

CHEMICAL CHARACTERIZATION, STRUCTURAL FEATURES, AND THERMAL BEHAVIOR OF SODIUM AND HYDROGEN OCTOSILICATE

G. BORBÉLY AND H. K. BEYER

Central Research Institute of Chemistry of the Hungarian
Academy of Sciences, Budapest, Hungary

H. G. KARGE

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

W. SCHWIEGER, A. BRANDT, AND K.-H. BERGK

Sektion Chemie, WB Technische Chemie, Martin-Luther-Universität, Halle, Germany

Abstract—The chemical composition and the thermal behavior of sodium and hydrogen octosilicate was studied by chemical and thermal analysis, infrared (IR), magic-angle-spinning nuclear magnetic resonance (MAS-NMR) spectroscopy, and X-ray diffractometry. Both compounds are layer silicates with basal spacings of 11.10 and 7.38 Å, respectively. In both forms the ratio of Q4 silicon (connected via oxygen bridges with four silicon atoms) to Q3 silicon (connected with only three other Si atoms) is 1. At least a small part of the Q4 silicon can be substituted by aluminum. Elimination of water coordinated to the cations in sodium octosilicate results in a concomitant structural collapse. Replacement of the sodium ions by protons affects the atomic arrangement in the sheets only to a minor degree, but results in a decrease of the periodicity along the crystallographic *c* axis. Upon heat treatment an endothermal structural rearrangement occurs at about 360 K as revealed by significant changes of the IR and ²⁹Si MAS-NMR spectra. Reexchange with Na ions largely, but not completely, restores the structure of the parent octosilicate.

The X-ray diffraction pattern of sodium octosilicate was indexed in the monoclinic system with $a = 7.345$ Å, $b = 12.74$ Å, $c = 11.25$ Å and $\beta = 99.3^\circ$. Based on conclusions drawn from the results of the present study, the X-ray pattern of hydrogen octosilicate was tentatively indexed in the monoclinic system with $a = 7.345$ Å, $b = 12.74$ Å, $c = 8.51$ Å and $\beta = 119.8^\circ$.

Key Words—Octosilicate, Sheet silicates, MAS-NMR spectroscopy, Thermal behavior.

INTRODUCTION

McCulloch (1952) reported the synthesis of a new crystalline sodium silicate, the chemical composition of which corresponds to the formula $\text{Na}_2\text{O} \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ (with x between 9.4 and 13.1). Later, Iler (1964) obtained with a similar preparation method a hydrated, crystalline sodium polysilicate $\text{Na}_2\text{O} \cdot 8\text{SiO}_2 \cdot 9\text{H}_2\text{O}$. No counterpart of this material has been found in nature.

Iler (1964) showed that the sodium ions of this silicate can be exchanged with Li^+ , Mg^{2+} , and some heavy-metal ions. It was also demonstrated that titration with acids results in the replacement of sodium ions by protons. The process proceeds in two well-defined steps at pH 7.0 and 4.5, both of which involve half of the total alkali. This process has been proven to be fully reversible if the undried material was back-titrated with sodium hydroxide solution. However, if the obtained crystalline silicic acid was washed with water and dried at 303 K, significant changes in the back-titration curve and X-ray diffraction pattern were observed.

Schwieger *et al.* (1985) showed by ²⁹Si magic-angle-spinning nuclear magnetic resonance (MAS-NMR)

spectroscopy that Iler's sodium silicate contains two different Si species. These occur in equal amounts, as revealed by signals at -101.9 and -112.2 ppm (referenced to tetramethylsilane). The latter signal was assigned to Si surrounded by tetrahedra, all containing Si as T atoms (so-called Si{4Si} or Q4), and the former to Si with 3 Si in its secondary coordination sphere (Si{3Si, O⁻} or Q3), and one OH or O⁻.

According to the chemical composition corresponding to $\text{SiO}_2/\text{Na}_2\text{O} = 8$, the material was named "octosilicate" by Schwieger *et al.* (1985). This terminology is somewhat misleading as it may imply an association with structural phenomena. Earlier, the term "ilerite" had been introduced by Wolf and Schwieger (1979) in honor of R. K. Iler who was, in 1964, the first to synthesize and study this particular sodium polysilicate. However, mineral terminology of this kind is generally restricted to compounds occurring in nature. Although we are aware of the inadequacy of the term "octosilicate," we use it in the present paper for lack of a more appropriate name.

Based on chemical composition and NMR results,

Table 1. Chemical composition of hydrated Na- and H-octosilicate.

Sample	Unit	Na ₂ O ^a	SiO ₂ ^a	Al ₂ O ₃ ^a	H ₂ O		T ^d	Na ^{Q3e}	Struct. H ₂ O
					Total ^b	Mol. water ^c			
Na-octosilicate	mmol/g	1.50	11.20	0.10	12.65	11.27	11.3	2.90	1.38
Na-octosilicate	atoms (molecules) per 8 T atoms	—	—	—	—	—	—	2.05	0.98
H-octosilicate	mmol/g	0.05	15.14	0.08	4.89	~0.83	15.24	0.02	~4.06
H-octosilicate	atoms (molecules) per 8 T atoms	—	—	—	—	—	—	0.01	~2.13

^a Obtained by AAS.

