The Topochemical Reaction of CaSi₂ to a Two-Dimensional Subsiliceous Acid Si₆H₃(OH)₃ (= Kautsky’s Siloxene)

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Topochemical Reaction, Calciumdisilicide, Subsiliceous Acid, Siloxene, Intercalation Reactions

Kautsky’s siloxene was prepared in a topochemical reaction from large crystals of CaSi₂. The structure model was revised. Siloxene is a subsiliceous acid [Si₆]H₃(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 alkoxyated derivatives Si₆H₃(OCH₃)₃ and Si₆H₃(OC₂H₅)₃ are also able to intercalate polar molecules.

The structure of calciumdisilicide CaSi₂ 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 Ca²⁺(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 CaSi₂ to react with conc. HCl. Hydrogen is evolved, leaving an insoluble yellow solid, for which Hönigschmid [5] found the composition Si₆O₂H₆. According to Kautsky [6–8] the solid is a polymeric cyclohexasiltrioxane (= siloxene) of idealized composition (Si₆O₂H₆)ₙ, in which six-membered Si₆ rings should be separated from each other by Si–O–Si bridges (I). Additionally each silicon should have an –Si–H bond.

A slightly different model was proposed by Wiberg [9a] with one-dimensional \( \text{Si} \sim \text{Si} \sim \text{Si} \) chains, interconnected by \( \text{Si} \sim \text{O} \sim \text{Si} \) 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.

* Reprint requests to Prof. Dr. Armin Weiss. 0340–5087/80/0100–25/$ 01.00/0
Materials and Methods

CaSi$_2$ 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 Ca = 1420 °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 the final experiments CaSi$_2$ 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$_2$O slowly to CH$_3$COCl, formic acid 100% and 50% with H$_2$O, acetic acid 100% and 50% with water, H$_2$SO$_4$ 96% and 50% with water, HF 40% aqueous and H$_2$PO$_4$. 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 CaSi$_2$ crystals were covered with the acid (ca. 5 mmoles per 2 mmoles of CaSi$_2$) and kept under dry nitrogen at room temperature, until H$_2$ evaporation was finished. With crystals 2 × 4 × 0.2 mm$^3$ 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 capillaries 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,N-dialkylformamides 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 CaSi$_2$ 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 yellow-green.

With nitric acid the reaction stops immediately after wetting, probably due to the formation of a stabilizing SiO$_2$ surface film. With HF (40% in water) the reaction does not stop at the yellow product, but proceeds rapidly to a white SiO$_2$ 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 mm$^2$) 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-, MgCl$_2$-, CaCl$_2$-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 elven 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

$$3\text{CaSi}_2 + 6\text{HCl} \rightarrow \text{Si}_6\text{O}_{3+x}\text{H}_x + 3\text{CaCl}_2 + (3+x)\text{H}_2\text{O}$$

$x$ 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 Si$_6$O$_{3+x}$H$_x$ 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 CaSi$_2$. 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. Diazot-
methane 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 less typical for Si\(_6\)- or Si–Si–H groups. In addition, broad bands at ~1625 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 (00l) 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 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\(_2\)H\(_5\))\(_3\) respectively are obtained with unaltered \(a\)-axes and increased layer distance. The increase in spacing is 150 pm with –OCH\(_3\) and 350 pm with –OC\(_2\)H\(_5\) instead of –OH.

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

\[
\text{[Si}_6\text{H}_3\text{(OH)}_3 + x\text{H}_2\text{O} \rightarrow [Si}_6\text{H}_{3-x}\text{(OH)}_{3a-x} + x\text{H}_2O]
\]

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

\[
2[\text{Si}_6\text{H}_{3-x}(\text{OH})_{3a-x} \rightarrow [\text{Si}_6\text{H}_{4-2x}(\text{OH})_{4+2x} + \text{H}_2\text{O}]
\]

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 I. Comparison of lattice dimensions of “siloxene” CaSi\(_2\) and silicon.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cell dimensions [pm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Siloxene”</td>
<td>(3n \times 656.5)</td>
</tr>
<tr>
<td>CaSi(_2)</td>
<td>(6 \times 510.5)</td>
</tr>
<tr>
<td>Si*</td>
<td>(384)</td>
</tr>
<tr>
<td>Siloxene from CH(_3)OH/HCl</td>
<td>(384) (3n \times 783.2)</td>
</tr>
<tr>
<td>Siloxene from C(_2)H(_5)OH/HCl</td>
<td>(383) (3n \times 983.2)</td>
</tr>
</tbody>
</table>
* Rhombohedral description.

