

Silicon

Amorphous Silicon: New Insights into an Old Material

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Dedicated to Prof. Dr. G. Roewer on his 75th birthday

Abstract: Amorphous silicon is synthesized by treating the tetrahalosilanes SiX₄ (X=Cl, F) with molten sodium in high boiling polar and non-polar solvents such as diglyme or nonane to give a brown or a black solid showing different reactivities towards suitable reagents. With regards to their technical relevance, their stability towards oxygen, air, moisture, chlorine-containing reaction partners RCl (R=H, Cl, Me) and alcohols is investigated. In particular, reactions with methanol are a versatile tool to deliver important products. Besides tetramethoxysilane formation, methanolysis of silicon releases hydrogen gas under ambient conditions and is thus suitable for a decentralized hydrogen production;

competitive insertion into the MeO–H versus the Me–OH bond either yields H- and/or methyl-substituted methoxy functional silanes. Moreover, compounds, such as Me_nSi(OMe)_{4–n} (n=0–3) are simply accessible in more than 75% yield from thermolysis of, for example, tetramethoxysilane over molten sodium. Based on our systematic investigations we identified reaction conditions to produce the methoxysilanes Me_nSi(OMe)_{4–n} in excellent (n=0:100%) to acceptable yields (n=1:51%; n=2:27%); the yield of HSi(OMe)₃ is about 85%. Thus, the methoxysilanes formed might possibly open the door for future routes to silicon-based products.

Introduction

Synthesis and reactivity of amorphous silicon: A historical background

Amorphous silicon was first nearly simultaneously described by Gay-Lussac^[1] and Sir Humphry Davy.^[2] They obtained a yellow to brown powder from reduction of SiF₄ with potassium that released hydrogen upon hydrolysis and gave SiO₂ after igniting in air. Similarly, Berzelius isolated that material starting from K₂SiF₆^[3] and in 1833 he replaced SiF₄ by its chlorine analogue SiCl₄ as silicon source.^[4] In 1855 Deville replaced sodium by potassium as reducing agent.^[5] In 1857 Buff and Wöhler reported an optimized synthesis of amorphous silicon starting from crystalline material that was treated with gaseous hydrogen chloride. Subsequent thermal decomposition of the chlorosilane-containing vapor resulted in the deposition of the brown silicon.^[6] First attempts to use anhydrous quartz sand and magnesium for silicon production were reported by Phipson,^[7] a deeper insight into this reaction was published by Gattermann.^[8] Vigouroux successfully isolated clean silicon not

only reacting sand and Mg,^[9] additionally he reported about the reduction of a SiO₂/K₂SiF₆ mixture with aluminum.^[10] More milestones in the history of amorphous silicon are reported in the literature: Reduction of SiF₄ with sodium^[11] and the addition of aluminum as “solvent” for silicon to separate from Na₂SiF₆. Similarly, the reduction of quartz by Al in the presence of cryolite is reported in reference [12]. The resulting Al/Si mixture was heated to a white glow and poured into cold water to give amorphous silicon separated from aluminum. Roll suggested that the different properties of amorphous silicon described in literature so far mainly depended on the kind of preparation and the work up methods. He claimed the amorphous material as a “solution of SiO₂ in silicon” and concluded that reactivity is “mostly determined by the different impurities introduced by the synthetic methods used”.^[13] In 1952 Köster and Schwarz were successful to produce amorphous silicon by pyrolysis of silicon chlorides and obtained first evidence for crystalline silicon resulting from thermal treatment of the amorphous material.^[14] Today the most common reaction for amorphous silicon production is the reduction of silicon tetrafluoride with potassium at 140–200 °C,^[15,16] or the pyrolytic decomposition of silane, SiH₄, at temperatures above 500 °C, whereas the pyrolysis of trichlorosilane, HSiCl₃, at T > 1000 °C and in the presence of hydrogen preferably leads to crystalline material.^[17]

In general, the chemical reactivity of amorphous silicon mostly depends on the synthetic conditions of its preparation and the different particle sizes obtained.^[13] Based on experiments performed in our laboratories it was found that amorphous silicon slowly starts to crystallize at temperatures

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higher than 800 °C, crystallization becoming faster with increasing temperatures. This crystallization was carefully investigated and proven by powder diffractometry and is thus generally implying that high reaction temperatures (e.g., melting temperature) or even ignition of the amorphous silicon might induce crystallization of the material. This effect might change the reactivity of the silicon samples originally used.

Oxidation with oxygen gives SiO₂: The smaller the particles, the higher is the silicon reactivity.^[1,18] Pure oxygen reacts more vigorously than air,^[19] although some brown amorphous silicon is even self-igniting in air.^[1,20] Halides react with amorphous silicon differently: Whereas tetrafluorosilane is formed in a vigorous reaction already at room temperature,^[21] in a reaction with chlorine the amorphous material obtained from SiF₄/K is self-igniting,^[1,22] but temperatures higher than 300 °C need to be applied for other silicon samples to achieve a reaction.^[10,22] However, after silicon activation with HF, this reaction is vigorous already at room temperature for these samples too.^[23] The same is true for a reaction with bromine.^[23] For iodination to SiI₄, temperatures as high as 800 °C are required.^[24] Reactions of silicon with sulfur,^[19] boron,^[25] and phosphorus^[19,26] occur at comparably high temperatures (600–1000 °C, electric arc conditions). As expected, silicon hydrolysis slowly releases hydrogen to give SiO₂,^[27] but obviously needs activation by OH⁻ ions^[28] and requires boiling water for completion of SiO₂ formation.^[29] Oxidation with diluted nitric acid fails,^[19] evidently because of protection of the material by the formed oxide layer on the surface.^[19] In contrast, concentrated acid reacts violently with NO_x formation, obviously caused by a low hydrogen content within the amorphous material: Heating in vacuo or under exclusion of air (CO₂, H₂, or Ar atmosphere) prevents subsequent silicon oxidation.^[20d,23] The reactivity against hydrofluoric acid depends on particle size^[20d,30] as well as on HF concentration.^[31] Aqueous hydrogen chloride reacts only slowly,^[32] and dissolution of Si–Al alloys in aqueous HCl yields small amounts of silane;^[33] oxidation with aqua regia occurs slowly at 100 °C,^[22] the same is observed for oxidation with sulfuric acid.^[34] Amorphous, brown silicon reduces the concentrated acid to elemental sulfur.^[35] Reactions with nitrogen oxides require high temperatures (≈800 °C), rapid heating of the mixture leads to ignition of the sample.^[22] NH₃ reacts with ignited amorphous silicon under formation of silicon nitride and H₂.^[21a,36]

Oxygen fluorides react with amorphous silicon vigorously,^[37] whereas sulfur fluorides such as SF₆ and S₂F₂ do not react even with the red glowing material;^[38] SiF₄ is formed with SeF₄ and SeOF₂; metastable subfluorides result from silicon under SiF₄ atmosphere at the melting temperature.^[39] With dry HCl gas, mono- and dichlorosilane are formed at relatively low temperatures,^[40] the temperatures required to react with hydrogen bromide to give SiBr₄ and HSiBr₃ are around 350 °C.^[41] Phosphorus-containing compounds, such as P₂O₅ or PF₃, react with red glowing silicon under ignition,^[22,42] with PCl₅ tetrachlorosilane and PCl₃^[43] being formed after ignition of the mixture.

Due to its high reactivity, this literature overview proves amorphous silicon to be a useful material for the synthesis of a wide range of different products. The main problem for

a “non-technical” use is obviously caused by the laborious process of synthesis, mostly involving solid/gas reactions at comparably high temperatures^[16] or metals like magnesium^[9] or aluminium^[10] for the high temperature reduction of SiO₂ to give mixtures of solids, for example, SiO₂/Si/MgO/Mg, that are difficult to separate from each other. These reasons motivated us to perform the studies described in this paper.

