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LAYERED SODIUM DISILICATES AS PRECURSORS OF MESOPOROUS SILICAS.
PART I: OPTIMISATION OF THE SYNTHESIS PROCEDURE OF δ-Na$_2$Si$_2$O$_5$ AND α-Na$_2$Si$_2$O$_5$

A b s t r a c t . Optimization of the synthetic procedures described in literature aimed at preparing pure δ-Na$_2$Si$_2$O$_5$ has been carried out. The results show that a substantial shortening of the calcination time of amorphous silicate precursor is required, in order to minimize the appearance of the thermodynamically stable α-Na$_2$Si$_2$O$_5$. The use of commercial water glass solution rather than freshly synthesized silica/NaOH slurry is the preferred source of the starting amorphous silicate. Optimized preparative routes for synthesis of single-phase δ-Na$_2$Si$_2$O$_5$ and α-Na$_2$Si$_2$O$_5$ have been described.

INTRODUCTION

An increasing interest of material scientists in the properties of crystalline layered disilicates stems from the fact that: a) the solids are excellent substitutes for sodium triphosphate in detergent manufacturing, as they possess high ion exchange capacity and selectivity but do not contribute to excessive fertilization (Rieck 1986, 1989; Bauer et al. 1999), and b) they serve as silica source for a novel class of adsorbents and catalysts, known as ordered mesoporous silicas (Kuroda 2004). These materials are chemically, mechanically and thermally stable due to the inorganic framework and exhibit not only high specific surface areas but also monomodal pore size distributions in the mesopore

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range (2–4 nm) and regular pore arrangements. Mesoporous silicas derived from layered silicates include FSM-16, KSW-1, KSW-2, SSW-1, and SSW-2 solids, and were all developed by the group of Kuroda (Yanigasawa et al. 1990; Inagaki et al. 1993, 1996; Kimura et al. 2000a,b, 2002, 2004; Kato et al. 2004, 2005; Tamura et al. 2007), who based the synthetic strategy on the concept of surfactant-driven self assembly. In most cases transformation to mesoporous silicas involved in the first step the formation of a layered silicate kanemite ($NaHSi_2O_5 \cdot 3H_2O$) as a precursor, because of kanemite ability to form interlayered compounds by cation exchange reaction with organoammonium ions (Beneke, Lagaly 1977). These authors described a number of synthetic routes leading to kanemite, including SiO_2-NaOH mixtures, sodium silicate solutions, or reactive transformation of other silicates. All of them in the first stage of synthesis consist in obtaining an amorphous sodium disilicate, which then is subjected to thermally induced crystallization. Wieker et al. (1995) demonstrated that it is the $Na_2Si_2O_5$ known as δ phase that reacts with water and undergoes a direct exchange of Na^+ for protons to yield kanemite. There are reports that synthesis of pure δ phase is very difficult, if not impossible, and that this phase is usually contaminated by other polymorphs, in particular by the thermodynamically stable α-$Na_2Si_2O_5$ (de Lucas et al. 2000, 2002; Falamaki 2003). In fact, both patents and open literature claim that the synthesis of δ phase-rich sodium disilicate requires seeding with δ-$Na_2Si_2O_5$ (Rieck 1986; de Lucas 2002; Falamaki 2003).

The aim of the present work was to investigate the seedless crystallization of amorphous sodium disilicate, in order to identify conditions favouring the synthesis of either δ or α phases, both of which are important in the synthesis of mesoporous silicas: the former as a source of kanemite, the precursor of FSM-16, KSW-1, KSW-2, the latter as a starting point of the SSW-1 and SSW-2 syntheses.

EXPERIMENTAL

Materials

Two methods were used for the synthesis of crystalline layered silicates, neither of them employing seeding. According to method A (Lagaly, Beneke 1977) 0.05 M of SiO_2 (Merck, Silica gel 60) dispersed in 5 ml methanol was mixed with 0.05 M of NaOH (POCh Gliwice, p.a.) dissolved in 1.75 ml of distilled water. The resulting dense slurry was dried at 100°C for 24 h. Crystallization was achieved by calcination at various temperatures (450–825°C) for different periods of time (0.3–24 h). The calcined samples are referred to as $Na_2Si_2O_5(X,Y)$-A, where X is the temperature of calcination, Y time of thermal treatment. In some experiments double volumes of methanol and water were used in amorphous silicate synthesis. Such samples are denoted $Na_2Si_2O_5(X,Y)$-2A. Method B involved the synthesis of amorphous silicate from water glass (Aldrich, reagent grade, molecular formula $Na_2Si_3O_7$), the Na/Si ratio being adjusted to 1 by addition of appropriate amount of 2 M NaOH solution. The liquid was dried at 100°C for 24 h and the remaining solid calcined as described for method B. The calcined samples are referred to as $Na_2Si_2O_5(X,Y)$-B.

