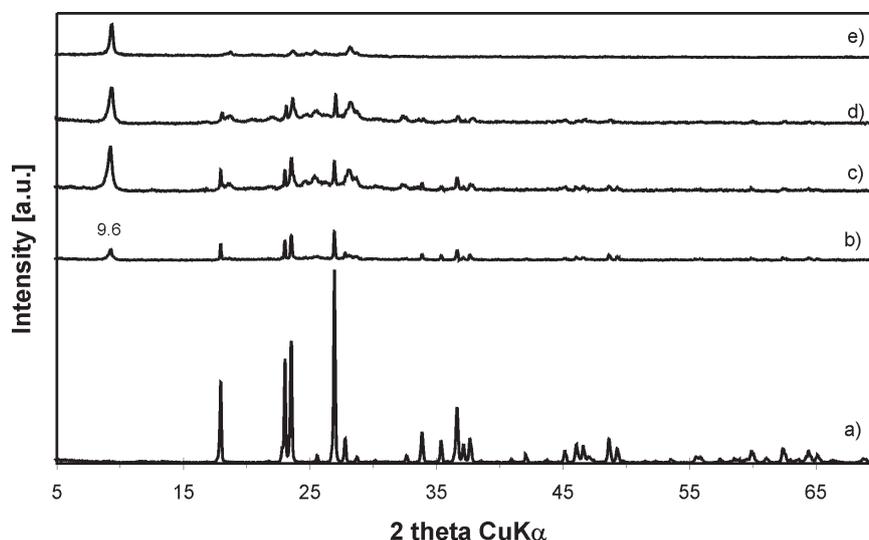


Fig. 2. XRD monitoring of α - $\text{Na}_2\text{Si}_2\text{O}_5$ hydration: a) parent α - $\text{Na}_2\text{Si}_2\text{O}_5$, b) after 5 min, c) after 1 h, d) after 5.5 h, e) after 8 h reaction with water (basal d spacing of the emerging hydrous silicate phase marked)

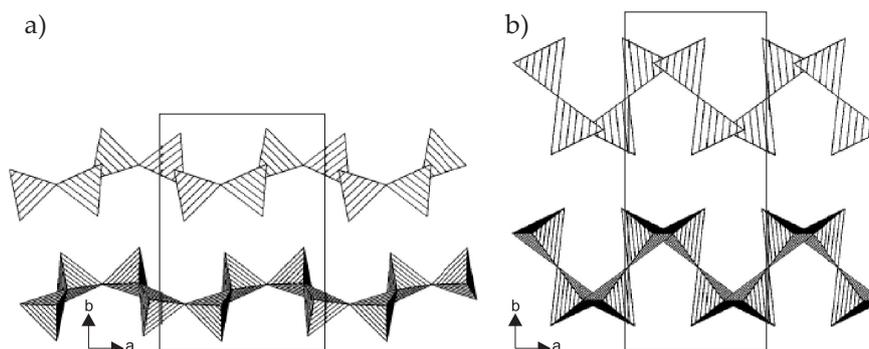


Fig. 3. Projection of crystal structures of a) δ - $\text{Na}_2\text{Si}_2\text{O}_5$ and b) α - $\text{Na}_2\text{Si}_2\text{O}_5$ along the c axis (after Kahlenberg et al. 1999)

axis (perpendicular to the silicate sheets) of δ - and α - $\text{Na}_2\text{Si}_2\text{O}_5$ phases presented by Kahlenberg et al. (1999) on the basis of the X-ray diffraction data. In the silicate layer, each tetrahedral silicon ion is bonded to other three tetrahedral silicon ions via bridging oxygen ions, leaving one coordinated oxygen ion in a non-bridging form. However, the corrugation of the layers in the α phase is much more pronounced than in the δ modification. δ - $\text{Na}_2\text{Si}_2\text{O}_5$ has silicate sheets with boat-type six-member rings (referred to as S6R), whereas the α phase possesses silicate sheets with chair-type six-member rings. As a result, the lattice constant b of the α disilicate, perpendicular to the layers, increases by about 27% relative to the δ phase, whereas the lattice constant a in the wavelength direction decreases by about the same factor. Figure 4 shows the projection of the silicate along the b axis. This projection allows for the proper view of six-member rings formed by the SiO_4 tetrahedra. The alignment of these openings in the disilicate structures with the channels generated by layer folding running along the $[001]$ direction provide routes for cation transport during exchange reactions. As pointed out by Kahlenberg et al. (1999), the S6R rings in δ - $\text{Na}_2\text{Si}_2\text{O}_5$ are larger than those in the α phase and assume a more circular shape, which is the likely reason for the superior ion exchange properties of the former phase. As the reaction with water is in essence a cation exchange process, the above would explain why the transformation of δ - $\text{Na}_2\text{Si}_2\text{O}_5$ to kanemite is more facile than that of α - $\text{Na}_2\text{Si}_2\text{O}_5$ to its hydrated form.