Results and Discussion

Amorphous silicon: Synthesis and properties

Tetrachlorosilane is easily available directly from SiO₂-based materials by using a carbohydrochlorination reaction^[44] and as a byproduct in industrial large-scale processes, such as the Rochow–Müller Direct Process for dimethyldichlorosilane production^[20c,45] or the Siemens Process to produce photovoltaic and/or electronic grade silicon.^[17] Thus, SiCl₄ might become a promising candidate for silicon and silicone production in an experimentally simple technical process. As reaction partner for silicon reduction, sodium metal is recommended because of its broad availability. Moreover, sodium chloride as byproduct of reaction [Eq. (1)] can easily be recycled. For a quantitative reduction finely dispersed and molten sodium is required to react with liquid tetrachlorosilane under controlled conditions; therefore, diethylene glycol dimethyl ether (diglyme) was chosen as a high boiling solvent (b.p. 162 °C) for silicon preparation. In comparison to the literature,^[46] larger amounts of solvent were used to achieve better reaction control.

Furthermore, for a complete consumption of sodium, tetrachlorosilane is used in excess. In Table 15 in the Experimental Section, a series of reactions of SiCl₄ with sodium under varying conditions is listed. According to [Eq. (1)] from eight reaction runs, a brown powdery product mixture consisting of amorphous silicon and sodium chloride was isolated in nearly quantitative yields (>90%). This mixture is highly reactive and ignites spontaneously when exposed to open air, possibly supported by remaining traces of sodium (the Supporting Information, Figure 1) in the material.



Separation from sodium chloride formed during the reduction [Eq. (1)] is therefore very difficult. Washing the product mixture with water immediately initiates SiO₂ formation with release of hydrogen. EDX analysis of the dried residue (atomic percent: O 44.25, Na 0.10, Si 55.38, Cl 0.27%) shows that 66% of SiO₂ had been formed, only 33% of silicon remained. X-ray powder diffractometry proves both components to be completely amorphous. This result is supported by ESCA investigations of the solids.^[47] Interestingly the pH value of the resulting aqueous solutions depends on the excess amount of SiCl₄ added (the Experimental Section, Table 15). With an increasing excess of SiCl₄ the pH becomes smaller (basic 21% excess; neutral 25% excess; acidic 30% excess and more, Table 15).

Our explanation for this behavior is that during the reduction with sodium in diglyme obviously a part of the introduced

SiCl_4 did not react with sodium, but with the freshly formed silicon particles, whereby the silicon surface is covered with SiCl or, more likely, with SiCl_3 groups.^[46] This differs from the observations made for reactions of silicon reduction in apolar solvents, which are described later. The surface-bound silicon chloride does not react with sodium, which results in a basic NaCl solution when only little excess SiCl_4 is used, because the product contains unreacted sodium metal. Indeed, upon heating of a respective sample to the melting point of sodium (98 °C), small drops of metal are observed, which then, in the absence of a polar solvent, react with the brown, chloride covered silicon to result in small black spots inside the brown powder. A rapid reaction detected for the sodium-containing brown powder after addition of ethanol at room temperature therefore most likely is merely catalyzed by sodium alcoholate, supporting the alkoxylation of silicon and thus releasing hydrogen gas. Instead, the brown, silicon chloride-covered silicon itself is reacting slowly, as confirmed by comparable reactivity studies with sodium-free samples isolated from experimental runs giving acidic pH values of the resulting water solutions (entries 3, 5, 7, and 8 in Table 15).

To get a deeper insight into the nature of the brownish amorphous silicon, a sample was hydrolyzed at room temperature and the resulting SiO_2 that is mixed with unreacted amorphous silicon, possibly deactivated by oxygen coverage of its surface, was filtered off. The obtained acidic aqueous solution was titrated with sodium hydroxide solution to give a molar ratio of 2.3 Si:1 Cl for the amorphous silicon ($\text{Si}_{2.3}\text{Cl}$).

For investigation of heterogeneous reactions and desorption processes from solid-state surfaces^[48] photoelectron (PE)- and mass (MS) spectroscopic techniques are well-described methods. Molecules or fragments released into the gas phase are identified by their typical ionization^[49] and mass fragmentation patterns under high and ultra-high vacuum conditions.^[50] Accordingly, a sample of the carefully vacuum dried amorphous material was heated or pyrolyzed, respectively, under vacuum and the gaseous desorption- and decomposition products were detected by He(I) PE and quadrupole mass spectroscopy and identified based on their characteristic ionization energies IE_v and the fragmentation patterns.^[49a,51] In a temperature range from about 50 to 350 °C the solvent diglyme and unreacted tetrachlorosilane desorb from the silicon surface. At about 300 °C thermal decomposition of the polyether starts, giving carbon monoxide, methane, ethene, ethine, methanol, ethanol, formaldehyde, and acetaldehyde.^[51] Besides traces of hydrogen chloride, methyl chloride is detected at temperatures above 350 °C.^[51] The formation might be explained by a bimolecular reaction of methyl radicals with HCl or SiCl_4 in the gas phase or at the surface of the amorphous silicon, respectively.^[50c,52,53] Between 500 and 700 °C quite remarkable amounts of hydrogen and of methyltrichlorosilane are detected besides SiCl_4 ^[49a,51b] that still remains the main desorption product. Obviously, hydrogen is formed besides carbon monoxide from the thermal decomposition of diglyme under exclusion of oxygen. In this temperature regime methyl radicals react with SiCl_4 in the gas phase or at the silicon surface to give MeSiCl_3 , in competition methyl chloride is formed. At temperatures

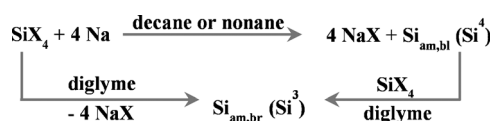
higher than 800 °C no further desorption of compounds from the silicon sample is observed.

To check the reactivity of the polar silicon–chlorine bonds in the amorphous material, samples were treated with ammonia, either in gaseous or in liquid form, to yield an amino-substituted derivative: The resulting black amorphous powder releases ammonia into the gas phase at temperatures higher than 100 °C as detected by PE and mass spectroscopy.

These results clearly prove that diglyme acts as a donor solvent that, as well as trichlorosilyl groups, is interacting with the silicon surface. The latter interaction obviously mainly determines the high reactivity of the material caused by the silicon chlorine functionality; moreover, surface chemistry occurs reacting the amorphous powder with donor molecules, for example, ethers or ammonia.

In contrast to the brown material described above, black amorphous silicon is prepared by reduction of SiCl_4 with molten Na metal in an inert, aprotic, non-polar solvent (e.g., toluene, *o*-xylene, nonane). Tetrachlorosilane is reduced quantitatively, the accruing NaCl amounts to 90 wt% of the generated powder.^[47] Reactivity studies are conducted with the NaCl/Si mixture without further purification.

Noteworthy, silicon tetrafluoride gas is reacting with alkali metals very similar to its chlorine counterpart. Bubbling of SiF_4 gas to the finely dispersed alkali metal, preferably sodium, in diglyme as donating and polar or, for example, toluene or decane as non-polar solvents, results either in a quantitative formation of the brownish or of the black amorphous silicon, admixed with sodium fluoride. The higher the reaction temperature, the faster the reduction occurs. Thus, the reaction rate of reduction increases corresponding to the increasing boiling points of toluene (b.p. 110 °C) < xylene (b.p. 143 °C) ≪ nonane (b.p. 148 °C) < decane (b.p. 171 °C) using potassium or sodium that are more reactive than magnesium and lithium: $\text{K} \approx \text{Na} > \text{Mg} \approx \text{Li}$. Dispersing the amorphous black silicon obtained in non-polar solvents in diglyme does not change the appearance of the material; after addition of some more SiX_4 (X = Cl, F), the material however completely changes into the yellow-brownish amorphous silicon. These results are summarized in Scheme 1 for sodium as a reducing agent.



Scheme 1. Reduction of tetrahalosilanes SiX_4 (X = Cl, F) with alkaline metals and magnesium. Reaction rates: $\text{K} \approx \text{Na} > \text{Mg} \approx \text{Li}$; decane > nonane ≫ xylene > toluene; am = amorphous, bl = black, br = brown.