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Methods

X-ray diffraction patterns were recorded with a Siemens D5005 powder diffracto-meter using CuKα radiation. Thermal analysis was carried out with a DSC/TG Netzsch STA 409 PC LUXX apparatus.

RESULTS AND DISCUSSION

The starting point for our studies was the synthesis of a crystalline silicate according to the method described in the first paper of Kuroda's group (Yanigasawa et al. 1990), which followed one of the preparative routes proposed by Beneke and Lagaly (1977). As the synthesis aims at obtaining a precursor of kanemite, the expected outcome should be the δ-$Na_2Si_2O_5$ phase. The first step involved the preparation of an amorphous sodium silicate from the mixture of the appropriate amounts of silica gel dispersed in methanol and NaOH solution, followed by drying and 5.5 h calcination in air at 700°C. The XRD pattern presented in Figure 1a shows that the sodium silicate obtained after drying at 100°C is an amorphous substance, producing only a very broad peak centered around 30°2θ. Analysis of the XRD pattern of the solid obtained after calcination reveals that the sample contains, as expected, δ-$Na_2Si_2O_5$ (ICDD 1998 – JCPDS 22-1396) but the α phase (ICDD 1998 – JCPDS 22-1397) is present as well, albeit in a lesser amount (Fig. 1c). In Table 1 the relative contributions of both phases are
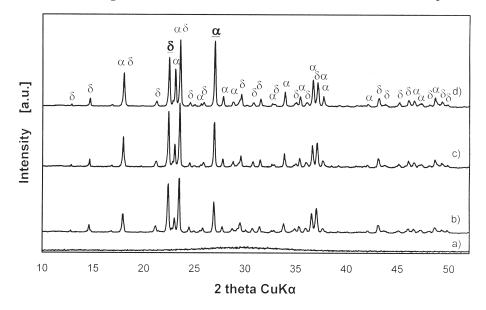

Fig. 1. XRD patterns of samples prepared according to method A,
showing the influence of the calcination time at 700°C:
a) amorphous $Na_2Si_2O_5$ dried at 100°C, b) $Na_2Si_2O_5(700,1)$-A, c) $Na_2Si_2O_5(700,5.5)$-A,
and d) $Na_2Si_2O_5(700,24)$-A (reflections belonging to δ and α phases are marked,
those used for determination of relative contributions are underlined)

TABLE 1

Relative contributions of δ-$Na_2Si_2O_5$ and α-$Na_2Si_2O_5$ phases expressed as the $I_{120}{}^{\delta}/I_{140}{}^{\alpha}$ XRD intensity ratio

Sample	$I_{120}{}^{\delta}/I_{140}{}^{\alpha}$
$Na_2Si_2O_5(700,1)$-A	1.58
$Na_2Si_2O_5(700,5.5)$-A	1.25
$Na_2Si_2O_5(700,24)$-A	0.75
$Na_2Si_2O_5(825,24)$-A	0.00
$Na_2Si_2O_5(825,24)$-2A	0.00
$Na_2Si_2O_5(450,1)$-A	amorphous
$Na_2Si_2O_5(550,1)$-A	0.62
$Na_2Si_2O_5(620,1)$-A	0.94
$Na_2Si_2O_5(700,1)$-B	22.71
$Na_2Si_2O_5(700,5.5)$-B	3.90

expressed as the ratio of $I_{120}{}^{\delta}/I_{140}{}^{\alpha}$, where $I_{120}{}^{\delta}$ and $I_{140}{}^{\alpha}$ are the most intensive, not overlapping reflections belonging to (120) and (140) planes of δ and α phases, respectively, appearing at d = 0.393 nm (22.6°2θ) and 0.330 nm (27°2θ). To check on dependence of the relative δ and α phases content on the time of the calcination, two additional samples were obtained at this temperature, thermally treated for 1 h and 24 h. The XRD patterns of the materials received are presented in Figure 1b and 1d, respectively. Comparison of the diagrams shows that the shortening of the calcination time results in an increase of the relative contribution of δ phase, while prolonged calcination leads to enhanced crystallization of the α phase.

