The Topochemical Reaction of $CaSi_2$ to a Two-Dimensional Subsiliceous Acid $Si_8H_3(OH)_3$ (= Kautskys' Siloxene)

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Kautsky's siloxene was prepared in a topochemical reaction from large crystals of CaSi₂. The structure model was revised. Siloxene is a subsiliceous acid $[Si_6]H_3(OH)_3$ and consists of two-dimensional corrugated Si-layers with three Si–Si bonds per silicon and an OH- or H-ligand, respectively. Ordering of adjacent layers is turbostratic. The layer lattice is capable of forming intercalation complexes. On intercalation only the layer distance is changed.

The alkoxylated derivatives $Si_6H_3(OCH_3)_{3n}$ and $Si_6H_3(OC_2H_5)_{3n}$ are also able to intercalate polar molecules.

The structure of calciumdisilicide $CaSi_2$ is characterized by two-dimensional corrugated layers of silicon, separated from each other by planar layers of Ca-atoms. The two modifications differ in stacking sequences with either three or six layers per unit cell [1, 2]. Within the Si-layers each atom has 3 neighbours at a distance of 239 pm, which is only 4 pm longer than the bonds in the element. The 3 equidistant neighbours correspond to the 8-N-rule: in an extreme formulation the compound may be looked at as $Ca^{2+}(Si^{-})_2$ [3]. Si⁻ is isoelectronic with group V elements and accordingly forms layers similar to those in As.

Due to this bond character the compound should undergo topochemical reactions, in which the two dimensional Si layers are conserved. In the last century Wöhler [4] had already observed $CaSi_2$ to react with conc. HCl. Hydrogen is evolved, leaving an insoluble yellow solid, for which Hönigschmid [5] found the composition $Si_6O_4H_6$. According to Kautsky [6–8] the solid is a polymeric cyclohexasiltrioxane (= siloxene) of idealized composition $(Si_6O_3H_6)_n$, in which six-membered Si_6 rings should be separated from each other by Si–O–Si bridges (I). Additionally each silicon should have an -Si-Hbond.

A slightly different model was proposed by Wiberg [9a] with one-dimensional Si Si chains,



interconnected by Si O Si bonds (II) and an additional H per silicon atom. In both models the two-dimensional Si-network of the starting material is assumed to be partially split and reconstructed as a regular sheet of mixed Si–Si and Si–O bonds [9b].



Whereas all these preparations were amorphous to X-rays, we now succeeded in preparing the compound in form of distorted large crystals, which permitted us to clarify its structure, showing the reaction to be topochemical, and the corrugated Si layers to remain unchanged.

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Materials and Methods

CaSi₂ was synthesized according to Evers et al. [10] crucible free in a copper boat at an argon pressure of 1.17 bar at 1400 °C. Evaporation of Ca during the synthesis (b.p. of Ca¹⁴²⁰ °C) was determined and the calculated excess added for a second melting run. Calcium used in the experiments was 99.5% (puriss.), silicon was of semiconductor quality (99.99%). For some of the final experiments CaSi₂ was synthesized from highest quality calcium (99.98% [11]). Single crystals with a diameter of 0.1-4 mm were used in most experiments. All of them were of the 6-layer polytype structure. The following acids were applied: aqueous HCl 37%, saturated HCl solution in methanol and ethanol (1 bar), HCl evolved by adding H_2O slowly to CH₃COCl, formic acid 100% and 50% with H_2O , acetic acid 100% and 50% with water, H_2SO_4 96% and 50% with water, HF 40% aqueous and H_3PO_4 . Solvents and acids were of analytical grade and purified and dried with standard procedures. HCl solutions were obtained from dry gaseous HCl and the solvent.

For "siloxene" preparations selected CaSi₂ crystals were covered with the acid (*ca.* 5 mmoles per 2 mmoles of CaSi₂) and kept under dry nitrogen at room temperature, until H₂ evaporation was finished. With crystals $2 \times 4 \times 0.2$ mm³ up to 24 h were necessary. Thereafter the samples were filtered and washed with water or another solvent, until all soluble Cl⁻ was removed. The samples were dried at 1×10^{-5} bar. For X-ray measurement crystals were placed in glass cappillaries previous to drying, together with solvent.