During the reactivity studies it became obvious that traces of bases like NaOH or Na_2O have tremendous influence on the reaction behavior of the Si/NaCl mixtures. Therefore, the initial preparation of the metal, cutting off the oxide layer of the commercial sodium pieces, weighing and transferring into the reaction flask immediately, did not result in sufficiently oxide-free metal surfaces. Even the small amount of oxide generated

during the initial workup, which definitely amounted to only a few ten mg, sufficed to determine the reactivity of the product mixture in subsequent reactions. The silicon produced from an oxide covered sodium is defined as $\text{Si}_{\text{am(ox)}}$. To produce an completely sodium oxide-free product mixture, a more sophisticated procedure is applied that is described in the Experimental Section.

Amorphous silicon generated from a oxide-free sodium is defined as $\text{Si}_{\text{am,bl}}$ and $\text{Si}_{\text{am,br}}$ (Scheme 1).

For comparison reasons we investigated the silicon stability towards a variety of reaction partners for different samples:

- Commercially available metallurgical grade silicon 99.5% purity, 0–70 μm , Si_{metr} denoted as Si^1 .
- Amorphous yellow-brownish silicon powders obtained from SiO_2 reduction with magnesium according to the literature^[7–9] and as described in the Experimental Section, listed as Si^2 and amorphous silicon $\text{Si}_{\text{am,br(ox)}}$ and $\text{Si}_{\text{am,bl(ox)}}$ for (ox) containing small traces of oxidized sodium (Na_2O , NaOH). These samples are denoted as $\text{Si}^3_{(\text{ox})}$ and $\text{Si}^4_{(\text{ox})}$, respectively, the respective oxide-free samples are Si^3 and Si^4 .

Reactivity studies of different silicon samples towards oxygen and air with the formation of silicon dioxide

For comparison reasons we first investigated the reactivity of the crystalline metallic silicon Si^1 and the amorphous material Si^2 towards pure oxygen.

The experiments were carried out inside a heated glass tube. The samples of 3–4 grams each were placed on a ceramic support and heated under a stream of oxygen to a constant temperature for 24 h. Afterwards the composition of the samples was analyzed by EDX and XRD measurements. The results of these experiments are listed in Table 1.

Table 1. Oxidation of Si^1 and Si^2 in a pure oxygen atmosphere.

T [$^{\circ}\text{C}$]	Si^1 Si_{oxid} [%]/XRD	Si^2 Si_{oxid} [%]/XRD
100	1.3/Si	6.1/Si
350	1.0/Si	6.8/Si, SiO_2
550	2.2/Si	8.2/Si, SiO_2
700	8.3/Si, SiO_2	37.0/Si, SiO_2
800	21.0/Si, SiO_2	48.5/Si, SiO_2
1000	25.2/Si, SiO_2	53.7/Si, SiO_2
1200	47.9/Si, SiO_2	59.8/Si, SiO_2

The largest increase concerning the oxidation grade is detected for Si^2 at 700 $^{\circ}\text{C}$, whereas significant oxidation of Si^1 occurs not before 800 $^{\circ}\text{C}$ and the largest increase is found at 1200 $^{\circ}\text{C}$. Even at that high temperature the oxidation grade of metallurgical silicon is significantly lower than for amorphous silicon, but both samples have not reacted completely.

For the oxidation with air, different silicon samples were placed on a support and stored inside a chamber oven for 24 h at a constant temperature. Then, the composition of the samples was analyzed by EDX measurements. Samples applied were metallurgical silicon Si^1 , Si^2 , a sample of amorphous sili-

con $\text{Si}^3_{(\text{ox})}$ and $\text{Si}^4_{(\text{ox})}$, both samples with only traces of oxidized sodium; oxide free samples Si^3 and Si^4 immediately react with air and are thus admixed to the already sodium oxide-containing materials.

In contrast to Si^1 and Si^2 both samples $\text{Si}^3_{(\text{ox})}$ and $\text{Si}^4_{(\text{ox})}$ are characterized by a very high reactivity towards oxygen: For $\text{Si}^3_{(\text{ox})}$, the increase in oxidation grade occurs at a slightly lower temperature, but it is steeper than that of $\text{Si}^4_{(\text{ox})}$, in which the increase in oxidation grade with temperature is smoother. For Si^3 and $\text{Si}^3_{(\text{ox})}$, washing with water leads to a high oxygen content already. The final oxidation grade is almost reached at 150 $^{\circ}\text{C}$. The Si^4 and $\text{Si}^4_{(\text{ox})}$ samples oxidize readily on contact to air even at room temperature. These samples have not been heated to temperatures above 500 $^{\circ}\text{C}$, because the results were similar to Si^3 and $\text{Si}^3_{(\text{ox})}$ and temperatures of more than 700 $^{\circ}\text{C}$ should not be applied to prevent melting of NaCl . The remaining samples Si^1 and Si^2 are not even converted completely at 1200 $^{\circ}\text{C}$ and the final oxidation grade is similar to that of the experiments in pure oxygen. The experimental results are listed in Table 2 and in the Supporting Information (Figure 4: SEM micrographs of samples of Si^1 – Si^3 before and after oxidation; Figure 5: Si^1 – Si^4 samples heated in air: oxygen content [%] of silicon vs. temperature).

Table 2. Oxidation of different silicon samples in air.

T [$^{\circ}\text{C}$]	Si^1 Si_{oxid} [%]	Si^2 Si_{oxid} [%]	$\text{Si}^3/\text{Si}^3_{(\text{ox})}$ Si_{oxid} [%]	$\text{Si}^4/\text{Si}^4_{(\text{ox})}$ Si_{oxid} [%]
25	–	–	42.0	40.6
100	2.0	5.0	54.8	47.6
150	2.5	6.4	58.0	52.0
200	2.9	6.4	55.4	56.6
300	3.1	8.3	56.5	59.6
500	3.4	11.6	58.7	58.0
550	3.5	12.4	59.3	–
700	6.2	21.2	59.8	–
850	13.3	41.5	61.5	–
950	33.9	56.6	60.0	–
1050	43.5	58.2	61.2	–
1200	50.8	59.8	62.9	–

The investigation of the reactivity towards air has been repeated with a fluidized bed containing 20–30 g of material (silicon or NaCl/Si mixture) inside a vertical tube (diameter 28 mm) heated to a constant temperature for 24 h (Table 3). Unlike the former investigation, the air was dried before it passed through the reaction tube from the bottom. The temperatures given were measured inside the samples. EDX investigations registered the oxidation grade of the samples.

Metallurgical silicon Si^1 is hardly oxidized in dry air up to temperatures of 900 $^{\circ}\text{C}$, in contrast to what was observed with oxygen and with storage in heated humid air. For Si^2 the oxidation behavior is similar to the one resulting for pure oxygen. Si^4 , which exhibited no change of color for 3 h in a stream of dried air at room temperature, showed oxidative color change within minutes when stored in contact with non-predried air. EDX measurements confirmed an Si oxidation grade of 32.8% after one week. When humid air was passed through a fluidized

Table 3. Oxidation of different silicon samples in dried air.

Si	T_{int} [°C]	Fraction of oxidized Si [%]	XRD
Si ⁴ /Si ⁴ _(ox)	150–350	change of color	
Si ⁴ /Si ⁴ _(ox)	400	70.7	amorphous
Si ⁴ /Si ⁴ _(ox)	460	80.1	amorphous
Si ²	100	0	Si
Si ²	460	6.0	Si
Si ²	700	37.0	Si, SiO ₂
Si ²	900	45.0	Si, SiO ₂
Si ¹	100	0	Si
Si ¹	400	1.2	Si
Si ¹	900	3.0	Si

bed of the same sample at room temperature, a color change was equally observed after a few minutes.

Reactivity of amorphous silicon Si⁴ with moisture

Furthermore, the reactivity of amorphous silicon Si⁴ with moisture was investigated. N₂ gas was saturated with water vapor at room temperature and then passed through a fluidized bed of the solid NaCl/Si mixture (20–30 g) for 24 h. The mixture exhibited a change of color after a few hours already at room temperature (Table 4). A white reaction mass (SiO₂/NaCl) was observed only at temperatures above 400 °C. EDX measurements reveal that even a white reaction product still contains unreacted amorphous silicon.