^b Obtained by thermogravimetry.

^c Obtained by Karl Fischer titration.

^d Si and tetrahedrally coordinated Al estimated from ²⁷Al MAS NMR (about half of the total Al content).

^e Na associated with Q3 sites (sodium content minus an amount equivalent to tetrahedrally coordinated Al).

a hypothetical structure model has been suggested (Schwieger *et al.*, 1985) in which two makatite sheets (as reported by Annehed *et al.*, 1982) are linked via 4 Si-O-Si bridges per formula unit. This results in 8-membered rings parallel to the *a-b* plane. Another hypothetical structure model for octosilicate, based on the structure of the zeolite, dachiardite, was proposed by Garcés *et al.* (1988). Neither of these hypothetical structures has been proven by exact structure analysis.

In the present paper, both sodium octosilicate and the crystalline silicic acid (H-octosilicate) obtained from it by ion exchange with mineral acids were characterized by different physico-chemical methods, and their X-ray patterns indexed on monoclinic cells. Structural changes occurring upon heat treatment were studied.

The observed crystallochemical phenomena and unit cell parameters must be consistent with tentative structure models, and hence, should be criteria for the correctness of such models.

MATERIALS AND METHODS

Sodium octosilicate was prepared by hydrothermal crystallization in the system Na₂O-SiO₂-H₂O. The molar ratio of the reactants was 4 SiO₂: 1 Na₂O: 30 H₂O. The crystallization mixture was prepared by adding 100 g silica sol (30 wt % SiO₂, obtained from VEB Chemiewerk Köstritz), while stirring, to 230 g aqueous NaOH solution (17.3 wt % NaOH). Crystallization carried out in closed polyethylene vessels at 373 K was complete after 28 days. The resulting crystalline product was separated from the mother liquor, washed, and dried at room temperature.

The decationization of sodium octosilicate was performed by ion exchange with 0.1 molar hydrochloric acid (100 ml/g) at room temperature. The resulting hydrogen form was washed until the effluent was acid-free, and then dried at room temperature.

Thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) were carried out simultaneously in a stream of dry nitrogen at a heating rate of 10 K min⁻¹ using a Derivatograph (MOM, Budapest). The weight loss was related to 1 g substance calcined at 1273 K.

The X-ray diffractograms were monitored using a Philips PW1130 diffractometer with graphite monochromator, CuK α radiation, and Si powder as an internal standard. The infrared (IR) spectra were obtained with a Nicolet FT-IR spectrometer 4100. The KBr pellet technique was used.

²⁹Si and ²⁷Al MAS-NMR spectra were run on a Varian XL-400 spectrometer equipped with a Doty cross-polarization MAS probe. The spinning frequency was 4.1 kHz and the number of scans was 512. The observed frequencies, external references and pulse intervals were as follows:

²⁹Si—79.46 MHz, TMS, 2 s

²⁷Al—104.21 MHz, Al₂(SO₄)₃·18H₂O, 0.2 s.

RESULTS AND DISCUSSION

Composition and thermal behavior of sodium octosilicate

The chemical composition of the sodium octosilicate used in this study is given in Table 1. The material contained a small amount of alumina present as a contaminant in the silica sol used as a silica source.

The total weight loss of sodium octosilicate at 1270 K substantially exceeded the amount of molecular water determined by Karl-Fischer titration (Table 1). The difference, corresponding approximately to a molar T/OH ratio of 4 and a Na/OH ratio of 1, must be due to water formed by elimination of structural hydroxyl groups.

Thermal analysis of sodium octosilicate (Figure 1) revealed two processes. Though both reactions overlap considerably, they can be readily distinguished by DTA and DTG. They are both endothermic, and the heat required for the second process is substantially greater than for the first. Neither of the two processes can be ascribed to the elimination of structural hydroxyl groups exclusively because the amount of water evolved in each step considerably exceeded the weight loss to be expected for dehydroxylation. Since the second step involved approximately 5 H₂O per 8 T atoms, or per two Na ions, it is obviously due to the removal of water