Table II. Effect of \(n\)-decanol on the basal spacing.

<table>
<thead>
<tr>
<th>Experimental conditions of preparation</th>
<th>Leaching or drying process and status, while X-rayed</th>
<th>Basal spacing [pm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaSi(_2) + HCl/H(_2)O</td>
<td>wet; leached with H(_2)O and dried over P(_4)O(_10)</td>
<td>656–703</td>
</tr>
<tr>
<td>CaSi(<em>2) + HCl/H(<em>2)O/n-C(</em>{10})H(</em>{21})OH</td>
<td>leached with H(_2)O/Et(_2)O; wet sample X-rayed</td>
<td>1163</td>
</tr>
<tr>
<td></td>
<td>leached with H(_2)O/Et(_2)O; air-dried sample X-rayed</td>
<td>1053</td>
</tr>
<tr>
<td></td>
<td>leached with H(_2)O/Et(_2)O; at 90 °C HV-dried</td>
<td>921</td>
</tr>
<tr>
<td></td>
<td>leached with Et(_2)O; wet sample X-rayed</td>
<td>1105</td>
</tr>
<tr>
<td></td>
<td>leached with Et(_2)O for 6 days; then at 90 °C HV-dried</td>
<td>643</td>
</tr>
<tr>
<td></td>
<td>leached with H(_2)O for 3 days; then at 90 °C HV-dried</td>
<td>762</td>
</tr>
</tbody>
</table>
all Si–H bonds may be hydrolysed to Si–OH \((\alpha; = 3.0)\) without condensation to Si–O–Si. Intercalated decanol molecules prevent adjacent layers from being condensed due to the increased basal spacing.

Composition of such samples corresponds to the formula \([\text{Si}_6\text{H}_3\text{(OH)}_3\text{]}_\alpha;\text{(n-C}_{10}\text{H}_{21}\text{OH})_{0.21}\). 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 \(\alpha; \approx 40^\circ\)) 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-diethylformamide and N,N-diethyldiamine 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$_2$Si$_4$O$_9$ × 5H$_2$O [13] (Table IV), representing silicic acids with layer structures. The lower value is also found on intercalation of N,N-diethylformamide 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

\[
\begin{array}{l|l|l|l}
\text{Guest component} & \text{Basal spacing} & \text{Increase in basal spacing} \\
& \text{d [pm]} & \text{A d [pm]} \\
\hline
\text{(H}_2\text{O)} & 656 & 23 \\
\text{N,N-dimethylacetamide} & 703 & 70 \\
\text{N,N-diethylformamide} & 1008 & 375 \\
\text{dimethylsulfoxide} & 1300 & 667 \\
\text{n-C}_{10}\text{H}_{21}\text{NH}_2\text{H}_2\text{O} & 2524 & 1891 \\
\text{n-C}_{12}\text{H}_{25}\text{NH}_2\text{H}_2\text{O} & 2845 & 2212 \\
\text{n-C}_{14}\text{H}_{29}\text{NH}_2\text{H}_2\text{O} & 3187 & 2554 \\
\text{N,N-dimethylacetamide} & 851 & 68* 218** \\
\text{N,N-diethylacetamide} & 851 & 68* 218** \\
\text{N,N-dimethylformamide} & 1141 & 358* 508** \\
\text{N,N-diethyldiamine} & 1326 & 543* 693** \\
\hline
\end{array}
\]

* (\(d – 783\) pm), ** (\(d – 633\) pm).
higher than that in DMSO-kaolinite ($\Delta d = 403$ pm) [16].

The methoxy derivative $[\text{Si}_6]_3\text{H}_2(\text{OCH}_3)_3$, prepared by HCl/CH$_3$OH is also capable of intercalating. The behaviour with N,N-dialkylformamide and N,N-dialkylacetamide 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**

CaSi$_2$ reacts topochemically with HCl/H$_2$O to an expandable layer compound $[\text{Si}_6]_3\text{H}_2(\text{OH})_3$ 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 Ca$^{2+}$-ions. Therefore the chemical behaviour is somewhat different from Si-compounds in homogeneous phase. The compound may be further oxidized to $[\text{Si}_6]_3\text{H}_{3-x}(\text{OH})_{3-x}$. 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 $-\text{OH}$ and $-\text{H}$. Thus the compound may be looked at as a subsiliceous acid. If CH$_3$OH or C$_2$H$_5$OH 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 IV.** Comparison of lattice expansions by intercalation of N,N-dimethylformamide or N,N-diethylformamide into various host lattices.

