A Puckered Layered Silicate, $KHSi_2O_5$: Hydrolysis Products and Alkylammonium Intercalated Derivatives

Z. Q. Deng, J. F. Lambert, and J. J. Fripiat*

Department of Chemistry and the Laboratory for Surface Studies, University of Wisconsin—Milwaukee, PO Box 413, Milwaukee, Wisconsin 53201

Received February 6, 1989

The layered silicate $KHSi_2O_5$, its hydrolysis product, and its alkylammonium intercalates are of interest as starting materials for the preparation of heterogeneous catalysts. However, some of these materials are difficult to characterize due to low long-range order. Their short-range ordering was investigated through solid-state proton and ^{29}Si NMR spectroscopy (including proton cross-polarization of ^{29}Si), in combination with IR spectroscopy, X-ray diffraction, weight loss, and surface area measurements. It is shown that stacking faults already exist in the parent $KHSi_2O_5$, together with very strong interlayer hydrogen bonding; on acid hydrolysis or alkylammonium intercalation, the structure undergoes considerable delamination, followed by reorientation of the layers and their partial condensation through the formation of siloxane bridges. Thus these reactions cannot be strictly considered as topotactic, contrary to what was previously believed.

Introduction

Among alkali-metal-layered silicates, $KHSi_2O_5$ has a well-characterized crystal structure because single crystals can be obtained. According to Le Bihan et al.[1] $KHSi_2O_5$ belongs to the space group *Pmnb* ($Z = 4$). The unit cell parameters are shown in Table I. Adjacent sheets are bonded by symmetrical hydrogen bonds (O···O distance = 2.489 Å) and interlayer K^+ in 4-fold coordination.

Upon acid hydrolysis, K^+ is easily removed, and a layered silicic acid with nominal composition $H_2Si_2O_5$ is reportedly[2] obtained. It is a rather well-crystallized powder with the cell parameters shown in Table I. Since acid hydrolysis results in a fragmentation of the initial crystals, it is by analogy with the starting material and indexation of powder patterns that these parameters were obtained. If hydrolysis yields one hydroxyl group per silicon, one wonders why the *b* parameter decreases (the axis *b* is normal to the layers). To avoid the strong repulsion between parallel Si–OH from adjacent silica sheets, translations along *a* and *c* could occur. However, the shortening of *a* and lengthening of *c* are most probably due to relatively slight changes in the Si–O–Si angle. Therefore, since *a* and *c* do not change dramatically, the strong OH dipoles' repulsive interaction along the axis perpendicular to the sheets should result in increasing *b*. There is obviously a problem here, and in addition, as shown further, weight losses on calcination suggest a smaller OH content than the theoretical value calculated for the formula $H_2Si_2O_5$. ^{29}Si high-resolution NMR spectroscopy should shed light on the structure of the acid hydrolysis product by allowing comparison between the silicon environments in both $KHSi_2O_5$ and $H_2Si_2O_5$. This is the first aim of this contribution. ^{29}Si NMR studies have been reported for magadiite,[3-5] hydrolyzed magadiite,[3,5] and hydrolyzed $Na_2Si_2O_5$[6] but not for $KHSi_2O_5$ and "$H_2Si_2O_5$ III" (the form derived from the potassium salt).

The second aspect developed here deals with the mechanism of the intercalation of alkylammonium cations within $KHSi_2O_5$. Kalt et al.[7] have suggested that the reaction may be written as

$$KHSi_2O_5 + 2zRNH_3^+ + (1-2z)H^+ + yH_2O \rightarrow (RNH_3^+)_{2z}H_{2-2z}Si_2O_5{\cdot}yH_2O + K^+ \quad (1)$$

in which all the potassium is removed, $2z$ is on average 0.3, and the compensating protons are introduced into the structure as H_3O^+. The *b* parameter increases with the alkylamine chain length. In the case of $C_2H_5NH_3^+$ the distance separating the planes has increased by about 2.9 Å with respect to that in $H_2Si_2O_5$. With $C_7H_{15}NH_3^+$ the increase is about 21 Å. Up to C_4 the alkyl chain is presumably oriented parallel to the *ac* plane, while longer alkyl chains are standing in the interlayer space and tilted with respect to the *b* axis. Increasing *b* should of course affect the OH dipole–dipole interaction between adjacent planes, and since hydrolysis and intercalation occur simultaneously, the silicon environment in the intercalated products should be different from that observed after acid hydrolysis.

Table I. Unit-Cell Parameters of $KHSi_2O_5$ and $H_2Si_2O_5$[1]

param, Å	$KHSi_2O_5$	$H_2Si_2O_5$
a	8.15	7.47
b	12.54	11.94
c	4.70	4.91

The high-resolution solid-state ^{29}Si NMR study is supplemented by data obtained from chemical analysis, IR spectroscopy, and surface area measurements.

Finally, mechanisms for hydrolysis and for intercalation are proposed.

Experimental Section

$KHSi_2O_5$ is obtained by hydrothermal synthesis at 300 °C as described by Wey and Kalt.[8] Its typical XRD spectrum shown in Figure 1a has been compared and found identical with that of a $KHSi_2O_5$ sample kindly provided by Professor Kalt.