To accomplish the synthesis of pure α phase, we decided to apply a more severe thermal treatment. The temperature of calcination was chosen on the basis of thermal analysis carried out for the amorphous sodium silicate precursor (Fig. 2). Differential scanning calorimetry (DSC) profile shows two effects in the high temperature region: an exothermic one around 630°C, attributed to the crystallization of δ-$Na_2Si_2O_5$ and an endothermic effect around 870°C, corresponding to the melting of the silicate (de Lucas et al. 2000). In consequence, the temperature of calcination was set at 825°C, the value considered sufficiently high for accelerating α-$Na_2Si_2O_5$ formation, and sufficiently low to avoid melting of the sample. Figure 3a shows the XRD pattern of the sample calcined at 825°C for 24 h. The diagram is dominated by the reflections of α-$Na_2Si_2O_5$, with no trace of the δ phase. However, low intensity peaks assignable to Na_2SiO_3 (ICDD 1998 – JCPDS 16-0818) impurity can be seen. To circumvent this problem, some modifications of the preparation procedure of amorphous silicate precursor were undertaken, of which doubling the amount of solvent turned out to bring the desired result. In the XRD pattern of $Na_2Si_2O_5(825, 24)$-2A presented in Figure 3b only peaks belonging to α-$Na_2Si_2O_5$ can be detected.

In search for conditions ensuring further enrichment in δ-$Na_2Si_2O_5$ phase, we have decided to stick to the 1 h calcination time while lowering the temperature of calcination, as to avoid the formation of the thermodynamically stable α phase. For this reason, the amorphous sodium silicate was calcined for 1h at 450, 550 and 620°C. The XRD patterns shown in Figure 4 demonstrate that lowering the temperature,
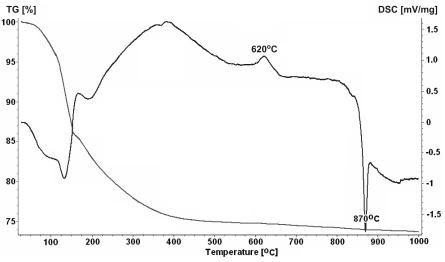

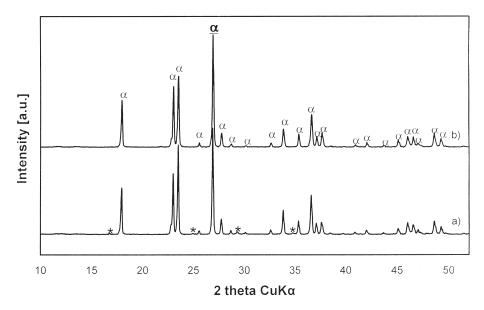Fig. 2. TG/DSC analysis profiles of amorphous $Na_2Si_2O_5$ obtained according to method A

Fig. 3. XRD patterns of the materials prepared according to method A and calcined for 24 h at 825°C,
showing the influence of the use of double volume of solvents:
a) $Na_2Si_2O_5(825,24)$-A, and b) $Na_2Si_2O_5(825,24)$-2A
(reflections belonging to the α phase are marked, * – Na_2SiO_3 impurity)
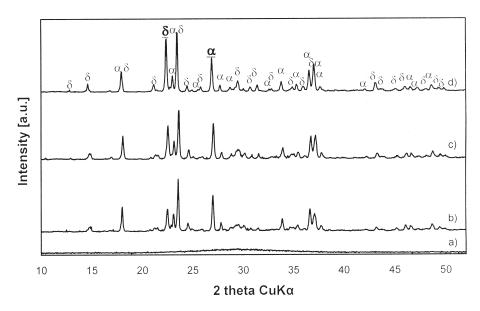
Fig. 4. XRD patterns of samples prepared according to method A and calcined for 1 h at different temperatures: a) $Na_2Si_2O_5(450,1)$-A, b) $Na_2Si_2O_5(550,1)$-A, c) $Na_2Si_2O_5(620,1)$-A, and d) $Na_2Si_2O_5(700,1)$-A (reflections belonging to the δ and α phases are marked respectively, those used for determination of relative contributions are underlined)

while maintaining short reaction time, did not result in enhanced contribution of the δ phase. A temperature of 450°C is not sufficient to induce crystallization, and for temperatures 550, 620, 700°C, the lower the temperature the lesser the relative content of the δ phase. Such behavior might point to the kinetic barriers associated with seed nucleation affecting the crystallization of δ-$Na_2Si_2O_5$. Indeed, as mentioned in the introduction, seeding is generally required to prompt crystallization of the δ phase (de Lucas et al. 2000, 2002; Falamaki 2003)

Thus, the series of experiments, in which we used as the substrate the amorphous sodium silicate obtained from the slurry of silica gel and NaOH, demonstrated that while preparing a pure α phase is possible, the preparation of δ-$Na_2Si_2O_5$ is associated always with the appearance of other phases (α and sometimes β), the best yield of the δ phase being obtained at 700°C at the shortest calcination time. The finding is important from the practical point of view, because it is at variance with the literature data reporting 5.5 h calcination time as appropriate (Beneke, Lagaly 1977).