Table 4. Oxidation of Si⁴ in humid N₂

T_{int} [°C]	Fraction of oxidized Si [%]
RT	change of color
400	72.6
460	72.8
550	77.8

Comparison of the results in the fluidized bed reactor with experiments in a chamber oven shows a reduced reactivity of Si⁴ towards dried air. A color change is not observed below 150 °C, whereas an experiment with humid air in a fluidized bed led to a change of color within minutes at room tempera-

ture. The still diminished oxidation rate of Si⁴ stored on air in comparison to Si⁴_(ox) is influenced by the absence of basic sodium oxide in the reaction mixture. Amorphous silicon Si³ and Si⁴ without an aqueous workup still show the highest reactivity of the tested silicon samples.

Reactivity of amorphous silicon samples towards chlorine-containing reaction partners with formation of chlorosilanes

Due to their silicon–chlorine functionality, chlorosilanes serve as unique starting materials for the synthesis of most silicon based compounds and materials. Technically they are produced in multi-ton processes reacting elemental silicon with chlorine gas, hydrogen chloride, or organochlorides. Especially trichlorosilane and dimethyldichlorosilane are used as building blocks for the production of highly pure silicon (Siemens process)^[17] or for the entry into silicones production by the Rochow–Müller-Direct Process.^[20c,45] Moreover, tetrachlorosilane serves as precursor for the synthesis a variety of the tetrafunctional silanes of less reactivity, for example, for the large-scale production of tetraalkoxy-^[54] or acetoxy silanes.^[55] Thus, the reactivity of amorphous silicon samples towards chlorinating agents is of very basic interest and was consequently studied. For the investigation of the different silicon powders Si³ and Si⁴, reactions were conducted with chlorine gas, gaseous hydrogen chloride, and methyl chloride. The reaction products formed were analyzed by using NMR and GC/MS spectroscopic methods. Performing the experiments, samples of Si³ and Si⁴ were filled into a vertical quartz tube (diameter 28 mm) under protective gas and heated to the given temperatures (Tables 5 and 6). Then, the reactant gas was introduced from the bottom of the tube. The reaction products were collected in a cooling trap from the top of the apparatus and analyzed accordingly. The temperatures given in Table 5 for the reactions of Si³ are the actual reaction temperatures T_{int} measured inside

Table 5. Reactions of Si³ with gaseous reactants.

Reaction gas	Si ³ [g]	t [min]	T_{int} [°C]	Products
Cl ₂	9.00	40	140	SiCl ₄
HCl	5.75	60	417	Cl _{<i>n</i>} SiH _{4–<i>n</i>} ($n = 1–4$)
MeCl	5.27	30	559	SiCl ₄

Table 6. Reactivity of different silicon samples towards methyl chloride under the conditions of the Direct Process in a fluidized bed reactor.^[a] opt: optimum; max: maximum.

Si sample	Catalyst	T_{start} [°C]	T_{opt} [°C]	T_{max} [°C]	SiMe ₄ [%]	Me ₃ SiCl [%]	Me ₂ SiCl ₂ [%]	MeSiCl ₃ [%]	SiCl ₄ [%]
Si ¹	CuCl (5%), Sn _{tr} , ZnCl ₂ (0.8%)	530/490	580–610	650	–	≈ 1	20	79	–
Si ²	CuCl (5%), Sn _{tr} , ZnCl ₂ (0.8%)	360	480	500	–	< 1	5	95	–
Si ² [b]	–	600	650	700	–	–	< 1	99	–
Si ⁴ [c]	CuCl (5%), Sn _{tr} , ZnCl ₂ (0.8%)	330	380	380	–	9	15	76	traces
Si ⁴ [c,d]	–	350	450–475	475	–	–	10	90	traces

[a] NMR chemical shifts (¹H/²⁹Si in ppm) SiCl₄ (–20); Me₃SiCl (0.43/30); Me₂SiCl₂ (0.8/32); MeSiCl₃ (1.12/12.2) Me₂SiClSiClMe₂ (0.40/17.5); MeSiCl₂SiCl₂Me (0.63/18.0), Me₃SiSiMe₃ (0.02/–19.5). Product compositions were determined by GC/MS analyses and integration of the NMR signals. [b] Due to the high temperatures formation of highly chlorinated hydrocarbons from CH₃Cl is observed. [c] 10% in NaCl. [d] Due to the high temperature different methylchlorosilanes are formed, among those Cl₃SiSiCl₃ and Me₃SiSiMe₃ (detected by GC/MS analysis).

the reaction mass. The difference of the heating temperature of the oven amounts up to 90 °C.

If a reaction of Si³ with the introduced gas occurred, a color change of the NaCl/Si mixture from brown to grey or white was observed and the weight of the sample decreased. As soon as the reactions started, a white "smoke" of condensed reaction products could be observed in the top part of the reaction tube. The reactions were abolished as soon as the reaction mass color changed to white. Up to external 150 °C, no change in color was detected and no products were found in the cooling trap.

At external 200 °C (140 °C internal) Si³ reacted completely with chlorine gas. For the experiments with HCl and MeCl reactions occurred at 417 and 559 °C, respectively.

The cooling trap in the successful HCl experiments had a temperature of -40 °C to prevent condensation of HCl (b.p. -85 °C). The amount of liquid inside the cooling trap decreased to approximately one quarter upon increasing the trap temperature to 0 °C. When the temperature exceeded 10 °C, the residual liquid evaporated also. Unfortunately, the products were not analyzed by GC/MS, but the evaporation behavior suggests a product mixture consisting of H₂SiCl (b.p. -30 °C) and H₂SiCl₂ (b.p. 8 °C). An EDX analysis of Si³ after the HCl reaction showed (atom%): O, 6.29; Na, 39.36; Si, 2.46; Cl, 59.90. The fraction of silicon inside the reaction mixture has decreased.

To overcome this problem of a definite product identification, the reactions of Si³ with gaseous hydrogen chloride were studied by using PE and MS spectroscopy.

Based on the fact that this material releases relatively large amounts of tetrachlorosilane and diglyme, the samples were heated in an increasing temperature range starting from 200 to 400 °C at 10⁻² mbar for two days before reacting with hydrogen chloride. The reactions were performed at temperatures between 350 and 500 °C. At 400 °C tri- and tetrachlorosilane, HSiCl₃ and SiCl₄, were detected by using PE spectroscopy (molar ratio HSiCl₃/SiCl₄ ≈ 2:1). With increasing temperature (T > 400 °C) the formation of di- and monochlorosilane (H₂SiCl₂ and H₃SiCl), became stronger, but HSiCl₃ remained the main product. These results were also confirmed by using mass spectroscopic techniques.

When product condensation (white "smoke") was observed in an experiment with MeCl at 559 °C, the solid mixture changed its color during the reaction. Besides traces of methyltrichlorosilane, SiCl₄ was the only isolated product.

The reactions of Si⁴ (3–5 g of a NaCl/Si mixture) with Cl₂ (40 L h⁻¹) occurs at 240–250 °C to give SiCl₄ as the sole product (GC/MS). The reaction was abolished after 40 min when the product formation, detectable by a white "smoke" in the upper part of the apparatus, ceased. Si was not converted completely. HCl gas (20–30 L h⁻¹) reacts with Si⁴_(ox) at temperatures between 360–420 °C. Below 370 °C only two reaction products are detected: H₂SiCl₂ (15%) and HSiCl₃ (85%). For temperatures of 370–420 °C, the product composition changes to 36.44% H₂SiCl₂, 58.48% HSiCl₃, and 5.08% SiCl₄ (GC/MS). In both cases the reaction ceased after 15–20 min. Silicon conversion was still incomplete.

MeCl (20–30 L h⁻¹) reacted with amorphous black silicon Si⁴ at 560 °C without any additive. The reaction tube was slowly heated, until condensation of the products was detected. After the reaction had ceased, silicon was not completely consumed. The reaction products MeSiCl₃ (¹H NMR δ = 1.022 ppm, 79%) and Me₂SiCl₂ (¹H NMR δ = 0.688 ppm, 21%) were identified by using ¹H NMR spectroscopy. During an experiment at 600 °C, decomposition of MeCl occurred; the gas stream leaving the apparatus contained brown particles and carbon precipitated on the fixed bed.