$H_2Si_2O_5$ has been obtained from $KHSi_2O_5$ either by repeated treatments in a slurry of 1.0 g of $KHSi_2O_5$ stirred at room temperature (RT) in 20 mL of a 1 N HCl solution (I) or by one exchange at RT in a suspension of 1.0 g of $KHSi_2O_5$ (stirred for 2 h) in 100 mL of a 0.2 N HCl solution (II).

For the alkylammonium exchange, 1.0 g of $KHSi_2O_5$ was contacted for 24 hours with 40 mL of a 1 M ethylammonium or

---

* To whom correspondence should be addressed at the Department of Chemistry.

(1) Le Bihan, M. T.; Kalt, A.; Wey, R. *Bull. Soc. Fr. Mineral. Cristallogr.* **1971**, *94*, 15.

(2) Wey, R.; Kalt, A. *C. R. Acad. Sci. Paris, Ser. D* **1967**, *265*, 1437.

(3) Schwieger, W.; Heidemann, D.; Bergk, K.-H. *Rev. Chim. Mineral.* **1985**, *22*, 634.

(4) Pinnavaia, T.; Johnson, I. D.; Lipsicas, M. *J. Solid State Chem.* **1986**, *63*, 118.

(5) Rojo, J. M.; Ruiz-Hitzky, E.; Sanz, J.; Serratosa, J. M. *Rev. Chim. Mineral.* **1983**, *20*, 807.

(6) Heidemann, D.; Grimmer, A.-R.; Huebert, C.; Starke, P.; Magi, M. *Z. Anorg. Allg. Chem.* **1985**, *528*, 22.

(7) Kalt, A.; Perati, B.; Wey, R. *International Clay Conference 1978*; Mortland, M. M., Farmer, V., Eds.; Elsevier: Amsterdam, 1979; p 501.

(8) Wey, R.; Kalt, A. *C. R. Acad. Sci. Paris, Ser. D* **1967**, *265*, 1.

0897-4756/89/2801-0375$01.50/0

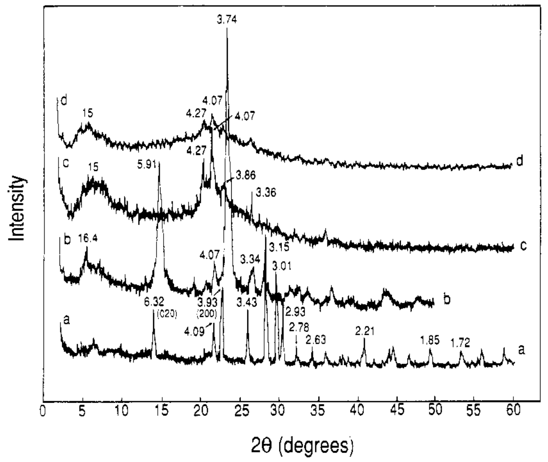

Figure 1. (a) XRD spectrum of nonoriented $KHSi_2O_5$. (b) XRD spectrum of RT-dried HP, oriented. (c) XRD spectrum of HP dried at 150 °C, oriented. (d) XRD spectrum of HP, calcined for 2 h at 500 °C, oriented. Cu Kα radiation, Ni filter.

heptylammonium chloride solution at RT. The exchange process was repeated three times to eliminate the potassium and to achieve complete exchange. The intercalation product was washed repeatedly to remove excess alkylammonium chloride.

Specific surface areas were measured by application of the BET technique to N_2 adsorption isotherms measured volumetrically at 77 K.

Weight losses upon calcination at different temperatures were determined gravimetrically.

The IR spectra were obtained on a Nicolet MX-1 FT-IR spectrometer, using KBr pellets.

XRD patterns were recorded (Cu Kα radiation) on a home-computerized Phillips diffractometer, using either oriented film or powder samples. The oriented films were prepared by depositing the wet solid (after washing) on glass slides.

High-resolution magic-angle-spinning (MAS) NMR spectra were recorded on a GN 500 spectrometer, in a magnetic field of 11.7 T. In such a field, the ^{29}Si and ^{1}H resonance frequencies are 99.3 and 500 MHz, respectively. The magic-angle-spinning frequency was typically between 7 and 9 kHz. For ^{29}Si, pulse lengths were between 3 and 7 μs, and the time between pulses varied between 1 and 4 s. The number of acquisitions was between 10^3 and 2×10^4. The acquisition time was 25 ms, and the radio frequency power was 60 W. For ^{1}H the number of acquisitions was between 200 and 2000 while the time between pulses was 1 s. In cross-polarization experiments the contact time was typically 3 ms.