The reaction was followed by measuring the volume of hydrogen evolved, the samples were characterized by chemical analysis, IR and mass spectroscopy, by optical and electron microscopy and by X-ray diffraction, both with powder and with rotation and Weissenberg techniques.

Intercalation capability was checked with acetylchloride, dimethylsulfoxide, *n*-alkylamines, *n*-alkylcarboxylic acids, various alcohols, pyridine, N.Ndialkylformamides and N.N-dialkylacetamides. For X-ray measurements single crystals were placed in glass capillaries after appropriate leaching and drying procedures, soaked with the liquid guest compound and sealed. Completion of the intercalation reaction was checked by X-ray diffraction after 1, 7 and 21 days.

Results

Most of our experimental results are similar to those of Kautsky. No reaction is observed if CaSi₂ crystals are exposed to water-free acids. After addition of water, however, hydrogen is evolved and the edges of the crystals start to become yellow. The final product is homogeneous yellow to yellowgreen.

With nitric acid the reaction stops immediately after wetting, probably due to the formation of a stabilizing SiO₂ surface film. With HF (40% in water) the reaction does not stop at the yellow product, but proceeds rapidly to a white SiO₂ gel, which is dissolved finally.

Suitable crystal flakes for X-ray studies are obtained, when single crystals of $CaSi_2$ of appropriate size $(0.05-1.5 \text{ mm } \emptyset)$ are treated with aqueous HCl (37%). Addition of water results in a colour change to orange, which lasts for 2–3 minutes. The colour disappears immediately on further addition of water. In the presence of salts (LiCl-, MgCl₂-, CaCl₂-saturated aqueous solutions) the orange colour becomes more intense, and instable red particles may be isolated.

During product formation the crystal dimensions remain unaltered parallel to the layers, but are expanded perpendicularly to them, the material looking similar to heat-expanded vermiculite. The flakes are easily cloven parallel to the layers, and are smooth, transparent yellow and lustrous like a brass foil, when prepared in a slow reaction. Otherwise they look crumpled. The reaction corresponds to

 $\begin{array}{l} 3 \operatorname{CaSi}_2 + 6 \operatorname{HCl} + (3+x) \operatorname{H}_2 \operatorname{O} \rightarrow \\ \mathrm{Si}_6 \operatorname{O}_{3+x} \operatorname{H}_6 + 3 \operatorname{CaCl}_2 + (3+x) \operatorname{H}_2 \end{array}$

x is close to 0 after a reaction time of 24 h and increases on aging. The hydrogen evolved during 24 h of HCl-attack in four independent experiments was 90%, 93%, 103% and 104% of the calculated value with x = 0. The hydrogen content in different samples Si₆O_{3+x}H₆ was 102.2%, 97.0% and 94.6% of the calculated value (x=0). After storage for several days, the value dropped to 85.2%, which corresponds to x = +1, i.e. the composition determined by Hönigschmid. Simultaneously the Si content decreased from 75.2% (75.7% with x=0) to 70.4% or even less. Mass spectrometric studies proved, that no volatile silanes were formed from pure CaSi₂. Obviously the freshly prepared siloxene is oxidized by water, increasing the mean oxidation number of Si.

The freshly prepared sample is highly reducing. In solutions containing Cu^{2+} or Ag^+ it is immediately covered with metallic copper or silver. Bromine in ether solution reacts rapidly, while the crystals start to expand also parallel to the layers. Diazomethane reacts vigorously at 0 °C, slightly decreasing the basal spacings, indicating interlayer water to be more acidic than free water.

IR-data show a very broad OH stretching band at 3400 cm^{-1} and a sharp Si-H stretching frequency at 2100 cm^{-1} . The low value of the latter is more or

addition, broad bands at $\sim 1625 \text{ cm}^{-1}$ and at 1035 cm^{-1} have been observed.