This result is even more interesting because the brown material Si³ gave only tetrachlorosilane during reactions at high temperatures, with the product formation obviously caused by pyrolytic decomposition of the gaseous methyl chloride.

Therefore, reactions of black Si⁴ were performed in a fluidized bed reactor passing a gas stream of MeCl through 4 to 5 g of Si⁴. Reaction products were collected in a cooled trap (-78 °C) and analyzed by using GC/MS and NMR (¹H, ²⁹Si) spectroscopy, quantification occurred by integration of signals against defined standards. In contrast to Si³ samples, Me₂SiCl₂ was formed from Si⁴ in 20% yield at a reaction temperature of 550 °C. MeSiCl₃ was isolated as main product (≈ 80%). Increasing reaction temperatures led to thermal decomposition of methyl chloride and to the formation of tetrachlorosilane, SiCl₄. The silicon conversion rate after a reaction time of about one hour was 49%.

For optimization of the technical Direct Process to give Me₂SiCl₂ in yields above 80% catalysts and promoters are added to the metallurgical silicon. According to literature information^[20c, 45] copper and/or copper(I) chloride play an important role as catalyst, whereas tin and zinc chloride are added as promoters. Performing comparable reactions of different silicon samples under Direct Process conditions prove that the yield of Me₂SiCl₂ from amorphous silicon Si² and Si⁴ is even lower compared to Si¹. In all cases, formation of MeSiCl₃ is strongly preferred. Even at a reaction temperature of 380 °C, nearly 10% of Me₃SiCl are formed from Si⁴ in the presence CuCl (5%), Sn, and ZnCl₂ (0.8%).

The results of our investigations are listed in Table 6 and show that in no experiment Me₂SiCl₂ could be synthesized in acceptable yields. Obviously the reaction conditions were not comparable to the technical Müller–Rochow-Process.

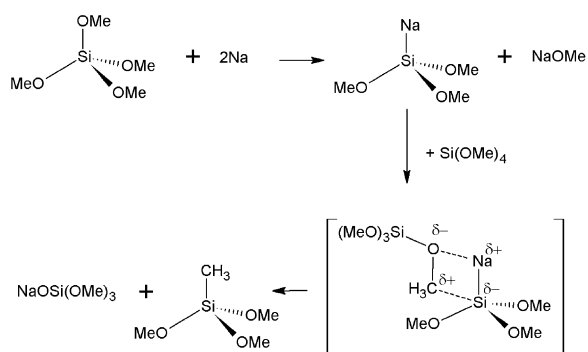
Reactivity of different silicon samples towards alcohols with formation of alkoxysilanes

Tetraalkoxysilanes are very important building blocks for products with a widespread field of different applications, for example, 1) they serve as suitable precursors for the production of colloidal sol–gel particles in sol–gel processes;^[56] 2) tetraethoxysilane is one of the main silicon based precursors for building ("stone") protection,^[57] and 3) most importantly, at temperatures above 200 °C, tetramethoxysilane is transferred into the substituted trimethoxysilanes (MeO)₃SiX (X = Me: 12.7%; X = H: 4.7%) by the use of sodium hydride,^[58] with sodium metal even the methyl-substituted derivatives

$\text{Me}_n\text{Si}(\text{OMe})_{4-n}$ are formed with an overall methylation degree of nearly 30% ($n=1$:22%; $n=2$:6.1%; $n=3$: possibly in traces).^[59]

As already mentioned, trichlorosilane and dimethyldichlorosilane are industrially most important feed stocks. The replacement of the silicon chlorine functionality against the less aggressive and less reactive alkoxy groups^[60] is heavily discussed as entrance into new technologies.^[61,62] Consequently, tremendous research efforts from both sides, academia and industry, focus on efficient synthetic routes for alkoxy silanes of the general formula $(\text{RO})_n\text{SiX}_{4-n}$ ($n=1-4$; $X=\text{Me}, \text{H}$; $\text{R}=\text{organo group}$) to replace the corresponding chlorosilanes in large-scale processes. Furthermore, compounds with hydrogen substituents at silicon serve as precursors for the synthesis of organosilanes through the addition of the Si–H functionality to carbon–carbon multiple bonds by the catalyst supported hydrosilylation reaction^[63] that may lead to new alkoxyfunctional organosilanes as starting materials for silicon-based polymers. For the classical synthesis of alkoxy- or aryloxysilanes, the corresponding chlorosilanes are treated with the respective alcohols to give the desired products.^[64]

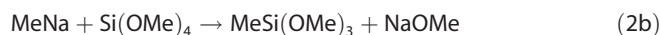
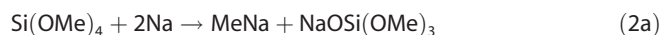
In the technically well-known “Crompton Process,” trialkoxysilane, $\text{HSi}(\text{OMe})_3$, is directly obtained from metallurgical grade silicon, methanol, and copper-based catalysts in a high-boiling aprotic solvent at temperatures between 150 and 450 °C in a “slurry phase reactor”. The yield of the product is nearly quantitative and the catalyst ammonium hydrogen difluoride, NH_4HF_2 , might be added as an activator.^[65] In addition, this reaction might open new entries for the synthesis of methyl-substituted alkoxy silanes $\text{Me}_n\text{Si}(\text{OR})_{4-n}$: $\text{MeSi}(\text{OMe})_3$ has been obtained as a byproduct in low yields during the synthesis of $\text{HSi}(\text{OMe})_3$. The methylation of silicon is best explained by a reduction of, for example, tetramethoxysilane at temperatures between 150–300 °C under the influence of a catalyst, for example, alkali metals, metal halides or hydrides, alkoxides, and amides or organic amines.^[59a,66] This is exemplarily shown in Scheme 2 for the treatment of tetramethoxysilane with metallic sodium.



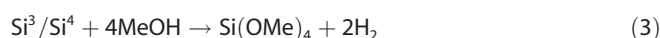
Scheme 2. Formation of methyl-substituted methoxysilanes from $\text{Si}(\text{OMe})_4$ and Na.

In the proposed three-step mechanism for the formation of $\text{MeSi}(\text{OMe})_3$, a sodium silyl derivative might be formed with

OMe abstraction to give NaOMe. Si–C bond formation obviously occurs from nucleophilic attack of a silyl group of $\text{Si}(\text{OMe})_4$. This reaction sequence might be duplicated to give the dimethoxy/dimethyl-substituted $\text{Me}_2\text{Si}(\text{OMe})_2$. Alternatively, Ryan favors a reaction sequence according to Equation (2 a, b).^[59a]



Summarizing and according to the literature methanol is a suitable reaction partner for highly reactive amorphous silicon for introduction of both, methoxy functionalities and methyl groups at silicon centers. Noteworthy, in the case of tetramethoxysilane hydrogen formation from Si^3 and/or Si^4 qualifies amorphous silicon as “hydrogen storage” material releasing this gas as a byproduct upon alcoholysis [Eq. (3)].



The reactions of amorphous Si^3 with methanol vapor were conducted in an externally heated vertical quartz tube (diameter 28 mm). Samples of Si^3 were filled into the tube and MeOH vapor from the boiling liquid was transported through the reaction mass by a stream of Ar at the given temperatures. The reaction products were collected in a cooling trap and analyzed by using GC/MS. Every reaction was abolished after 45 min.

First signs of a reaction were observed at 373 °C ($\text{MeSi}(\text{OMe})_3$ 16%, $\text{Si}(\text{OMe})_4$ 84%). All of the investigated reactions delivered only these two alkoxy silanes as products in different ratios. The maximum fraction of monomethylated silane was detected for a reaction temperature of 513 °C with more than 41% ($\text{Si}(\text{OMe})_4$, 59%). Higher temperatures were not applied because the alcohol decomposed.

Performing reactions of Si^3 with liquid methanol or ethanol, 50 mL of the respective alcohol were added to 3 g of the brown powder. If no reaction was observed, indicated by release of hydrogen, the mixture was heated to reflux.