Results

There is little noticeable difference by any of the characterization techniques employed between preparations with diluted or more concentrated acids in acid hydrolysis of $KHSi_2O_5$. It was hoped that a short and mild hydrolysis treatment would reduce the delamination of the lattice (see the surface area measurements), but the application of either treatment I or II has no effect on the final products. The XRD spectrum of the RT-dried nominal $H_2Si_2O_5$ is shown in Figure 1b, where it can be compared with that of $KHSi_2O_5$. It agrees with the XRD pattern observed by Wey and Kalt[2] except for the broad and weak reflection near 16 Å. The XRD spectrum of the hydrolysis product heated at 150 °C is shown in Figure 1c, and the XRD spectrum of the product calcined for 2 h at 500 °C is shown in Figure 1d. A broad and weak reflection is observed at about 15 Å. It is accompanied by three sharper but weaker reflections at 4.27, 4.07, and 3.84 Å.

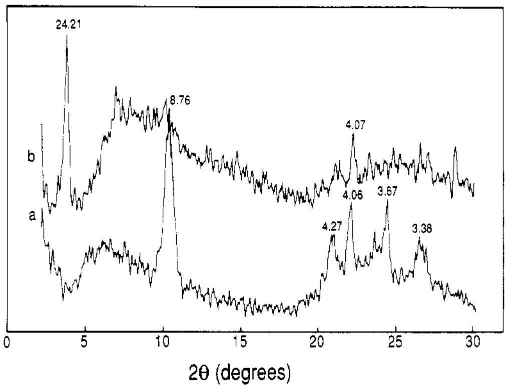

Figure 2. XRD spectra of oriented (a) ethylammonium and (b) heptylammonium intercalates of $KHSi_2O_5$ after complete exchange of the potassium.

Figure 2a,b shows the XRD patterns obtained for ethylammonium and heptylammonium intercalates. The sharp reflections at 8.76 and 24.2 Å, respectively, agree with those reported by Kalt et al.[7] However, for both intercalates, a broad reflection is observed in the 5–10° 2θ range, while the weaker reflections in the 20–30° 2θ range are distinct from those of spectra in Figure 1, especially in the case of the ethylammonium intercalate (Figure 2a).

Chemical Composition of "$H_2Si_2O_5$". The theoretical weight losses upon calcination would be 5.1% for the formula $KHSi_2O_5$ and 13% for $H_2Si_2O_5$. Experimentally, we observed that air-dried $KHSi_2O_5$ loses 4.8% (w/w) of constitutional water upon calcination between RT and 500 °C. Further calcination at 800 °C does not result in further weight loss. In contrast, the agreement is not good for the hydrolysis product. Weight loss figures are consistently lower than the theoretical value of 13%. The air-dried hydrolysis products that we have examined have a weight loss of 11.5 ± 0.1% between RT and 500 °C; between 100 and 500 °C, it is 9.9 ± 0.6%. Calcination at 800 °C of the product calcined at 500 °C does not yield any further weight loss. These gravimetric results may be compared with the thermogravimetric analysis (TGA) trace in ref 9 showing an ill-defined plateau at 125 °C followed by a rapid weight loss from about 200 to 400 °C. The difference between the weight losses at 500 and 125 °C in the TGA experiment in ref 9 was 8.6% (w/w RT-dried material).

As shown later, the surface areas measured for the hydrolysis products are 22 ± 2 m^2/g. On such a hydrophilic surface two monolayers of physically adsorbed water would produce a weight loss of $\sim$1%, whereas the loss measured in this work between RT and 100 °C is 1.6 ± 0.6%. Thus attributing the weight loss below 100 °C to physisorbed water elimination, we may retain a weight loss of $\sim$9.9% due to calcination proper.

The chemical composition of the RT-dried hydrolysis product should then be $H_{2(1-x)}Si_2O_{5-x}\cdot yH_2O$, the structural (and intercalated) water contents being appreciably lower than those of $H_2Si_2O_5$. Thus from now on, the hydrolysis product will be called HP (HP contains less than 1% of the original K content).

Surface Area Measurements. The average results are shown in Table II. Clearly the acid hydrolysis of $KHSi_2O_5$ or the intercalation of alkylammonium within the lattice results in an extensive delamination since the initial surface area is multiplied by about 100.

Spectroscopic Results. IR Data. The IR-active vibrational bands recorded in KBr pellets are shown in Figure 3. In the region between 800 and 1300 cm^{-1}, $KHSi_2O_5$ (spectrum a) and RT dried HP (spectrum b) are markedly different. A triplet of bands can be observed between 894 and 957 cm^{-1}, as already noticed by Wey and

---

(9) Guth, J. L.; Hubert, Y.; Perati, B.; Wey, R. *C R. Acad. Sci. Paris, Ser. D* **1978**, *286*, 5.

Table II. Surface Area Measurements for $KHSi_2O_5$ and Its Hydrolysis Product

sample	T_{th},[b] °C	T_{pret},[a] °C	S, m²/g
$KHSi_2O_5$	RT	100	<0.2
	500	100	3.7
HP	RT	100	24 ± 2
	500	100	42
C_2HP	RT	70	29.9[c]
C_7HP	RT	70	27[c]

[a] T_{pret} refers to the outgassing temperature prior to the surface area measurement. [b] T_{th} refers to the temperature of the thermal treatment undergone by the sample prior to the measurement. [c] In spite of the low T_{pret}, the intercalated amine is removed, and in fact the product is probably comparable to HP.