The main differences to Kautsky's results are the X-ray patterns. Single crystal data show a hexagonal unit cell with $(00 \ l)$ and (hk0)-reflections. (hkl)-reflections are absent with the exception of (hkl) with l=3n. The stacking sequence is more or less turbostratic; the shift of adjacent layers however is not fully at random. Dislocations of $n/3 \ a$ are slightly favoured.

The *a*-axes are very similar to a of the starting material (Table I) and of silicon, when described in a rhombohedral cell. Therefore, one has to assume, that the corrugated Si layers are the same in the

Table I. Comparison of lattice dimensions of "siloxene" $CaSi_2$ and silicon.

Compound	Cell dimensions $[pm]$ a = b = c =			
"Siloxene"	382	3n imes 656.5		
CaSi ₂	385	6 imes510,5		
Si*	384			
Siloxene from CH ₃ OH/HCl	384	3n imes 783,2		
Siloxene from C ₂ H ₅ OH/HCl	383	3n imes 983,2		

* Rhombohedral description.

3 structures and no oxygen is inserted into the Si–Si bond system. Consequently there are no Si–O–Si bonds in the primary product. Insertion of oxygen into the Si–Si layers should be accompanied by an expansion of the crystals parallel to the layers. However, such an expansion is observed by Br_2 or I_2 treatment only, when the Si layers are destroyed.

Absence of Si–O–Si in the basic layers is substantiated by syntheses in HCl/methanol or HCl/ethanol. In this case samples of composition $(Si_6)H_3(OCH_3)_3$ and $(Si_6)H_3(OC_2H_5)_3$ respectively are obtained with unaltered *a*-axes and increased layer distance. The increase in spacing is 150 pm with –OCH₃ and 350 pm with –OC₂H₅ instead of –OH.

On storage in the presence of water the subsiliceous acid is slowly oxidized according to

$$[\operatorname{Si}_{6}]\operatorname{H}_{3}(\operatorname{OH})_{3} + x\operatorname{H}_{2}\operatorname{O} \rightarrow \\ [\operatorname{Si}_{6}]\operatorname{H}_{3-x}(\operatorname{OH})_{3+x} + x\operatorname{H}_{2}$$

At relatively low values of x condensation starts to compete with further oxidation. In the first step of the condensation adjacent layers become interconnected via Si-O-Si bonds, which may be written as

$$2 [Si_6]H_{3-x}(OH)_{3+x} \rightarrow [Si_6]_2OH_{6-2x}(OH)_{4+2x} + H_2O$$

On prolonged storage this reaction may take place even with x = 0 on the crystal edges, which has a detrimental effect on intercalation reactions.

Preparation with 37% HCl in the presence of *n*-decanol yielded yellow-green products with the same *a*-axes, but highly increased *c*-axes. Depending on the leaching process higher basal spacings can be observed, caused by intercalated decanol molecules, which may be removed by prolonged leaching with ether (Table II). In the decanol-expanded sample

Table II.	Fluect of	<i>n</i> -decanor	on	tne	Dasal	spacing.	

Experimental conditions of preparation	Leaching or drying process and status, while X-rayed	Basal spacing [pm]
$\overline{\mathrm{CaSi}_2 + \mathrm{HCl/H}_2\mathrm{O}}$	wet	656-703
	leached with H_2O and dried over P_4O_{10}	633
$\mathrm{CaSi_2} + \mathrm{HCl/H_2O}/n\text{-}\mathrm{C_{10}H_{21}OH}$	leached with H_2O/Et_2O ; wet sample X-rayed	1163
	leached with H ₂ O/Et ₂ O; air-dried sample X-rayed	1053
	leached with H ₂ O/Et ₂ O; at 90 °C HV-dried	921
	leached with Et ₂ O; wet sample X-rayed	1105
	leached with Et ₂ O for 6 days; then at 90 °C HV-dried	643
	leached with H_2O for 3 days; then at 90 °C HV-dried	762

all Si-H bonds may be hydrolysed to Si-OH (x=3.0) without condensation to Si-O-Si. Intercalated decanol molecules prevent adjacent layers from being condensated due to the increased basal spacing.