Kanemite and hydrated α - $\text{Na}_2\text{Si}_2\text{O}_5$ show also striking differences in crystal morphology. SEM micrographs of both compounds presented in Figure 5 reveal that while kanemite is present in the form of agglomerated platy particles with dimensions in the range of tenths of a μm , the hydrated α - $\text{Na}_2\text{Si}_2\text{O}_5$ forms clusters of long ($>1 \mu\text{m}$) needle-like crystallites.

As discussed in the introduction, the crystal structure of the compound formed after hydration of α - $\text{Na}_2\text{Si}_2\text{O}_5$ has not yet been resolved. However, analysis of the d values

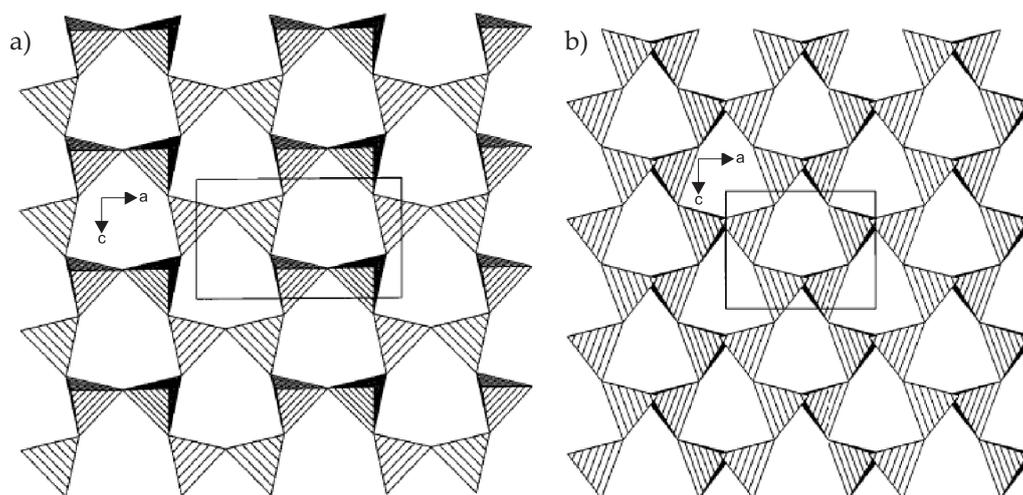


Fig. 4. Projection of crystal structures of a) δ - $\text{Na}_2\text{Si}_2\text{O}_5$ and b) α - $\text{Na}_2\text{Si}_2\text{O}_5$ along the b axis (after Kahlenberg et al. 1999)

associated with the first low angle reflections observed for the hydrated α phase and for kanemite leads to some interesting observations. In kanemite, the first low angle reflection at $d = 1.03$ nm is the most intensive one and corresponds to the basal d spacing of the layered structure (Garvie et al. 1999). It seems reasonable to assume that the most intensive low angle reflection in the pattern of hydrated α - $\text{Na}_2\text{Si}_2\text{O}_5$ corresponds also to the basal d spacing. The value of this spacing, 0.96 nm, is lower than that in kanemite. However, comparison of the parent structures of anhydrous disilicates shows that the lattice constant b of α - $\text{Na}_2\text{Si}_2\text{O}_5$ (1.542 nm), perpendicular to the layers, is larger than