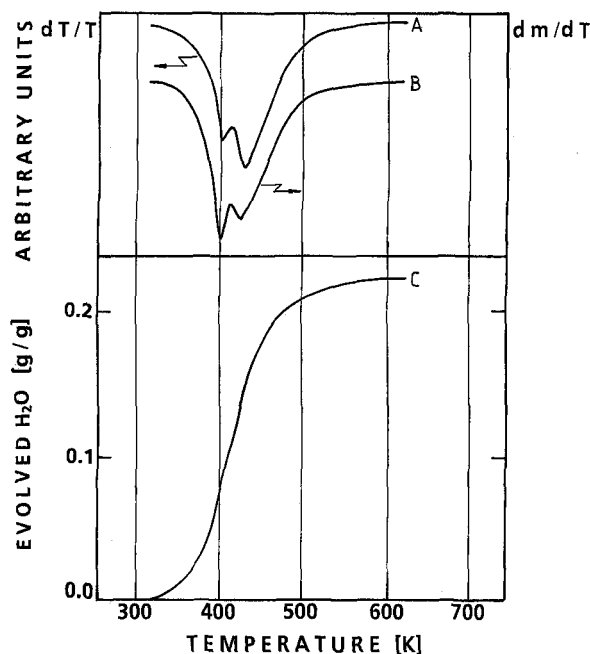


Figure 1. Differential thermogravimetric curve of sodium octosilicate, and evolution of water vs temperature. Heating rate: 10 K min⁻¹.

bound in the coordination sphere of the sodium cations (2 H₂O per Na⁺), and to the simultaneous elimination of structural hydroxyl groups (1 OH per 4 T atoms). Hence, the first process must be the desorption of physically adsorbed water.

This interpretation of the thermoanalytical results is in line with the X-ray crystallinity of sodium octosilicate heated in the thermoanalyzer up to particular temperatures. The crystallinity was not affected until the end of the first weight-loss step (up to about 400 K), but it gradually decreased during the second weight loss.

The ²⁷Al MAS-NMR spectrum of the prepared sodium octosilicate (Figure 2) consists of 3 central signals at 8.6, 29.5 and 54.4 ppm (external reference: [Al(H₂O)₆]³⁺). All the other signals can be assigned as spinning side bands relative to one of the 3 centerbands. By analogy to results obtained with zeolites (Gilson *et al.*, 1987), the signals at 8.6 and 29.5 ppm may be associated with extra-framework aluminum species, whereas the line at 54.4 ppm is indicative of aluminum located in framework T sites. It can be roughly estimated from the signal intensity ratios that about half of the aluminum occupies framework sites.

The ²⁹Si MAS NMR spectrum of the prepared sodium octosilicate shows two lines of equal intensity at -100.5 and -111.7 ppm from external TMS (Figure 3). According to the assignment of Heidemann *et al.* (1987) these signals are indicative of Si{3Si,O⁻} and Si{4Si}, respectively. Thus, ²⁹Si MAS-NMR spectroscopy

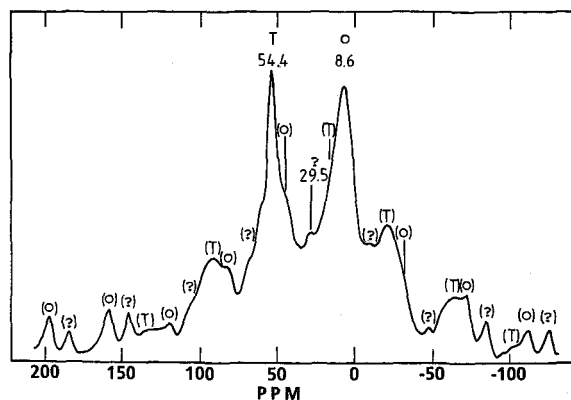
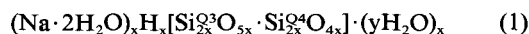


Figure 2. ²⁷Al MAS-NMR spectrum of sodium octosilicate (reference: [Al(H₂O)₆]³⁺). Center bands of tetrahedrally and octahedrally coordinated Al species are marked by T and O, respectively, and an unassigned band by a question mark. Spinning side bands are marked by the respective designation enclosed in parentheses.

copy provides strong evidence that in the octosilicate structure the Q4/Q3 ratio is equal to unity. A less intense signal appears as a shoulder at about -99.5 ppm. It is tentatively assigned to Si{3Si,Al} because the amount of tetrahedrally-coordinated framework aluminum, estimated from the intensity of this signal, corresponds to the value obtained from wet-chemical analysis and ²⁷Al MAS-NMR spectroscopy. No signal indicative of Si{2Si,Al,O⁻} appears in the spectrum, which points to the substitution of framework Si by Al exclusively in Q4 sites. It is to be expected that negative charges associated with framework aluminum are preferentially compensated by sodium ions, since such sites should be more acidic than Si{3Si,OH} sites.

Considering the chemical composition as well as thermal and MAS-NMR spectroscopic results, and neglecting the relative low aluminum content, the idealized unit-cell composition of sodium octosilicate can be written as



where x is an integer ≥ 1 , and y amounts to about 2 in the fully hydrated state. The subscripts Q3 and Q4 indicate silicon in Si{3Si,O⁻} and Si{4Si} sites, respectively. The adsorbed water ($x \cdot y$ molecules) can be removed reversibly. In contrast, elimination of water from the coordination sphere of the sodium ions results in structural collapse and simultaneous dehydroxylation. The question is whether the structural breakdown is caused primarily by elimination of water from the coordination sphere of the sodium cations or by dehydroxylation.