Composition of such samples corresponds to the formula $[Si_6](OH)_6(n-C_{10}H_{21}OH)_{0.21}$.

Analysis

Calcd Si 54.51 C 9.81 H 3.45, Found Si 55.37 C 9.97 H 3.50.

Extraction of the decanol is reversible immediately after preparation, but hindered after storage for weeks. Even in these samples hydrolyses and condensation occur on storage over several weeks.

Intercalation Complexes

The two-dimensional structure of the compound is also substantiated by its capability for intercalation reactions (Table III). However, all intercalations are superimposed with condensation of adjacent layers, by which further intercalation is hindered for steric reasons.

After preparation in 37% aqueous HCl a small amount of H₂O is trapped, which may be removed over P₄O₁₀ or by reaction with diazomethane. The drop in basal spacing is only 23 pm. With methanol, ethanol and N,N-diethylacetamide a small increase in spacing is observed (70 pm, 87 pm and 70 pm). Again the difference is too small to accommodate the intercalated moieties in each interlayer. Correspondingly the (001)-reflections are non-integral.

An expansion of 1891 pm is observed with *n*-decylamine in aqueous emulsion. This increase is higher than the space requirement of fully extended molecules with their long axes perpendicular to the matrix layers. Thus bilayers with tilted (tilting angle $ca. 40^{\circ}$) or coiled chains have to be assumed. The linear increase of the spacings from the *n*-decyl-to the *n*-tetradecylamine-intercalate points to a regular arrangement within the bilayers. Experiments with amines of shorter chain length, *i.e.* less hydrophobicity were accompanied with a fast decomposition of the lattice and hydrogen formation.

With N,N-dimethylformamide and N,N-diethylformamide the spacings are increased by 375 and 562 pm, respectively. The (001)-reflections are integral, indicating regular intercalation into each interlayer region. The absolute increases are similar to those in the intercalating natural H-magadiite [12] and synthetic $H_2Si_{14}O_{29} \times 5H_2O$ [13] (Table IV), representing silicic acids with layer structures. The lower value is also found on intercalation of N,Ndimethylformamide into transition metal dichalcogenides [14, 15], but is different from that found on intercalation in kaolinite [16], FeOCl, CrOCl, TiOCl, InOCl and InOBr [17]. The lattice expansion, brought about by dimethylsulfoxide (DMSO) is

Table III. Dasai spacings of intercalation complex	II. Basal spacings of intercalation con	mplexes
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[Si ₆]H ₃ (OH) ₃ prepared by reaction of	Guest component	Basal spacing d [pm]	Increase in basal spacing ⊿ d [pm]
$ \begin{array}{l} \hline & \\ \text{CaSi}_2 + \text{HCl} ~(37\%) \\ \text{,,} ~~ \text{after dehydration} \\ \text{CaSi}_2 + \text{CH}_3\text{OH} + \text{HCl} ~(= [\text{Si}_6]\text{H}_3(\text{OCH}_3)_3) \\ \text{CaSi}_2 + \text{C}_2\text{H}_5\text{OH} + \text{HCl} ~(= [\text{Si}_6]\text{H}_3(\text{OC}_2\text{H}_5)_3) \end{array} $	(H ₂ O) — —	656 633 783 983	$\begin{array}{r} 23\\ \hline 150\\ 350 \end{array}$
$CaSi_2 + H_2O + HCl (37\%)$	N.N-diethylacetamide CH ₃ OH C ₂ H ₅ OH N.N-dimethylformamide dimethylsulfoxide n-C10H21NH2/H2O n-C12H25NH2/H2O n-C14H29NH2/H2O	703 703 720 1008 1300 1300 2524 2845 3187	$\begin{array}{c} 70 \\ 70 \\ 87 \\ 375 \\ 562 \\ 667 \\ 1891 \\ 2212 \\ 2554 \end{array}$
$CaSi_2 + CH_3OH + HCl$	N.N-dimethylacetamid N.N-diethylacetamide N.N-dimethylformamide N.N-diethylformamide	851 851 1141 1326	68* 218** 68* 218** 358* 508** 543* 693**

* (d - 783) pm, ** (d - 633) pm.