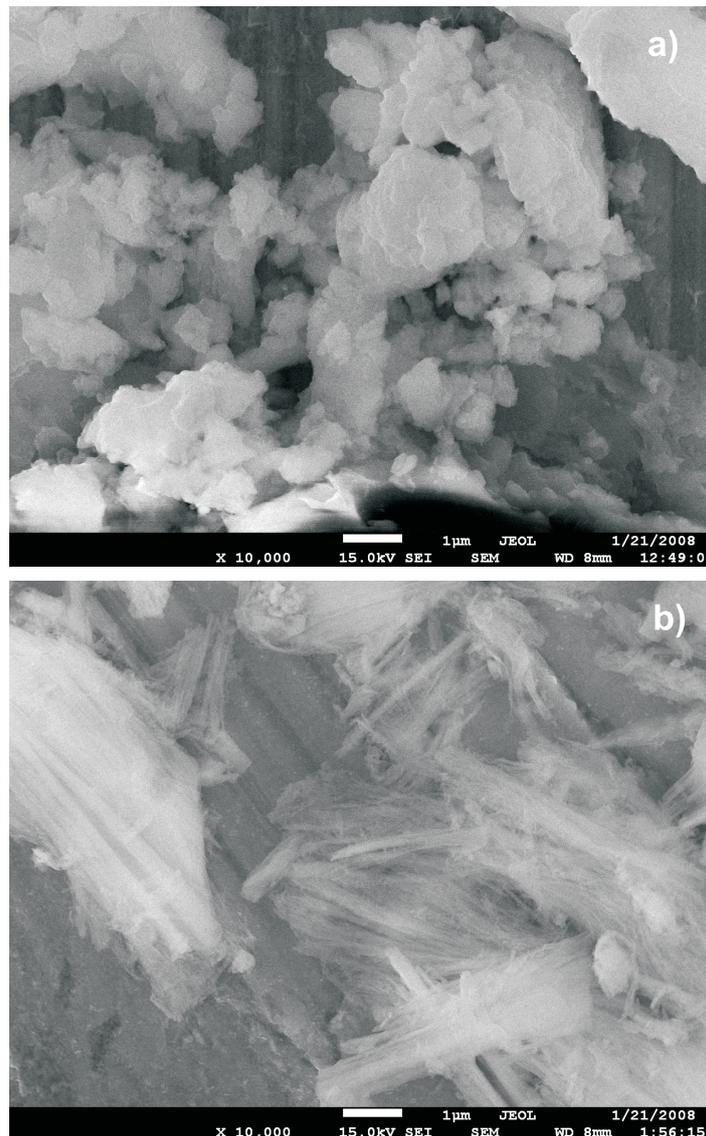


Fig. 5. SEM micrographs of a) kanemite, b) hydrated α - $\text{Na}_2\text{Si}_2\text{O}_5$

that of δ - $\text{Na}_2\text{Si}_2\text{O}_5$ (1.207 nm). As discussed above, the difference is due to the stronger folding of the silicate layers in α - $\text{Na}_2\text{Si}_2\text{O}_5$. Thus, after hydration the relation becomes reversed. Two explanations of the observed phenomenon may be proposed: either the geometry of the layers in the hydrated α phase is different than in the parent material, or, if it is similar, the packing of interlayer cations and water is different. The first option seems less likely in view of the fact that the phase transformation occurs in very mild conditions at room temperature. Additionally, according to Kahlenberg et al. (1999), the SiO_4 tetrahedra in the δ phase display higher strain than the structural units in α - $\text{Na}_2\text{Si}_2\text{O}_5$, nevertheless in kanemite the character of the layer folding is preserved (Garvie et al. 1999). For this reason we suggest that it is the different packing of the interlayer cations and water that is responsible for the lower value of basal spacing in hydrated α - $\text{Na}_2\text{Si}_2\text{O}_5$. In such a case it might be expected that the release of water from both hydrous silicates may proceed in different manner. Figure 6a and 6b shows the DSC/TG profiles of kanemite and hydrated α - $\text{Na}_2\text{Si}_2\text{O}_5$. Two main endothermic effects