Phase transitions and loss of crystallinity occur at relatively low temperatures in the zeolites, stilbite and heulandite. This is shown to be dependent on both the nature of the structural cations and, after elimination

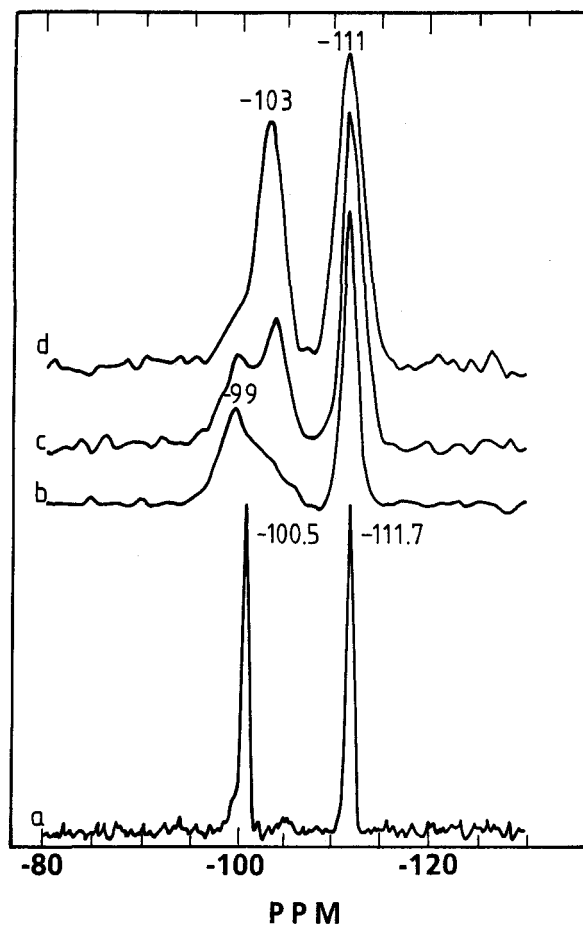


Figure 3. ^{29}Si MAS-NMR spectra of the as-synthesized sodium octosilicate (reference: TMS) dried at 300 K (a), and hydrogen octosilicate dried at 300 K (b) and heated to 350 K (c) and 373 K (d).

of the physically adsorbed water, the dehydration degree (Beyer *et al.*, 1980). The thermal stability of these zeolitic structures is, hence, obviously related to the coordination state of the structural cations. This conclusion is supported by the finding that decationized stilbite and heulandite, i.e., the hydrogen forms of these zeolites, are much more thermostable than the respective cation forms. They gradually undergo a structural collapse, with progressing dehydroxylation (Jacobs *et al.*, 1979). By analogy to the thermal behavior of these zeolites, we suggest that the change in the coordination state of the sodium cations during the dehydration causes the structural collapse that is associated with dehydroxylation.

The IR spectrum of sodium octosilicate undergoes significant change when the material is heat-treated at 373 K (compare spectra a, b; Figures 4, 5). The same characteristic changes are also observed when Na-octosilicate is first converted to the hydrogen form by treatment with acids and then reexchanged by titration

Table 2. X-ray powder data for hydrated sodium octosilicate.

hkl	d (calc.), Å	d (obs.), Å	$\Delta d/d$, %	Rel. int.
001	11.10	11.10	0.0	320
100	7.25	7.25	0.0	8
101	5.66	5.66	0.0	16
002	5.55	5.55	0.0	22
012	5.09	5.09	0.0	7
102	4.80	4.80	0.0	105
102	4.10	4.10	0.0	100
130	3.664	3.664	0.00	14
20 $\bar{1}$	3.622	3.623	0.03	30
10 $\bar{3}$	3.535	3.538	0.08	23
210	3.486	3.487	0.03	51
032	3.373	3.375	0.09	8
20 $\bar{2}$	3.288	3.287	0.03	49
023	3.200	3.206	0.19	26
103	3.099	3.100	0.03	26
041	3.062	3.062	0.00	100
140	2.916	2.916	0.00	19
004	2.776	2.776	0.00	45
10 $\bar{4}$	2.744	2.745	0.04	14
23 $\bar{2}$	2.600	2.600	0.00	9
104	2.463	2.463	0.00	5
14 $\bar{3}$	2.366	2.367	0.04	16

with NaOH solution, even if the temperature during the successive preparation steps never exceeded 300 K. In the lattice vibration region, the poorly-resolved band around 950 cm^{-1} is shifted to smaller wave numbers forming a new, broad band at $850\text{--}920\text{ cm}^{-1}$ (Figures 4a, and 4b).

Characteristic changes of the stretching vibrations of structural hydroxyl groups associated with Q3 sites are illustrated in Figure 5. In the IR spectrum of the as-synthesized sodium octosilicate an intense hydroxyl stretching band appears at 3620 cm^{-1} . Heat treatment results in the formation of new hydroxyl types vibrating at 3585 and 3640 cm^{-1} . These form at the expense of the OH-groups associated with the band at 3620 cm^{-1} . Interaction between neighboring hydroxyl groups via hydrogen bridges may contribute to the broad band centered at 3440 cm^{-1} , normally indicative of OH in water.