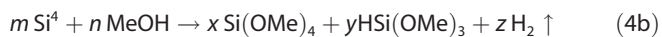
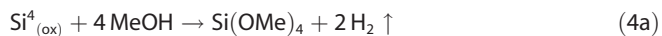
The “acidic” and the “neutral” brown powders did not react with alcohols, even after several days of boiling no silicon containing reaction product was identified in the solvent. The “basic” brown powder on the other hand produced hydrogen already at room temperature, but the reaction was finished (change of sediment color to white) only after several days of boiling. After the precipitate was filtered off under protective atmosphere, the major part of the alcohols were removed from the solution by distillation and $\text{Si}(\text{OMe})_4$ or $\text{Si}(\text{OEt})_4$, respectively, were identified by using $^1\text{H}/^{29}\text{Si}$ NMR spectroscopy in the remaining colorless liquid residue.

The explanation of this reaction behavior has been already discussed at the beginning of the manuscript when describing the syntheses of the amorphous brown silicon Si^3 .

For the investigation of the reactivity of amorphous silicon samples Si^4 and $\text{Si}^4_{(\text{ox})}$ with liquid alcohols, a weighed amount of the NaCl/Si product mixture (3–4 g) in general was transferred to a dried reaction flask under inert atmosphere and an

excess of the alcohol was added. The reactions proceeded while stirring.

Sodium oxide-containing NaCl/Si mixtures $\text{Si}^4_{(\text{ox})}$ [Eq. (4a)] and oxide-free Si^4 [Eq. (4b)] exhibit a distinctly different reaction rate and a different product composition with an excess of methanol at room temperature.



Sodium oxide catalyzes the reaction of silicon with methanol by the formation of sodium methoxide. The reaction proceeds under vigorous development of H_2 gas and the exothermal process heats the reaction mixture up to the boiling point of methanol. Depending on the specific amount of base inside the product mixture NaCl/Si, the reaction is finished after 30 min to a few hours. In the course of the reaction the formerly black powder first turns to dark brown, the color becomes brighter, and finally only white to light-gray NaCl remains. $\text{Si}(\text{OMe})_4$ is the only product of the reaction (^{29}Si NMR $\delta = -79.91$ ppm, GC/MS corresponds).

The reaction of Si^4 under the same conditions is distinctly slower. The volume of the powder increases upon addition of the alcohol and the temperature of the reaction mixture changes only moderately. Generation of hydrogen gas is slow. The color of the solid changes from black to brown, but the brightening of the color is too slow to be observed. The reaction has neither stopped nor is it finished after 3 d at room temperature. In contrast to the reaction in the presence of a base, the solvent *n*-hexane contains not only $\text{Si}(\text{OMe})_4$ (^{29}Si NMR $\delta = -79.91$ ppm, $\approx 84\%$), but also $\text{HSi}(\text{OMe})_3$ (^{29}Si NMR $\delta = -55.24$ ppm, $\approx 16\%$). Only after addition of a catalytic amount of sodium methoxide the reaction becomes rapid and proceeds to the end.

A similar reaction with ethanol and $\text{Si}^4_{(\text{ox})}$ leads to an exothermal generation of hydrogen. The reaction takes 2–3 h until completeness and $\text{Si}(\text{OEt})_4$ (^{29}Si NMR $\delta = -82.24$ ppm) is the only product. Oxide-free Si^4 reacts with ethanol slower compared with the reaction in methanol. After about 2 weeks, only 20% of the silicon is consumed to give $\text{HSi}(\text{OEt})_3$ (29%) and $\text{Si}(\text{OEt})_4$ (71%).

Reaction of amorphous silicon with methanol: Si–H versus Si–Me bond formation

The direct reaction of methanol with metallurgical silicon Si^1 , catalyzed by copper compounds and in a slurry with an inert solvent, is an established technical process.^[65,67]

The major product of the optimized reaction is trimethoxysilane $\text{HSi}(\text{OMe})_3$. The literature describes a variety of different inert solvents with high boiling points as suitable for the process, for example, biphenyls, oligophenylenes, dialkoxybenzenes, alkylated benzenes, polycyclic aromatic hydrocarbons, diphenyl ether, isoparaffine, tri- and tetraluene, dibenzylbenzene, as well as mixtures of these compounds. Comparatively low amounts of solvent are used for preparing the slurry, often

less than double of the silicon amount by weight. The influence of amine addition as a promoter to the slurry has been investigated.^[68] Copper metal and a number of different copper compounds, organic complexes as well as inorganic compounds, have been tested for the process, but often CuCl , Cu_2O , $\text{Cu}(\text{OH})_2$, or CuO are considered as most appropriate.^[69] Commonly, silicon grain sizes smaller than 500 μm are applied for the reaction. Sometimes pretreatment of the silicon with hydrofluoric acid is suggested to improve the reactivity. Reported laboratory-scale reactions are conducted with up to 1 kg of silicon. The described catalyst content of the slurry varies in the wide range of 0.005 up to 5%. The pressure during reaction experiments does not exceed 2 bar and usually atmospheric pressure is preferred. Reaction times can be as low as 1.5 h but may also exceed 24 h to improve the silicon conversion. Applied reaction temperatures are in general between 150 and 300 °C, with preferred values of about 200–240 °C. Methanol is introduced either as a liquid or as a vapor. Silicon conversions of more than 80% and $\text{HSi}(\text{OMe})_3$ contents of more than 90% in the product mixture are obtained. The indicated advantages of the slurry-phase reactors compared to fluidized bed setups are better control of the reaction temperature and the absence of a “fines” loss, which allows to apply smaller catalyst particle sizes to improve the results.^[70]

In addition, reactions of silicon with MeOH vapor in fixed or fluidized beds or in closed vessels are reported. For the open systems, silicon charges of up to 300 g for experimental runs are described and catalyst contents of up to 40% are reported. The selectivity for $\text{HSi}(\text{OMe})_3$ is similar to the slurry-phase reactions. Admixing thiophene or sulfur-containing compounds to the MeOH vapor results in the additional formation of $\text{MeHSi}(\text{OMe})_2$ in up to 22% yield, but with decreased silicon conversion.^[71]

Investigations in sealed tubes in general react amounts of only 0.1 g Si_{met} with grain sizes < 100 μm or atomized silicon. Besides 1–3% of the catalyst, an activator is also introduced to remove the SiO_2 layer from the silicon. This activators are HF or a HF-containing salt, like NH_4HF_2 or an alkaline hydrogen difluoride. The initially introduced liquid MeOH is 0.1 to 1 N in HF content. After the reaction starts at 150 °C for up to 10 h, the product mixture contains up to 17% $\text{H}_2\text{Si}(\text{OMe})_2$ in addition to $\text{HSi}(\text{OMe})_3$ and $\text{Si}(\text{OMe})_4$ depending on the reaction conditions. Other experiments yield up to 89% $\text{HSi}(\text{OMe})_3$.^[71,72]

As can be seen from Table 7, reproduction of the conversion in inert solvents was tried in dodecylbenzene or paraffin oil. Prior to the reaction, silicon and catalyst were heated to 220 °C under stirring in the solvent for 1 h. The products were not removed continuously and MeOH was very slowly added in 10% excess (up to 3 equiv of MeOH) by means of a dropping funnel and the products were distilled from the high boiling solvent after additional heating at reflux for 5–8 h. As expected, $\text{Si}^4_{(\text{ox})}$ and methanol reacted at 230 °C completely to $\text{Si}(\text{OMe})_4$, comparable to a reaction in *n*-hexane at room temperature. The currently best product composition with respect to trialkoxysilane formation was obtained by treating 4.19 g Si^4 in 40 mL dodecylbenzene with 4 wt% of Cu_2O (regarding Si amount) as catalyst. Si was not consumed completely. Accord-

Table 7. Reactions of amorphous silicon Si⁴_(ox) with methanol in a high boiling solvent.