<table>
<thead>
<tr>
<th>Host layer lattice</th>
<th>Increase in basal spacings $\Delta d$ [pm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Si}_6]_3\text{H}_2(\text{OH})_3$ (this work)</td>
<td>$375$ $562$</td>
</tr>
<tr>
<td>$[\text{Si}_6]_3\text{H}_2(\text{OCH}_3)_3$ (this work)</td>
<td>$358$ $543$</td>
</tr>
<tr>
<td>H-magadiite [12]</td>
<td>$350$ $520$</td>
</tr>
<tr>
<td>H$_2$Si$_3$O$_2$ $\times$ $5\text{H}_2\text{O}$ [13]</td>
<td>$550$ $520$</td>
</tr>
<tr>
<td>kaolinite [16]</td>
<td>$480$</td>
</tr>
<tr>
<td>TiS$_2$ [14]</td>
<td>$386$ $389$</td>
</tr>
<tr>
<td>Nb$_2$ [15]</td>
<td>$373$ $370$</td>
</tr>
<tr>
<td>TaS$_2$ [15]</td>
<td>$383$ $376$</td>
</tr>
<tr>
<td>TiOCl [17]</td>
<td>$1136$ ($= 2 \times 568$) $830$ ($= 2 \times 415$)</td>
</tr>
<tr>
<td>VOCl$_2$ [17]</td>
<td>$856$ ($= 2 \times 478$) $1130$ ($= 2 \times 565$)</td>
</tr>
<tr>
<td>FeOCl [17]</td>
<td>$508$ $1022$ ($= 2 \times 511$)</td>
</tr>
<tr>
<td>InOCl [17]</td>
<td>$599$ $636$ ($= 2 \times 318$)</td>
</tr>
<tr>
<td>InOBr [17]</td>
<td>$547$ $628$ ($= 2 \times 314$)</td>
</tr>
</tbody>
</table>

**Conclusions**

CaSi$_2$ reacts topochemically with HCl/H$_2$O to an expandable layer compound $[\text{Si}_6]_3\text{H}_2(\text{OH})_3$ 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 Ca$^{2+}$-ions. Therefore the chemical behaviour is somewhat different from Si-compounds in homogeneous phase. The compound may be further oxidized to $[\text{Si}_6]_3\text{H}_{3-x}(\text{OH})_{3-x}$. 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 $-\text{OH}$ and $-\text{H}$. Thus the compound may be looked at as a subsiliceous acid. If CH$_3$OH or C$_2$H$_5$OH 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.

<table>
<thead>
<tr>
<th></th>
<th>Kautsky's model</th>
<th>Our model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>$\text{Si}_3\text{O}_3\text{H}_5$</td>
<td>$\text{Si}_3\text{O}_3\text{H}_5$</td>
</tr>
<tr>
<td>Basic layers</td>
<td>${\text{(Si}<em>6/\text{O)}</em>{4/2}}$</td>
<td>${\text{(Si}_6}$</td>
</tr>
<tr>
<td>Ligands on the layers</td>
<td>$6\text{H}$</td>
<td>$2\text{H}$ and $3\text{OH}$</td>
</tr>
<tr>
<td></td>
<td>${\text{(Si}<em>6/\text{O)}</em>{6/2}\text{H}_6}$</td>
<td>${\text{(Si}_6\text{O})_3(\text{H}_3\text{OH})_3$</td>
</tr>
<tr>
<td></td>
<td>oxygen constituent of the basic layers</td>
<td>oxygen within OH ligands</td>
</tr>
<tr>
<td>Oxidation number</td>
<td>all equivalent $0$</td>
<td>alternatingly $+1$ and $-1$</td>
</tr>
<tr>
<td>Methoxy- or ethoxyldervative</td>
<td>${\text{(Si}<em>6/\text{O)}</em>{6/2}\text{H}_{6-x}\text{(OR)}_x$</td>
<td>${\text{(Si}_6\text{H})_3(\text{OR})_2$</td>
</tr>
</tbody>
</table>

**Fig. 1.** Topochemical reaction of CaSi$_2$ with HCl/solvent.
The subsiliceous acid is unstable on storage. Condensation of \([\text{Si}_6\text{H}_3(\text{OH})_3]\) on edges of the crystals yields free water, which in a second step causes oxidation to \([\text{Si}_6\text{H}_2(\text{OH})_4]\). 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 \(\text{OH}^–\) 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.