These changes in the stretching of hydroxyl groups bound to Q3 Si atoms also point to structural changes in the surface layers of tetrahedra in the silica sheets.

In the X-ray pattern these changes are reflected only by a more-or-less pronounced increase or decrease in the intensity of particular reflections, and/or peak broadening.

IR and NMR spectra of sodium octosilicate given in the literature differ from the respective spectra of the as-synthesized material in Figures 3 and 4. Garcés *et al.* (1988) presented an IR spectrum identical with that of the re-exchanged sample (spectrum b, Figure 4). The ^{29}Si MAS-NMR spectra published by Schwiager *et al.* (1985) and Garcés *et al.* (1988) are in accordance with our findings because the Q3 and Q4 signals are

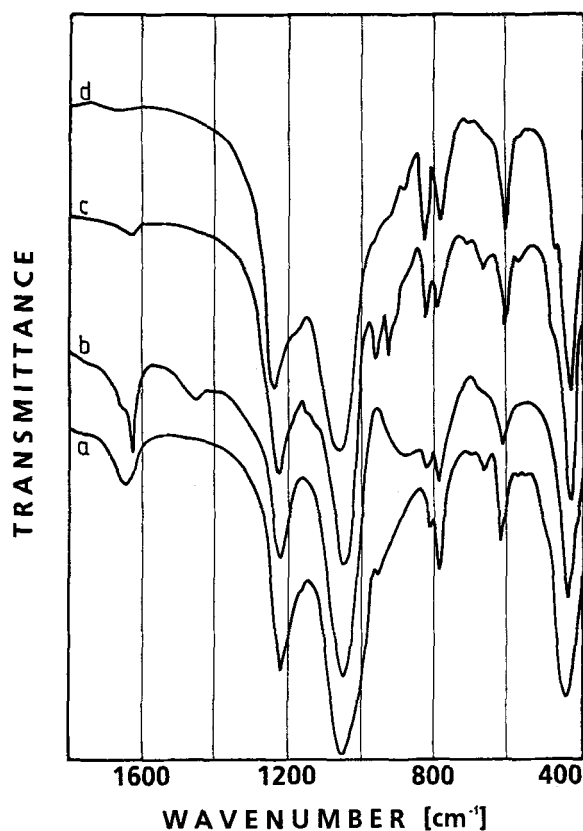


Figure 4. IR transmission spectra in the lattice vibration region of sodium octosilicate (a, b) and H-octosilicate (c, d), dried at 300 K (a, c) and heated to 373 K (b, d). Spectrum b is identical with the spectrum of the reexchanged Na-octosilicate not treated at higher temperatures.

of equal intensity. However, in their spectra the high-field signal is about twice as broad and only half as high as the low-field signal. In contrast, the respective spectrum of our material shows two extremely sharp lines of equal line width (50 Hz) and height. This indicates a higher degree of structural order, at least in the direct surroundings of the $\text{Si}\{3\text{Si},\text{O}^-\}$ sites. Thus, in these earlier studies of sodium octosilicate, structural changes of the same type as outlined above may have occurred already during one of the preparation steps.

Unit-cell parameters of sodium octosilicate

The X-ray diffraction data of the as-synthesized sodium octosilicate is given in Table 2. The data could

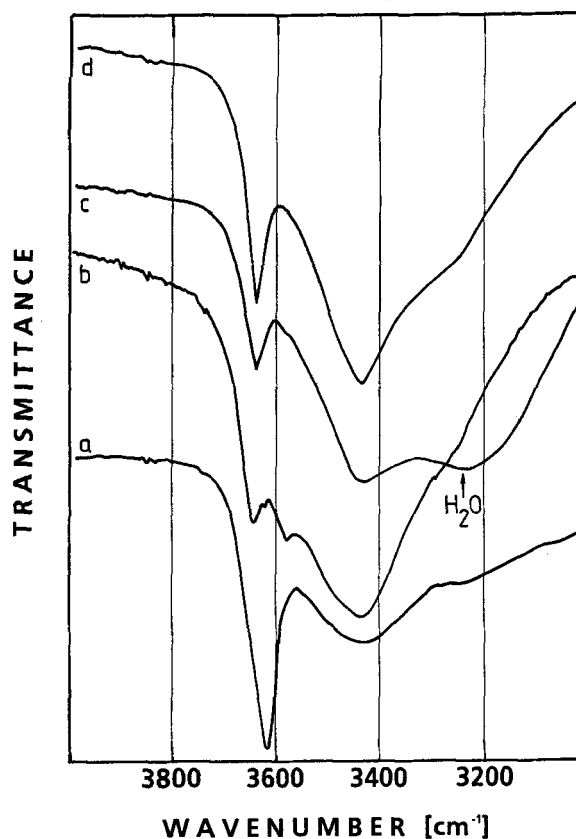


Figure 5. IR transmission spectra in the hydroxyl stretching region of sodium octosilicate (a, b) and H-octosilicate (c, d), dried at 300 K (a, c) and heated to 373 K (b, d).