Solvent	Amorphous silicon and reaction conditions	A ^[a]	B ^[a]	C ^[a]	D ^[a]
Paraffin oil	Si ⁴ _(ox) , 230 °C	–	–	–	100
Paraffin oil	Si ⁴ , 230 °C, 5 h, reflux	66.3	traces	traces	33.7
Paraffin oil	Si ⁴ , 230 °C, 8 h, CuCl, reflux	46.9	traces	traces	53.1
Paraffin oil	Si ⁴ , 230 °C, 8 h, Cu ₂ O, reflux	41.9	traces	traces	58.3
Dodecylbenzene	Si ⁴ , 230 °C, 8 h, Cu ₂ O, reflux	59.1	traces	0.8	38.1
Paraffin oil	Si ⁴ , 300 °C, "slurry phase"-reactor ^[b]	–	3.0	37.2	59.8
Paraffin oil	Si ⁴ , 300 °C, 3 h, T _{MeOH} = 150–200 °C, "slurry phase"-reactor ^[b]	–	2.3	51.3	46.4
Paraffin oil	Si ⁴ , 300 °C, CuCl, "slurry phase"-reactor ^[b]	–	10.1	31.8	45.1

[a] Values given are in percent. A: HSi(OMe)₃, B: Me₂Si(OMe)₂, C: MeSi(OMe)₃, D: Si(OMe)₄. [b] The conversion rate of silicon is ≈49%. Waxy to solid siloxanes are formed from side reactions, for example, hydrolysis of Si-methoxy groups to give silanols that condense with SiOSi formation.^[65] Product compositions were determined by GC/MS analyses.

ing to GC/MS analysis the product mixture consisted of 59.05 % HSi(OMe)₃, 38.11 % Si(OMe)₄, 0.82 % MeSi(OMe)₃, and 2.01 % of byproducts.

In contrast to the reactions giving trimethoxysilane in yields up to nearly 70 %, higher reaction temperatures using the "slurry phase conditions" (see the Experimental Section) and providing preheated methanol vapor to the amorphous silicon Si⁴ delivers trimethoxymethylsilane in yields up to 51 %. Admixing CuCl as catalyst to the silicon sample, even at 300 °C the dimethyldimethoxysilane is formed in 10 % yield besides MeSi(OMe)₃ (32 %) and Si(OMe)₄ (45 %). Under these conditions, silicon-carbon bond formation is strongly preferred over the Si-H formation; HSi(OMe)₃ cannot be detected in the product mixture at all. The addition of the catalyst and preheating of the alcohol seems to support the insertion of silicon into the Me-OH bond, finally giving methylsilanes.

To prove the general validity of the results described above, we treated samples of Si⁴ and Si⁴_(ox) with methanol vapor in a temperature range of 130 to 350 °C. For fixed bed reactions, the steam generated by boiling methanol was transported through the previously described vertical tube by a stream of Argon (6 L h⁻¹) to prevent recondensation, and the reaction products were collected in a cooling trap. Experiments have been conducted with and without addition of a catalyst to the sodium oxide-containing NaCl/Si mixture Si⁴_(ox) (3–5 g) and with sodium oxide-free Si⁴. The results obtained are listed in Tables 8 for Si⁴ and 9 for Si⁴_(ox). Table 10 contains the product mixture obtained for Si⁴_(ox) in the presence of CuCl (20 and 40 wt %, respectively) as catalyst.

As can be seen from Tables 9 and 10, the only reaction product of Si⁴_(ox) and methanol at temperatures below 130 °C is tetramethoxysilane. In the non-catalyzed reactions, the relative amount of Si(OMe)₄ decreases whereas the formation of methyltrimethoxysilane increases with higher temperatures. Although the same is true for both silicon samples Si⁴ (Table 8) and Si⁴_(ox), this trend is expectedly much stronger for Si⁴.

Interestingly, reactions with Si⁴ also yield HSi(OMe)₃ and Me₂Si(OMe)₂ as products: While the amount of trimethoxysilane is decreasing with increasing temperature, the yield of the dimethylsilane increases. Both products are not (or only in traces) formed from Si⁴_(ox). The presence of CuCl as catalyst

seems to support H- and methylsilane formation, but this effect is not very distinctive; Si(OMe)₄ by far remains the main product (Table 11).

Obviously, smaller amounts of the catalyst favor the formation of MeSi(OMe)₃ whereas bigger amounts increase the contents of HSi(OMe)₃ and of Me₂Si(OMe)₂ in the product mixture.

From Si⁴ and Si⁴_(ox), trimethoxysilane was obtained only in small yields from reactions with

Table 8. Reactions of Si⁴ with methanol/Ar without catalyst in an open system (fixed bed)^[a].

T [°C]	HSi(OMe) ₃ [%]	Me ₂ Si(OMe) ₂ [%]	MeSi(OMe) ₃ [%]	Si(OMe) ₄ [%]
150	5.21	2.59	12.59	79.62
200	7.30	2.60	17.45	72.65
240	2.67	1.34	19.08	76.91
260	1.91	5.09	27.36	65.64
300	0.13	7.22	36.95	55.70
350	0.22	12.72	36.87	50.19

[a] Product compositions were detected by GC/MS analyses.

Table 9. Reactions of Si⁴_(ox) with methanol/Ar in an open system (fixed bed, without catalyst)^[a].

T [°C]	HSi(OMe) ₃ [%]	Me ₂ Si(OMe) ₂ [%]	MeSi(OMe) ₃ [%]	Si(OMe) ₄ [%]	Byproducts [%]
132	–	–	–	≈100	traces
170	–	0.18	1.83	97.74	0.26
220	–	0.15	4.70	94.51	0.64
260	–	0.19	7.78	91.94	–
280	–	–	17.75	77.97	4.28
320	–	–	21.99	78.01	–
350	–	–	26.29	73.71	–

[a] Product compositions were detected by GC/MS analyses.

Table 10. Reactions of Si⁴_(ox) with methanol/Ar and 20 (top)/40 (bottom) wt % CuCl as catalyst in an open system (fixed bed)^[a].

T [°C]	HSi(OMe) ₃ [%]	Me ₂ Si(OMe) ₂ [%]	MeSi(OCH ₃) ₃ [%]	Si(OMe) ₄ [%]	Side products [%]
220	0.03	0.03	9.37	88.17	2.39
	0.86	0.47	7.87	90.41	0.40
280	0.07	0.05	11.09	88.59	0.18
	2.48	1.85	5.57	89.41	0.68
320	0.17	0.89	30.08	68.35	0.50
	1.86	1.60	15.38	80.02	1.14
350	–	–	27.37	59.81	12.82
	2.27	1.40	18.94	74.80	2.50

[a] Product compositions were detected by using GC/MS analyses.

Table 11. Reactions of sodium oxide/hydroxide free Si⁴ with methanol in sealed tubes^[a].

T [°C]	n (Si/MeOH)	HSi(OMe) ₃ [%]	Me ₂ Si(OMe) ₂ [%]	MeSi(OMe) ₃ [%]	Si(OMe) ₄ [%]
150	1:1	37.66	1.18	1.50	59.66
	1:2	46.56	1.11	1.74	50.59
	1:3	48.59	15.98	0.31	35.26
	1:4	64.55	2.15	0.58	32.72
200	1:1	25.08	0.39	0.40	74.12
	1:2	63.95	3.01	traces	33.04
	1:3	67.66	2.68	1.09	28.57
	1:4	58.16	1.68	0.30	39.86
250	1:8	69.47	1.05	0.99	28.49
	1:1	30.20	0.13	0.34	69.33
	1:2	62.28	0.32	traces	37.40
	1:3	1.96	0.36	0.57	97.11
300	1:4	4.26	0.53	0.19	95.02
	1:1	21.11	0.16	1.01	77.73
	1:2	23.27	0.15	0.35	76.28
	1:3	9.59	0.69	0.46	89.25
350	1:4	traces	0.68	0.32	98.99
	1:8	–	0.79	0.20	99.01
	1:1	12.61	0.52	6.26	80.61
	1:2	26.26	0.40	0.71	72.64
	1:3	9.25	0.54	0.91	89.30
	1:4	–	0.36	0.60	99.04

[a] The composition of the liquid product mixture was determined by using GC/MS analysis. Waxy to solid residues contained some amorphous silicon but mostly siloxanes (see footnote of Table 7 and ref. [65]).