Table IV. Comparison of lattice expansions by intercalation of N,N-dimethylformamide or N,N-diethylformamide into various host lattices.

Host layer lattice	Increase ⊿d [pm] H-C N	in basal spacings CH ₃) ₂ H-C N(C ₂ H ₅) ₂
[Si ₆]H ₃ (OH) ₃ (this work)	375	562
[Si ₆]H ₃ (OCH ₃) ₃ (this work)	358	543
H-magadiite [12]	350	520
$H_2Si_{14}O_{29} \times 5H_2O[13]$	550	520
kaolinite [16]	480	
TiS ₂ [14]	386	389
NbS_{2} [15]	373	370
TaS ₂ [15]	383	376
TiOC1 [17]	1136(=2)	$\times 568) 830(=2 \times 415)$
VOCI [17]	956(=2)	$\times 478)1130(=2 \times 565)$
FeOC1 [17]	508	$1022(=2 \times 511)$
InOCI [17]	599	$636(=2 \times 318)$
InOBr [17]	547	$628(=2\times 314)$

higher than that in DMSO-kaolinite ($\Delta d = 403 \text{ pm}$) [16].

The methoxy derivative $[Si_6]H_3(OCH_3)_3$, prepared by HCl/CH₃OH is also capable of intercalating. The behaviour with N,N-dialkylformamide and N,Ndialkylacetamide is similar to that of the free OH-derivative. With DMSO and *n*-decylamine however, intercalation into the methoxy compound is followed by a rapid destruction of the lattice.

Conclusions

CaSi₂ reacts topochemically with HCl/H₂O to an expandable layer compound $[Si_6]H_3(OH)_3$ according to Fig. 1. The first step of this solid state reaction is mainly determined by the nucleation of the expanded layer lattice, which is enhanced by the solvation of the Ca²⁺-ions. Therefore the chemical behaviour is somewhat different from Si-compounds in homogeneous phase. The compound may be further oxidized to $[Si_6]H_{3-x}(OH)_{3+x}$. However, condensation to a three-dimensional, randomly interlinked system competes with this oxidation.

Within the layers the two-dimensional, corrugated Si-Si bond system is unchanged. Each Si-atom has 3 equivalent Si neighbours at a distance very close to that observed in silicon. Perpendicular to the layers every Si atom has a ligand L, which in the most stable form is alternatingly -OH and -H. Thus the compound may be looked at as a subsiliceous acid. If CH₃OH or C₂H₅OH are used as solvents for HCl instead of water, the alkoxylated compound is obtained directly. The differences to Kautsky's model are summarized in Table V.

Table V. Comparison of Kautsky's model of siloxene with our data.

	Kautsky's model	Our model
Composition	$Si_6O_3H_6$	Si ₆ O ₃ H ₆
Basic layers	$\{(Si_6)O_{6/2}\}$	{Si6}
Ligands on the layers	6 H [(Si ₆)O _{6/2} H ₆] oxygen constituent of the basic layers	3 H and 3 OH [Si ₆]H ₃ (OH) ₃ oxygen within OH ligands
Oxidation number	all equivalent 0	alternatingly $+1$ and -1
Methoxyl- or ethoxylderivative	$[(\mathrm{Si}_6)\mathrm{O}_{6/2}]\mathrm{H}_{6-x}(\mathrm{OR})_x$	$[(Si_6)]H_3(OR)_3$



Fig. 1. Topochemical reaction of CaSi₂ with HC1/solvent.

The subsiliceous acid is unstable on storage. Condensation of $[Si_6]H_3(OH)_3$ on edges of the crystals yields free water, which in a second step causes oxidation to $[Si_6]H_2(OH)_4$. At this stage formation of Si–O–Si linkages between adjacent layers starts to affect the layer characteristics, and the intercalation capability is lost. In the presence of OH^- the silicon layers are rapidly oxidized to a silica gel. However, alkylammonium salts can be prepared with long chain amines. Probably the surfactant character of these amines gives a protective surface layer, which prevents chemical attack at the Si–Si bonds.

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