Kuroda and co-workers, in the later paper describing the synthesis of FSM-16 materials (Inagaki et al. 1996), modified the procedure of obtaining crystalline $Na_2Si_2O_5$ by starting from amorphous material prepared by drying a solution obtained from the commercial water glass, with Si/Na ratio adjusted by addition of NaOH solution. The recommended calcination conditions were 6 h at 700°C. We decided to test this procedure and a sample referred to as $Na_2Si_2O_5(700, 5.5)$-B was obtained. Its XRD pattern presented in Figure 5c shows a distinct enrichment in δ-$Na_2Si_2O_5$ relative to the α phase, as compared to the best yields obtained with the procedure A (Table 1).
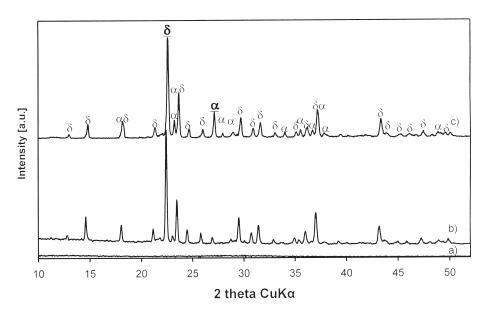
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Fig. 5. XRD patterns of samples prepared according to method B, showing the influence
of the calcination time at 700°C: a) amorphous $Na_2Si_2O_5$ dried at 100°C obtained according to method B,
b) $Na_2Si_2O_5(700,1)$-B, c) $Na_2Si_2O_5(700,5.5)$-B
(reflections belonging to the δ and α phases are marked,
those used for determination of relative contributions are underlined)

Bearing in mind that the procedure A resulted in better yields of the δ phase when shorter periods of calcination were applied, we decided to check on the time dependence of the crystalline phases evolution for the procedure B by shortening the thermal treatment time. The XRD pattern obtained for sample prepared from water glass and calcined for 1 h is presented in Figure 5b and shows that after only 1 h of calcination at this temperature an almost pure δ-$Na_2Si_2O_5$ is obtained. Further shortening of the thermal treatment does not increase the yield of the δ phase, and results in a material of poorer crystallinity. Thus, also in the case of the preparation procedure starting from water glass, it appears that the synthesis parameters proposed in the literature (6-h calcination) are far from optimum.

CONCLUSIONS

The synthetic procedures described in the literature aiming at preparation of pure δ-$Na_2Si_2O_5$ phase have been verified. The results show that a substantial shortening of the calcination time of an amorphous silicate precursor is required (e.g., from 5–6 h to 1 h), in order to minimize the formation of the thermodynamically stable α-$Na_2Si_2O_5$. The use of commercial water glass solution rather than freshly synthesized silica//NaOH solution is the preferred source of the starting amorphous silicate. Application of the water glass-based procedure and short calcination time at 700°C led to the

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synthesis of an almost single-phase δ-Na$_2$Si$_2$O$_5$ material. The α-Na$_2$Si$_2$O$_5$ could be obtained in a pure form by calcination of the amorphous sodium silicate at 825°C.

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Warstwowe krzemiany sodu jako prekursory mezoporowatych krzemionek.
I: Optymalizacja syntezy δ-Na$_2$Si$_2$O$_5$ i α-Na$_2$Si$_2$O$_5$

Streszczenie

Zweryfikowano opisaną w literaturze procedurę syntezy czystego δ-Na$_2$Si$_2$O$_5$. Stwierdzono, że skrócenie czasu kalcynacji amorficznego prekursora krzemianowego z 5–6 godz. do 1 godziny zapewnia otrzymanie niemal czystego δ-Na$_2$Si$_2$O$_5$, przy minimalnej ilości termodynamicznie stabilnej fazy α-Na$_2$Si$_2$O$_5$. Preferowanym źródłem wyjściowego amorficznego krzemianu sodu jest szkło wodne w miejsce syntetyzowanego roztworu SiO$_2$/NaOH. Użycie szkła wodnego i krótki czas kalcynacji w 700°C prowadzą do otrzymania monofazowego δ-Na$_2$Si$_2$O$_5$. Czysty α-Na$_2$Si$_2$O$_5$ można otrzymać kalcynując amorficzny krzemian sodu w temperaturze 825°C.