be indexed in the monoclinic system with the lattice parameters $a = 7.345 \text{ \AA}$, $b = 12.74 \text{ \AA}$, $c = 11.25 \text{ \AA}$ and $\beta = 99.3^\circ$. A set of 001 reflections, generally appearing in the diffractograms of layer silicates, may be due to a sheet structure with the basal spacing of 11.10 \AA . A sheet structure is supported by the increase in the basal spacing upon cation exchange with organic cations (Table 3).

The length of the monoclinic cell in the a direction is equal to the respective lattice parameter of the layer silicate, magadiite that also shows monoclinic symmetry (Brindley, 1969). Moreover, the basal spacing and the monoclinic angle are related in both structures in such a way that the displacement of the basal faces of the unit cell, compared with an orthorhombic arrange-

Table 3. Basal spacings of octosilicate after incorporation of organic cations.

Exchanged cation	Spacing, \AA	Exchange conditions
Cetylpyridinium	34.7	Ion exchange of Na-octosilicate with the respective chlorides (0.026 molar).
Cetyltriethylammonium	27.6	Weight ratio of solution/octosilicate: 100
n-Hexylammonium	27.2	Treatment of H-octosilicate with equivalent amounts of the respective hydrox-
n-Tetrapropylammonium	19.8	ides in aqueous solution

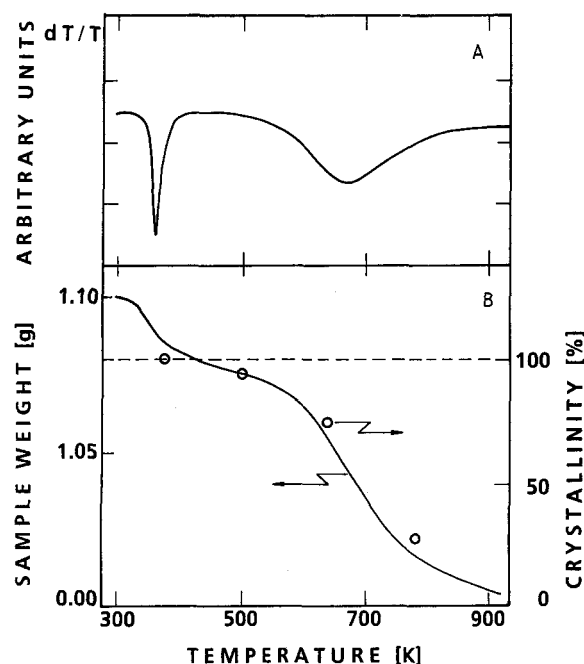


Figure 6. A) DTA curve of hydrogen octosilicate. B) Weight loss (full line) and degree of X-ray crystallinity (empty circles) of H-octosilicate vs temperature. Heating rate: 10 K min⁻¹.

ment, corresponds exactly to one quarter of the lattice constant, a . This may reflect a structural relationship between octosilicate and magadiite, as already proposed by Schwieger *et al.* (1985). However, their structural model is not consistent with the unit-cell parameters of octosilicate determined in the present work. In any case, the findings suggest an orthorhombic arrangement in the single sheet, but an overall monoclinic symmetry due to dislocation of the sheets in the a direction, corresponding to 25% of the a parameter.

Chemical composition of hydrogen octosilicate

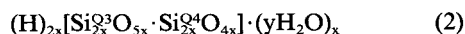
The analytical data presented in Table 1 show that a nearly sodium-free product is obtained from Na-octosilicate by acid treatment. Within the limits of the experimental error in the determination of molecular water by Karl-Fischer titration, the Si/OH ratio of the decationized octosilicate is 2, suggesting a simple replacement of sodium ions by protons.

The ²⁹Si MAS-NMR spectrum of H-octosilicate dried at 300 K consists of a relatively sharp line at -111 ppm (line width 127 Hz) and a set of overlapping signals, the most intense of which appears at -99 ppm, followed by at least one more line appearing as a shoulder at about -103 ppm (spectrum b, Figure 3). The signal at -111 ppm undoubtedly represents silicon in Q4 sites, whereas the set of high-field signals has to be assigned to Q3 silicon (Si{3Si,O⁻}), probably located in different crystallographic lattice positions. The areas

under the Q4 peak and the set of Q3 peaks are approximately equal.

The thermogravimetric curve of H-octosilicate shows two well-separated steps (Figure 6B). The first process, proceeding up to about 500 K, is due to the desorption of physically adsorbed water. The second one, starting at about 600 K, is ascribed to the dehydroxylation of the structure. The amount of water evolved during the second step corresponds to a molar SiO₂/H₂O ratio of exactly 4.