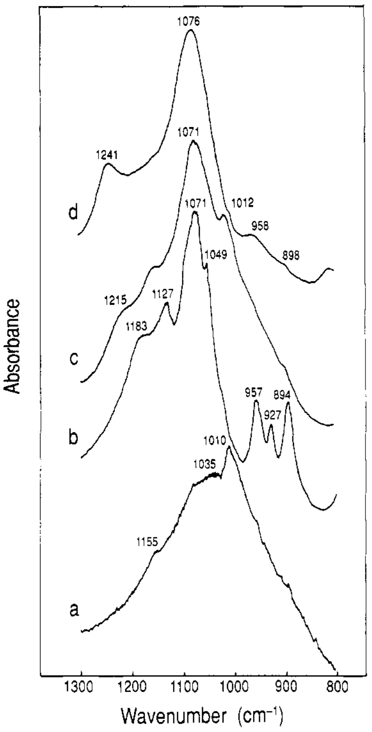

Figure 3. Infrared spectra between 800 and 1300 cm⁻¹ of (a) $KHSi_2O_5$, (b) RT-dried HP, (c) ethylammonium-exchanged $KHSi_2O_5$, and (d) heptylammonium-exchanged $KHSi_2O_5$.

Kalt.[2] Also the main asymmetric Si–O stretching band shifts from 1010 to 1071 cm⁻¹, and weaker bands appear at 1127 and ~1180 cm⁻¹. Note that in quartz, in which each SiO_4 unit shares corners with four adjacent SiO_4 units, namely, a Q^4 environment according to the ^{29}Si NMR nomenclature,[10] the Si–O asymmetric stretches are observed at 1097, 1150, and 1176 cm⁻¹.[11] From this comparison, we suggest that the shift of the Si–O stretch is not due primarily to some variation in the Si–O–Si angles but to a deeper reorganization of the lattice. The triplet at 957, 927, and 894 cm⁻¹ is most probably attributable to Si–O–H bending since the intensity of these bands is reduced in the alkylammonium intercalates (spectra c and d).

^{29}Si and ^1H High-Resolution MAS NMR Spectra. $KHSi_2O_5$. As shown in Figure 4a, the ^{29}Si one-pulse spectrum exhibits a single resonance line at −89.3 ppm, the width at half-height ($\nu_{1/2}$) being 2.7 ppm.

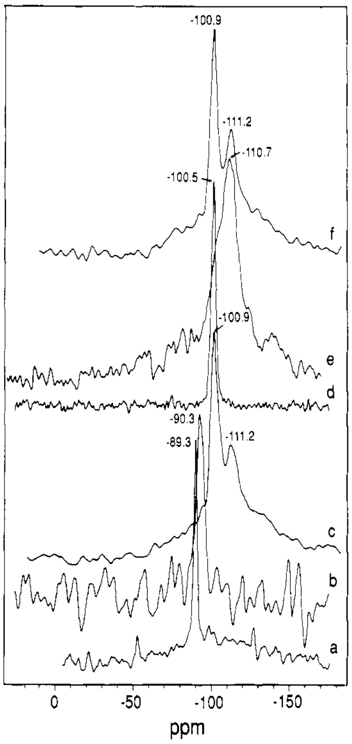

Figure 4. ^{29}Si NMR spectra of puckered layered silicates: (a) MAS spectrum of $KHSi_2O_5$; (b) CP MAS spectrum of $KHSi_2O_5$; (c) MAS spectrum of HP dried at RT; (d) CP MAS spectrum of HP; (e) MAS spectrum of dehydroxylated HP; (f) MAS spectrum of the ethylammonium intercalate of $KHSi_2O_5$ (C_2HP).

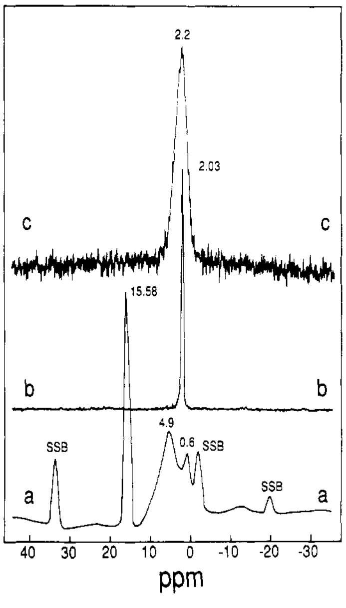

Figure 5. The 500-MHz ^1H NMR (a) MAS spectrum of $KHSi_2O_5$, (b) MAS spectrum of HP, and (c) static spectrum of HP.

The proton resonance spectrum in Figure 5a shows a sharp line with a huge chemical shift at +15.6 (±0.8) ppm with respect to TMS and another, broader band at about +4.9 ppm with a shoulder at about +0.6 ppm. Besides, at least 2 orders of spinning side bands (SSB) of the sharp peak are discernible.