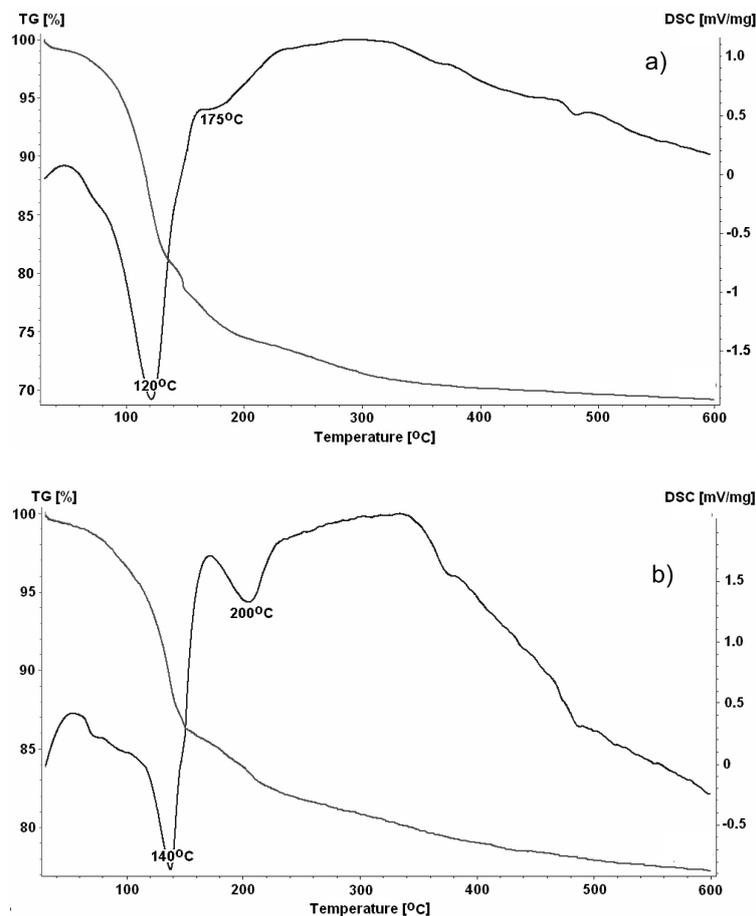


Fig. 6. TG/DSC analysis profiles of a) kanemite, b) hydrated α - $\text{Na}_2\text{Si}_2\text{O}_5$

with maxima at 120 and 175°C observed in kanemite are associated with the stepwise release of interlayer water, the dehydroxylation of the layers proceeding in a continuous manner as the temperature continues to increase (Johan, Maglione 1972; Beneke, Lagaly 1977; Wieker et al. 1995). The DSC/TG diagram of hydrated α - $\text{Na}_2\text{Si}_2\text{O}_5$ is qualitatively similar, but the maxima of the two effects are both shifted to higher temperatures, the first one having the maximum at 140°C, the second at 200°C. This shows that the water of hydration is more strongly bound in the interlayer space of the hydrated α phase than the water in kanemite. Additionally, the weight loss corresponding to the total loss of water of hydration (sum of both effects) amounts to *ca* 26% in the case of the kanemite sample, whereas in the case of the hydrated α phase it is only 17.5%. The removal of three water molecules from the molecular unit of kanemite $\text{NaHSi}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ would give 25.2% weight loss, which agrees well with the observed value. Under assumption that the chemical formula of the hydrated α phase is $\text{NaHSi}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, the observed weight loss can be explained by fitting $n = 2$ as the expected weight loss would then correspond to 18%, i.e., the value very close to the experimental one (17.5%). Thus, thermal analysis data suggest that the lower basal spacing observed for hydrated α phase is due to the lesser amount of water of hydration trapped between the layers. It is likely that smaller interlayer distances contribute to the stronger binding of water in this material.

CONCLUSIONS

Reaction of δ - $\text{Na}_2\text{Si}_2\text{O}_5$ and α - $\text{Na}_2\text{Si}_2\text{O}_5$ with water at ambient conditions leads in the first case to kanemite, in the other to a crystalline solid, assumed to be the layered hydrated α phase of yet unknown structure. Important differences have been observed in the kinetics of δ - $\text{Na}_2\text{Si}_2\text{O}_5$ and α - $\text{Na}_2\text{Si}_2\text{O}_5$ reactions with water. The former substrate undergoes hydration very swiftly, the latter is distinctly slower to transform, but the process is eventually completed. The difference in the hydration behaviour is assigned to the different structural properties of the disilicates investigated. Larger six-member rings in the δ phase facilitate cation exchange required for the phase transformation. Hydrated δ - $\text{Na}_2\text{Si}_2\text{O}_5$ and α - $\text{Na}_2\text{Si}_2\text{O}_5$ possess, respectively, the platy and the needle-like morphology. The interlayer water is more strongly bound in the hydrated α phase. The smaller basal spacing of the latter, as compared to kanemite, is tentatively attributed to the lower content of interlayer water of hydration.

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**Warstwowe krzemiany sodu jako prekursory mezoporowatych krzemionek.
II: Hydratacja $\delta\text{-Na}_2\text{Si}_2\text{O}_5$ i $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$**

Streszczenie

Reakcje $\delta\text{-Na}_2\text{Si}_2\text{O}_5$ i $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$ z wodą prowadzą do powstania uwodnionych krzemianów sodu, odpowiednio – kanemitu (z fazy $\delta\text{-Na}_2\text{Si}_2\text{O}_5$) i z fazy α – jej uwodnionej formy o nieznannej strukturze. Kinetyki hydratacji tych krzemianów są zdecydowanie różne; faza δ ulega szybkiej transformacji, faza α – wolnej. Różne szybkości hydratacji można wiązać z różnicami strukturalnymi obu krzemianów sodu. Uwodniony $\delta\text{-Na}_2\text{Si}_2\text{O}_5$ wykształcony jest w formie płytek, podczas gdy uwodniony $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$ ma morfologię typu igieł. Różna jest również ilość wody międzypakietowej w obu hydratách; uwodniony $\delta\text{-Na}_2\text{Si}_2\text{O}_5$ posiada jej więcej ale słabiej związanej, natomiast uwodniony $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$ mniej, lecz związanej silniej.