From the experimental results the following unit cell formula can be deduced for hydrogen octosilicate:



where x is a integer ≥ 1 , as in (1), and y amounts to 0.33 in the hydrated state.

Structural changes of octosilicate upon decationization

The X-ray pattern of H-octosilicate exhibits only a few reflections (Table 4). Moreover, compared with the pattern of the as-synthesized sodium octosilicate, most of the peaks are considerably broadened, and no common reflections appear in the diffractograms of the two forms. It is, therefore, believed that because of the weak binding forces (hydrogen bridges) between the sheets, hydrogen octosilicate is poorly ordered in the c crystallographic direction. The relatively sharp peaks at $d = 7.38$ and 3.69 Å obviously represent basal reflections.

Back-titration of hydrogen octosilicate with NaOH solution results in a product that gives nearly the same X-ray pattern as the parent sodium form. Thus, decationization seems to result in complete exchange of Na ions by protons without substantial changes of the sheet framework topology. Also the lattice vibration IR spectrum of H-octosilicate (Figure 4, spectrum c) points to a highly-ordered atom arrangement in the sheets since it consists of a relatively large number of well-resolved and sharp bands. It is obvious that imperfect periodicity along the c axis has serious consequences for the scattering of X-rays, but hardly affects the lattice vibrations in sheets with regular arrangements of atoms.

Thus, sheet topology is expected to be identical in sodium and hydrogen octosilicate. Nevertheless, some minor structural differences must exist, as revealed by ²⁹Si MAS-NMR and IR spectroscopy. Since decationization splits and broadens the sharp Q3 signal observed in the spectrum of sodium octosilicate at -100.5 ppm (Figure 3), replacement of sodium by protons must result in a decrease in crystal symmetry and degree of lattice ordering. The Q4 sites are also affected, as indicated by the increase of the line width of the respective signal from 50 to 127 Hz.

The small but significant shift of the hydroxyl stretching band at 3620 cm⁻¹ (spectrum a, Figure 5) to 3640 cm⁻¹ upon decationization (spectrum c, Figure

Table 4. X-ray powder data for hydrogen octosilicate.

hkl	H-octosilicate as-synthesized; dried at 300 K			H-octosilicate heated to:					
	d (calc.), Å	d (obs.), Å	Intensity	373 K		493 K		633 K	
				d (obs.), Å	Intensity	d (obs.), Å	Intensity	d (obs.), Å	Intensity
001	7.380	7.38	144	7.1	48	7.0	15	—	—
11 $\bar{1}$	5.977	5.92	15	—	—	—	—	—	—
110	5.698								
12 $\bar{1}$	4.639	4.62	83	4.6	18	4.6	14	4.6	7
120	4.505								
002	3.690	3.69	113					3.7	4
13 $\bar{1}$	3.597	3.58	63	3.6	59	3.6	31	3.6	6
012	3.544								
121	3.356	3.31	48	3.3	16	3.3	8	—	—
21 $\bar{2}$	3.271								
131	2.892	2.89	18	—	—	—	—	—	—
14 $\bar{1}$	2.882								
Reflections due to scattering related to the magnitude of the interatomic vectors of X-ray amorphous materials				6.63	86	6.62	87	6.62	69
				4.01	30	4.02	19	4.02	22
				3.44	126	3.44	117	3.44	100
				3.31	16	3.30	8	3.30	5

* Calculated with lattice parameters $a = 7.345$ Å, $b = 12.74$ Å, $c = 8.51$ Å, and $\beta = 119.8^\circ$.

5) does not necessarily indicate structural rearrangements. However, the considerable differences in the lattice vibration spectra, especially in the range from 900 to 1020 cm^{-1} (compare a and c, Figure 4), suggest structural differences between both forms of octosilicate. As already mentioned, these changes are reversible only to some extent because after reexchange of H-octosilicate with Na, spectrum b in Figure 4 is obtained. It is identical with the IR spectrum of Na-octosilicate heated to 373 K. These findings are in line with observations made by Iler (1964) who found striking differences between the titration curves monitored during decationization and subsequent reexchange of octosilicate.

Thermal behavior of hydrogen octosilicate

The dehydroxylation of H-octosilicate proceeds at higher temperatures than in the case of the sodium form (Figure 6B), and it is accompanied by a gradual loss in crystallinity. At about 360 K a small weight loss indicates desorption of some adsorbed water. This process obviously coincides with another reaction revealed by a relatively intense and rather sharp DTA peak at 360 K (Figure 6A). This endothermic effect cannot be attributed exclusively to a water desorption process proceeding over a much wider temperature interval. Moreover, the endothermic reaction is accompanied by structural changes reflected by ^{29}Si MAS-NMR and mid-infrared spectra (Figures 3, 4). Most of the 10 IR bands of H-octosilicate between 900 and 1000 cm^{-1} disappear, or are only nominally present, when the sample is heated above the critical temperature of about 360 K. On the other hand, the bands at 606 and 830 cm^{-1} gain in intensity. Heidemann *et al.*

(1987) published a spectrum of hydrogen octosilicate identical with spectrum d in Figure 4. Their sample was obviously heated to temperatures above 353 K prior to measurement of the spectrum. In the ^{29}Si MAS-NMR spectrum, a new signal developed at -103 ppm at the expense of the -99 ppm line when the sample is heated up to 353 K. In conjunction with other data, this indicates definitive structural changes in the two-dimensional crystal sheets. It seems that only the Q3 sites, i.e., the surface tetrahedra layers on both sides of a sheet, are involved.