Upon irradiating the proton at the frequency of the band at 15.6 (±0.8) ppm, the cross-polarization ^{29}Si spectrum shows a line (Figure 4b) at −90.3 ppm, with a reduced intensity as evidenced by the lower S/N ratio. After complete dehydroxylation of $KHSi_2O_5$ at 500 °C, the one-pulse ^{29}Si spectrum shows only a very broad band ($\nu_{1/2}$ = 31 ppm) shifted by about −116 ppm with respect to TMS (not shown).

---

(10) Lippmaa, E.; Magi, M.; Samoson, A.; Engelhardt, G.; Grimmer, A. R. *J. Am. Chem. Soc.* **1980**, *102*, 4889.

(11) Lippincott, E. R.; van Wallenburg, A.; Weir, C. H.; Bunting, E. N. *J. Res. Natl. Bur. Stand.* **1958**, *61*, 61.

Table III. Products Formed by Acid Hydrolysis of $KHSi_2O_5$

drying temp, °C	aging	R^a (from ^{29}Si NMR)	wt loss, % (air dried)	composition
20	fresh[b]	2.3	11.6	$H_{1.4}Si_2O_{4.7}0.18H_2O$
20	1 month	0.7	11.4	$H_{0.8}Si_2O_{4.41}0.45H_2O$
100	1 month	0.3	9.3	$H_{0.46}Si_2O_{4.23}0.45H_2O$
160	1 month	0.8	8.6[c]	$H_{0.9}Si_2O_{4.45}0.19H_2O$

[a] $R = Q^3/Q^4$ as defined in the text. [b] "Fresh" means aged for a few days at 20 °C. [c] Estimated from ref 9.

Hydrolysis Products. The MAS and static NMR ^1H spectra of HP are shown in Figure 5, parts b and c, respectively. One single line is observed at about 2 ppm.

The RT-dried hydrolysis products consistently gave one-pulse ^{29}Si spectra containing two lines, one at −101 ppm ($\nu_{1/2} = 5$ ppm) and one at −111 ppm ($\nu_{1/2} = 6$ ppm) as shown in Figure 4c. Upon cross polarization the ^{29}Si MAS NMR spectrum of HP contains only one line at −100.5 ppm, its width being about 3.5 ppm (Figure 4d). Thus the line at −111 ppm is completely suppressed under the CP MAS (and decoupling) conditions. This clearly shows that the line at about −101 ppm must be associated with silanol groups, while the second line at −111 ppm corresponds to a silicon without a proton neighbor. After heat treatment at 500 °C (Figure 4e), the one-pulse ^{29}Si spectrum of totally dehydroxylated HP has one single line at −111 ppm ($\nu_{1/2} \approx 14$ ppm). Thus the line at this frequency must be associated with siloxane bridges, i.e., a Q^4 environment.

The ratio R of the intensity of the Q^3 (3Si–SiOH) line at −101 ppm to the Q^4 line (4Si–Si) at −111 ppm depends upon the drying conditions and the aging time as shown in Table III. The composition of $H_{2(1-x)}Si_2O_{5-x}{\cdot}yH_2O$ (≡ HP) can be easily computed from R and the weight loss. Indeed $x = 1/(1 + R)$. Upon aging at RT and drying at $T \geq 100$ °C, the number of silanol groups decreases whereas the number of siloxane bridges increases. Thus HP is a very unstable compound in which siloxane bridges form spontaneously.

The one-pulse ^{29}Si spectrum recorded for the ethylammonium intercalate (C_2HP) is shown in Figure 4f. Qualitatively, this spectrum is very similar to that observed for HP (Figure 4c). Quantitatively, R is on the order of 2 even after aging. The intercalation of ethylammonium seems to reduce the tendency to form siloxane bridges.

Discussion

First, it will be assumed that the structure obtained for $KHSi_2O_5$ single crystals is correct. In this structure the silicon atoms are in a Q^3 environment, half of them bearing OH. In fact, the shift being a function of the group electronegativity and the group electronegativities of OK and OH being quite close, ^{29}Si resonance does not distinguish between silicon atoms linked to oxygens whose charges are balanced by either K^+ or H^+.

The observed shift of −89.4 ppm may appear unusually low (in absolute value) for a Q^3 environment. However, it is highly dependent on the Si–O–Si angle, as shown in the data collected by Janes and Oldfield;[12] the Q^3 ^{29}Si resonance line is observed at −89.2 ppm in wollastonite with an average Si–O–Si angle of 140° and at −86.3 ppm in pectolite where the average Si–O–Si angle is 135.7°.

The huge shift of the proton line in $KHSi_2O_5$ is also interesting. According to the structural analysis, the distance between near oxygen neighbors belonging to adjacent silicate sheets is 2.489 Å. Therefore the O–H–O bond should be almost symmetrical and thus very strong. What is remarkable is that in such a strongly hydrogen-bonded solid, the main ^1H resonance line is shifted by about 50% of the shift calculated for a "naked proton", namely, about +30 ppm.[13,14]

The observation of a distinct peak at +4.9 ppm indicates a second proton population that is not in fast exchange with that observed at ~15 ppm. According to the structure there should be only one proton site in $KHSi_2O_5$ and thus one single ^1H line. The observation of two main ^1H signals suggests that there are stacking faults in the potassium salt. Stacking faults would result in a rotation of one plane with respect to its neighbor with the consequence that beside the symmetric strong hydrogen bond, there are weaker hydrogen bonds attributable to longer O–H—O distances. Other hypotheses such as assuming the presence of trapped H_3O^+, besides being improbable under the conditions of synthesis, would lead to a large increase in the weight loss of the potassium salt in contradiction with the experimental weight loss, which is near the theoretical one.

In the hydrolysis product (b in Figure 5), a single ^1H MAS NMR line is observed at about +2 ppm with respect to TMS. Thus the silanol group and the intercalated water are in fast exchange. A chemical shift of 2.3 ppm lies in the range observed for protons in silica gel.

The comparison with MAS NMR data from HP and $KHSi_2O_5$ shows that upon hydrolysis, a deep structural rearrangement has occurred. Indeed the ^{29}Si MAS NMR spectrum now has a line at −111 ppm, in a range corresponding to silicon in a Q^4 environment. In silicalite, for instance, this line is at −109.2 ppm and the average Si–O–S angle is 150.7°, whereas in mordenite it is observed at −112.2 ppm, the average angle being about 150° too.[12] The most likely conclusion is that a noticeable fraction of the OH groups produced upon hydrolysis have condensed, creating siloxane bridges between adjacent silicate sheets. On completion of the present study, we became aware of very similar conclusions reached by Heidemann et al.[6] on the hydrolysis product of $Na_2Si_2O_5$, which is known as $(H_2Si_2O_5)_x$–I. This is a layered silicate with a structure distinctly different from that of $KHSi_2O_5$, but it seems that under certain circumstances, hydrolysis can cause a partial condensation of the silicate sheets, manifested in the appearance of a Q^4 ^{29}Si NMR signal. Indeed the ^{29}Si NMR spectrum of one of the $(H_2Si_2O_5)$–I samples in ref 6 is very similar to that of HP; however, the proton NMR spectrum is markedly different, with two distinct components.

In HP, the remaining hydroxyls are attached to silicon nuclei whose chemical shift is at −101 ppm, as compared with −89.3 ppm in the initial $KHSi_2O_5$. The opening of the Si–O–Si angle from 137° to 150° and the decrease of the strength of the hydrogen bond are most probably responsible for the shift of the Q^3 [$(Si–O)_3Si–OH$] line from about −90 to −101 ppm.

The modifications in the average Si–O–Si angles are also most probably at the origin of the changes in the unit-cell parameters reported in Table I, while the formation of siloxane bridges explains why the weight loss observed for HP is smaller than the nominal composition suggested by the formula $H_2Si_2O_5$. The main point however is that the hydrolysis of $KHSi_2O_5$ does not produce a structure with inverted tetrahedra bearing OH groups facing one another.

---

[12] James, N.; Oldfield, E. *J. Am. Chem. Soc.* **1985**, *107*, 6769.

[13] Freude, D.; Hunger, M.; Pfeifer, H. *Chem. Phys. Lett.* **1982**, *91*, 307.

[14] Thomas, J. M.; Klinowsky, J. *Adv. Catal.* **1985**, *33*, 199.

Table IV. Q^3/Q^4 Ratio in Some Crystalline Alkali-Metal Sheet Silicates and Some of Their Hydrolysis Products

silicate	composition	Q^3/Q^4	$-\nu(Q^3)$	$-\nu(Q^4)$	ref
octosilicate	$Na_2O{\cdot}8SiO_2{\cdot}10{\cdot}2H_2O$	1.1	101.9	112.2	3
kenyaite	$Na_2O{\cdot}20SiO_2{\cdot}10H_2O$	0.25	101.1	109–117	3
kanemite	$NaHSi_2O_5{\cdot}3H_2O$	∞	101		4
magadiite	$Na_2Si_{14}O_{29}{\cdot}10H_2O$	0.5	101	112–117	3
magadiite	$Na_2Si_{14}O_{29}{\cdot}9H_2O$	0.33	102	113	4
H magadiite	$H_2Si_{14}C_{29}{\cdot}5–4H_2O$	0.35 → 0.22	105	115	4
α-$(H_2Si_2O_5)_xI$	nominal $H_2Si_2O_5$	∞	101.5		5
δ-$(H_2Si_2O_5)_xI$	nominal H_2Si_2O5	3	~100	~110	5
this work	$KHSi_2O_5$	∞	89.4		this work
RT-dried HP	$H_{2(1-x)}Si_2O_{5-x}{\cdot}yH_2O$ $(0.175 \le y \le 0.448)$	2.3 → 0.7	100.9	111.2	this work

The strong dipole–dipole repulsion generated within such a structure is avoided through the formation of siloxane bridges between the layers and by rearranging the layer stacking so that the remaining OH are not strongly hydrogen bonded.