These structural changes are also reflected in the X-ray pattern of H-octosilicate. The intensities of the peaks indicative of this sheet structure decrease drastically at relatively low temperatures (Table 4). On the other hand, reexchange with sodium ions restored the X-ray pattern of the parent sodium octosilicate. Thus, in thermally-treated H-octosilicate the periodicity in the c crystallographic direction is not maintained over distances sufficiently large to give scattering effects typical of matter highly ordered in all three dimensions. However, the "two-dimensional crystallinity" of the sheets must be retained.

Upon heat treatment of H-octosilicate at 360 K several new reflections appear (Table 4), the intensities of which gradually decrease with progressing dehydroxylation (Figure 6). The four most intense reflections are listed in Table 4. These new peaks obviously reflect scattering in a non-directional sense, as the scattering is related to the magnitude of the interatomic vectors, but not to their direction. Calculation of the radial distribution function (e.g., Klug and Alexander, 1974) would probably provide information on the structure of the crystal sheets after heat treatment.

The intensities of the Na-octosilicate reflections, restored by reexchange with sodium cations, also depend on the degree of dehydroxylation obtained during the preceding heat treatment of the hydrogen form. Thus, dehydroxylation of H-octosilicate is accompanied by a gradual collapse of sheet crystal structure.

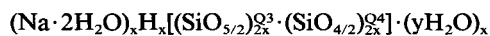
Unit cell parameters of hydrogen octosilicate

The X-ray pattern of hydrogen octosilicate consists of only a few rather broad reflections that are unsuitable for precise indexing. Nevertheless, information may be obtained in an indirect way. The aforementioned findings indicate that the replacement of the Na ions by protons affects the sheet structure only to a minor degree. Only a decrease in the periodicity along the *c* axis takes place, i.e., perpendicular to the sheets. Thus, it can be assumed that the lattice constants *a* and *b* are identical with the respective parameters of the sodium form (7.345 and 12.74 Å) and, further, that the atomic arrangement in the sheet is orthorhombic.

However, the overall symmetry must be lower than orthorhombic. The *d*-values, obtained with the *a* and *b* parameter of the sodium form, and the basal spacing of the hydrogen form (7.38 Å) as lattice constant *c*, do not give satisfactory agreement. An overall monoclinic symmetry may exist due to dislocation of the orthorhombic unit cell of the "two-dimensional" sheets. Supposing distinct dislocations along the crystallographic *a* and *b* axes, the *c* parameter and the monoclinic angle can be calculated from the experimentally-obtained basal spacing. The comparison of the calculated *d*-values with experimentally-observed values shows that a satisfactory agreement is only obtained when an assumed dislocation along the *a* axis amounts to half of the unit cell *a* parameter. For this case, which probably correctly reflects the unit cell of hydrogen octosilicate, the lattice parameters are: *a* = 7.345 Å, *b* = 12.74 Å, *c* = 8.51 Å and $\beta = 119.8^\circ$.

CONCLUSIONS

Sodium octosilicate is a layer silicate. The ideal chemical composition of the unit cell is:



where *x* is an integer ≥ 1 , and *y* amounts to ~ 2 .

The physically-adsorbed water (*x*·*y* molecules per unit cell) can be removed reversibly. However, heat treatment at 373 K causes minor, but irreversible structural changes in the surface layers of the sheets consisting of Q3 Si tetrahedra. Elimination of water from the coordination sphere of the sodium cations occurs at temperatures above 400 K and results in a gradual structural collapse.

At least a small part of the Q4 silicon can be isomorphically substituted by aluminum during crystallization.

The crystal symmetry is monoclinic with *a* = 7.345 Å, *b* = 12.74 Å, *c* = 11.25 Å and $\beta = 99.3^\circ$.

Treatment with dilute acids leads to the replacement of the sodium cations by protons. The resulting crystalline silicic acid contains two structural hydroxyl groups per four silicon atoms. Compared to the sodium form, its structure is less ordered in the *c* crystallographic direction. However, the arrangement of the atoms in the *a* and *b* directions is not affected by decationization. At temperatures of about 360 K an endothermic process proceeds that is associated with a nearly complete loss in ordered orientation of the sheets in the *c* direction. Nevertheless, upon reexchange with sodium ions the periodicity in the *c* direction is restored. The "two-dimensional" crystal structure of H-octosilicate is gradually destroyed with a progressive dehydroxylation that starts at about 500 K.

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