Upon complete dehydroxylation, all the layers are bonded by siloxane bridges. This dehydroxylation process gives rise to a distribution of Si–O–Si angles and to the broadening of the ^{29}Si line ($\nu_{1/2}$ = 14 ppm) centered at –110.7 ppm. The above description of HP is qualitative and the question is what is the number of siloxane bridges and how are they distributed? The information is partially contained in the ratio Q^4/Q^3, where Q^3 stands for [$(Si-O)_3Si-OH$], but the measurement of this ratio is complicated by the fact that neither line is narrow enough to assume that it is made of one single component. This broadening is probably due to a distribution of Si–O–Si angles. For instance, in spectrum c in Figure 4, one can observe that there is a shoulder at –105 ppm on the right wing of the –101 line and both main lines are superimposed onto a broad background. Moreover, as emphasized earlier, HP is unstable.

Interestingly, HP dried at 150 °C shows a poor XRD diagram (Figure 1c), which contains the same reflections still observed after complete dehydroxylation (Figure 1d), namely, a broad peak at about 15 Å and four sharper reflections at 4.27, 4.07, 3.84, and 3.34 Å, respectively. Thus the characteristic 020 reflection at 5.91 Å in RT-dried HP is totally missing, and the 200 reflection at 3.74 Å (in RT-dried HP) is also missing or strongly reduced in both HP treated at 150 °C and HP calcined at 500 °C. The delamination of acid-hydrolyzed $KHSi_2O_5$ evidenced by the large increase in the specific surface area (Table II) and the formation of siloxane bridges are likely to be at the origin of the modification of the $h0l$ Bragg reflections.

It is not possible to predict or to compute a regular structure for HP, but some schematic representation can be suggested. First, it is easy to draw a structure derived from the $KHSi_2O_5$ layers in which all silanol groups have condensed to yield 100% Q^4 Si even without changing the Si–O–Si angle: a displacement of every second layer by $c/2$ in the c direction will bring the silanol oxygens into coincidence, and the resulting completely condensed product has the formula SiO_2. Thus, any intermediate degree of condensation could be explained by the coexistence of the totally condensed and uncondensed domains.

But it is also possible to draw regular structures with an intermediate value of the $Q^3/Q^4 = R$ ratio. For example, the model presented in Figure 6 has the structural formula $H_{1.5}Si_2O_{4.75}{\cdot}yH_2O$, and the Q^3/Q^4 ratio is 3.

In this model, each ring contains on the average 1.5 siloxane bridges and 4.5 silanol groups. The puckered Si_2O_5 planes are rotated by 60° with respect to each other. The remaining silanol groups are not facing each other, but they point to the center of the rings in the opposite plane. Therefore, there are no hydrogen bonds (or only very weak hydrogen bonds) between the layers, which agrees well with the NMR results. This model has an ABAB repeating pattern; the repeat distance spans two layers. In RT-dried and -aged C_2HP (see Figure 4f) the presence of both Q^3 and Q^4 environments is obvious; the Q^3/Q^4 intensity ratio remains higher than in RT-dried and -aged HP.

Even if intercalation props the silicate sheets apart, hydrolysis and the formaion of siloxane bridges (although to a lower extent) occur simultaneously. Therefore the actual intercalation reaction should be rewritten as

$$2zRNH_3^+ + (y - x')H_2O + KHSi_2O_5 \rightarrow K^+ + (2z - 1)H^+ + (RNH_3)_{2z}H_{2(1-x'-z)}Si_2O_{5-x'}{\cdot}yH_2O \quad (2)$$

This would account for (i) the formation of siloxane bridges, (ii) the decrease in the intensity of the Si–O–H bending vibration, and (iii) the shift of the Si–O stretch toward higher frequency. An alternative chemical structure for the reaction product could be $(RNH_2)_{2z}H_{2(1-x')}Si_2O_{5-x'}{\cdot}yH_2O$, the intercalated alkylammonium transferring its proton to the lattice and being, in that alternative, hydrogen bonded to silanols.

We have pointed out earlier that in HP ($H_{2(1-x)}Si_2O_{5-x}{\cdot}yH_2O$), $x = 1/(1 + R)$, and we have outlined that in the alkylammonium intercalate R is about 2. Remember that the degree of exchange, or $2z$, is about 0.3. The –101 ppm ^{29}Si resonance line would contain in that case two kinds of Q^3 silicon environments, namely, $2z((Si-O)_3-SiO^-NH_3^+R)$ and $2(1 - x')((Si-O)_3Si-OH)$. It is possible but not evident that both have the same resonance frequency. If proton transfer occurred, then the –101 ppm resonance line would have contributions from $2z((Si-O)_3-SiOH—NH_2R)$ and of $2(1 - x')((Si-O)_3-SiOH)$ environments. It is most likely that both have the same resonance frequency. In the case where $1/(1 + R) = x' \approx 0.33$, we cannot reach a conclusion about proton transfer on the basis of the ^{29}Si NMR data.

However what is certain is that siloxane bridges exist in the alkylammonium intercalate. A $C_2NH_3^+$ chain has a diameter of about 3.3 Å, and when lying flat on the ac plane it covers an area of 16.8 $Å^2$. Since the unit cell area is ac = 36.7 $Å^2$ and contains four Si, steric hindrance cannot account for the limitation of the degree of exchange to about z = 0.15. However if x' = 0.33, that is, for the model shown in Figure 6, the area between siloxane bridges should be the unit cell area minus the cross-section area of the oxygen, that is, $36.8\ Å^2 - \pi(1.4)^2\ Å^2 = 30.6\ Å^2$. Thus, for steric reasons, the maximum degree of exchange should already be reduced to $30.6/(4 \times 16.8) = 0.45$. Of course, a larger number of siloxane bridges would lower the degrees of exchange below 0.45. Such calculations presuppose that the alkylamine molecules are lying flat in the open channels left between the siloxane bridges of the silicate structure (such channels are apparent in the right-hand part of Figure 6); they would also predict decreasing maximum degree of exchange with increasing chain length. This contradicts the experiment since the degree of ex-

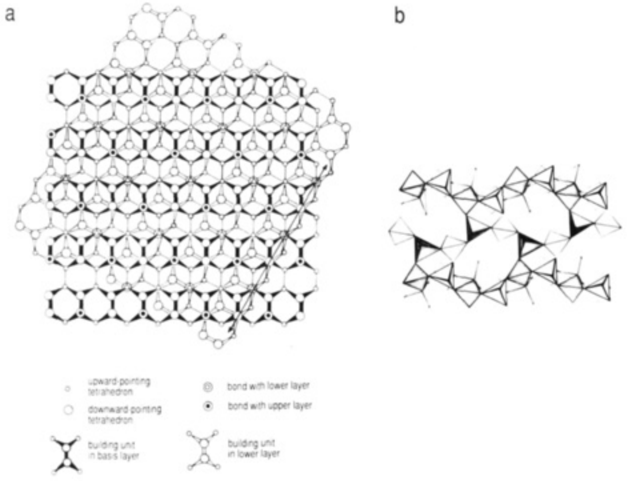

Figure 6. Idealized structural model for the RT-dried acid hydrolysis product of $KHSi_2O_5$, model suggested for $R = Q^3/Q^4$ ratio = 3. (a) Projection on plane 010. The arrows indicate the 101 plane, a section of which is shown in Figure 6b. (b) Projection on plane 101. Shaded tetrahedra are those forming siloxane bridges with adjacent layers; unshaded tetrahedra have free silanol groups.

change seems to be independent of the alkylammonium. Besides, alkyl chains longer than C_5 are no longer lying flat in the *ac* plane but are tilted out of it, as evidenced by the high *d* value in the XRD spectrum of the heptylammonium intercalate (Figure 2b). This would prevent the formation of siloxane bridges by holding the layers apart.

In fact, the presence of a broad background in the XRD spectra in Figure 2 would suggest an alternate picture, with interstratification of layers with a higher density of siloxane bridges and unbridged layers, which have a higher degree of exchange than the experimentally observed average. It therefore seems probable that intercalation of alkylammonium is not a topotactic reaction.

Finally, it is interesting to compare the ^{29}Si NMR data obtained in this work with those reported for other alkaline or hydrolyzed crystalline silicas. This survey is made in Table IV. First we note that in kanemite as well as in $KHSi_2O_5$ there is no line attributable to a Q^4 environment. In both cases the Q^3 resonance line does not distinguish between $(Si–O)_3SiOH$ and $(Si–O)_3SiONa$ or $(Si–O)_3SiOK$ environments. The important difference between kanemite and $KHSi_2O_5$ is in the chemical shift of their single Q^3 line. Most probably in kanemite the intercalated water prevents the formation of the strong symmetric H bond which is characteristic of $KHSi_2O_5$.

Hydrolysis of magadiite does not affect very significantly the number of siloxane bridges. According to Pinnavaia et al.,[4] in hydrolyzed magadiite heated at 230 °C the Q^3/Q^4 ratio decreases from 0.35 to 0.22, indicating some layer cross-linking. Note that in the original magadiite, with 10 H_2O per structural formula,[3] Q^3/Q^4 was 0.5. According to ref 4, in sodium magadiite as well as in hydrolyzed magadiite, the Q^4 layers would contain some inverted tetrahedra forming the Q^3 ($(Si–O)_3SiOH$) units.

The characteristic layer of $KHSi_2O_5$ is made of pairs of inverted tetrahedra. It is therefore not surprising that RT-dried HP has a much higher Q^3/Q^4 ratio than hydrogen magadiite.

Therefore, it may be concluded that NMR results are consistent with the structural data. The instability of HP results from the puckered structure of the $KHSi_2O_5$ layer silicate, and because of the easy formation of siloxane bridges the exchange of potassium by alkylammonium yields a randomly interstratified structure of intercalated and siloxane-bridged domains.

Acknowledgment. An NSF grant (DIR-8719808) and an NIH grant (RR04095) which have partly supported the purchase of the GN-500 NMR instrument are gratefully acknowledged. J.J.F. thanks Professor A. Kalt for providing a sample of $KHSi_2O_5$.