Table 12. Reactions of Si⁴ and Si⁴_(ox) with MeOH in sealed tubes.^[a]

Reaction conditions	HSi(OMe) ₃ [%]	Me ₂ Si(OMe) ₂ [%]	MeSi(OMe) ₃ [%]	Si(OMe) ₄ [%]	Byproducts [%]
150 °C, 3 MeOH	45.72	10.14	–	43.80	remaining silicon
150 °C, 4 MeOH	–	–	0.03	≈ 100	–
	63.85	2.09	0.32	32.36	1.38
150 °C, NH ₄ HF ₂ , 3 MeOH	–	0.04	0.15	≈ 100	traces
	82.75	0.77	3.88	12.12	0.48
150 °C, NH ₄ HF ₂ , 4 MeOH	–	–	–	≈ 100	traces
	25.05	0.62	0.91	71.42	2.00
150 °C, CuCl, 3 MeOH	–	–	–	≈ 100	traces
	84.71	0.93	0.12	13.45	0.79
150 °C, Cu ₂ O, 3 CH ₃ OH	82.12	0.87	0.14	16.64	0.23
	64.34	0.82	0.18	31.32	3.34
150 °C, CuCl, 4 MeOH	–	–	–	92.46	7.54
	63.24	1.13	0.08	33.60	1.95
150 °C, Cu ₂ O, 4 MeOH	70.23	2.03	0.48	27.17	0.10
	58.60	1.78	0.08	38.80	0.74
150 °C, CuCl, NH ₄ HF ₂ , 3 MeOH	–	–	–	95.47	4.53
	58.59	0.14	0.04	37.42	3.81
150 °C, Cu ₂ O, NH ₄ HF ₂ , 3 MeOH	–	–	0.36	95.74	3.90
	79.73	–	0.05	14.91	5.31
150 °C, CuCl, NH ₄ HF ₂ , 4 MeOH	–	0.05	0.02	98.33	1.60
	53.29	–	–	43.37	3.34
150 °C, Cu ₂ O, NH ₄ HF ₂ , 4 MeOH	–	–	–	90.23	9.77
	43.59	0.33	–	54.56	1.52
220 °C, 3 MeOH	–	–	–	–	–
	14.03	–	–	73.96	12.01
220 °C, CuCl, 3 MeOH	–	–	–	–	–
	47.15	–	–	52.23	0.62
220 °C, Cu ₂ O, 3 MeOH	–	–	–	–	–
	42.16	–	–	56.66	3.18

[a] Reactions conducted under identical conditions with Si⁴ (top) and Si⁴_(ox) (bottom), for side reactions see footnote of Table 7 and ref. [65]. Product compositions were determined by GC/MS analyses.

methanol. This might be due to the dilution of Si by NaCl, which diminishes contact between catalyst and silicon or to the sodium oxide/hydroxide content of the reaction mixture that may catalyze the decomposition of HSi(OMe)₃. Upon the formation of Si–OR groups from silicon and alcohol, hydrogen gas is released that possibly is necessary to increase the yield of trimethoxysilane. Therefore conversions in sealed tubes were tested; simultaneously, the molar amount of methanol was varied to check a possible effect on product formation. The results are listed in Table 11.

The reactions in closed vessels require sealed tubes of appropriate size to prevent breaking due to the pressure at elevated temperatures. Ampoules of approximately 50 mL volume made from Duran glass were selected to conduct experiments with Si⁴/Si⁴_(ox) amounts inside the NaCl mixtures in the range of 100 mg. In a second series, a catalyst was added in amounts resulting in 5 wt% of Cu in comparison to Si⁴/Si⁴_(ox); the amount of activator was 5 wt% of the total sample weight and the reactions were abolished after 5 h. The pressure during reactions was calculated to stay below 8 bar. Reaction

conditions and results of these experiments are summarized in Tables 11 and 12, respectively. For comparison, conversion of metallic Si¹ under some of the experimental conditions was attempted, but without success.

As can be seen from Table 11 the molar ratio between tri- and tetramethoxysilane formed from reactions of base-free Si⁴ and methanol is mainly influenced by the reaction temperature and in the low temperature region by the molar ratio of silicon to methanol. In a temperature range from 150 to 200 °C, HSi(OMe)₃ (70%) is the main reaction product. Interestingly, a stoichiometric excess of methanol does not favor Si(OMe)₄ formation, but temperatures higher than 200 °C increase the amount of this silane by simultaneously diminishing that of HSi(OMe)₃. In a temperature region of 150–200 °C, a molar excess of methanol seems to strongly support HSi(OMe)₃ formation, already at T=250 °C the highest yield is obtained for a molar ratio Si/MeOH=1:2, the addition of more methanol results in

a nearly quantitative $\text{Si}(\text{OMe})_4$ formation. As expected, the course of reactions is influenced by use of a catalyst (Table 12). CuCl -catalyzed reactions gave higher yields of $\text{HSi}(\text{OMe})_3$ compared with those catalyzed by copper(I) oxide.

However, the molar amount of methanol seems to play a quite important role: An excess of alcohol yields tetramethoxysilane to greater extent. This result is also confirmed running the experiments in the presence of 5 wt% NH_4HF_2 . With a molar ratio MeOH/Si of 3:1 nearly 83% $\text{HSi}(\text{OMe})_3$ is formed. Instead, only 25% are obtained from a stoichiometric ratio of 4:1. Generally, the addition of NH_4HF_2 as an activator shifts the product composition in CuCl -catalyzed reactions to a stronger $\text{Si}(\text{OMe})_4$ formation. In contrast, the NH_4HF_2 activation in copper(I) oxide-catalyzed reactions with a Si/MeOH ratio of 1:3 increases $\text{HSi}(\text{OMe})_3$ formation, which is obtained in about 80% yield (Table 12).

Summarizing this series of experiments, the product compositions of $\text{Si}^{4(\text{ox})}$ reactions in the sealed tube confirm the hydride-decomposing effect of the base content. These reactions often deliver almost pure $\text{Si}(\text{OMe})_4$, which was to be expected considering the extended contact times of the primary reaction products with the solid. Only with CuCl as a catalyst is $\text{HSi}(\text{OMe})_3$ achieved from the conversion of MeOH with $\text{Si}^{4(\text{ox})}$. This indicates a reaction of the base with the metal chloride to give NaCl and less basic cuprous or copper oxide or hydroxide.

In contrast, the conversion of base-free Si^4 yields up to more than 80% of $\text{HSi}(\text{OMe})_3$ under appropriate reaction conditions. For a reaction without catalyst and activator, the formation of more than 10% of the dimethylated $\text{Me}_2\text{Si}(\text{OMe})_2$ is remarkable, whereas the monomethylated compound was not detected at all.

For comparison reasons, a series of experiments was run with ethanol and phenol instead of methanol. Silicon-ethyl or phenyl substitution was never detected, obviously because of steric reasons. The results of the reactions of Si^4 with ethanol are presented in Table 13 and clearly show a clean triethoxysilane formation at 150 °C. Increasing reaction temperatures diminish the yields of $\text{HSi}(\text{OEt})_3$, but this effect might be compensated with an molar excess of the alcohol. Condensation reactions of the ethoxysilanes formed obviously gave 1,3,5-triethoxycyclosiloxane as a side product besides some hexaethoxydisiloxane from decomposition reactions. Whereas the yield of $\text{HSi}(\text{OEt})_3$ only changes slightly with reaction temperatures, the yield of $\text{Si}(\text{OEt})_4$ is much higher at 300 °C compared with a reaction temperature of 150 °C. This is possibly best explained by the thermolysis of the main side product 1,3,5-triethoxycyclosiloxane, which is mostly formed at a temperature of 250 °C.

Experiments to react an excess of molten phenol with $\text{Si}^{4(\text{ox})}$ at temperatures between 70–220 °C (temperature limit of the heating bath) did not yield $\text{Si}(\text{OPh})_4$. For investigations at higher reaction temperatures, $\text{Si}^{4(\text{ox})}$ was placed inside a vertical reaction tube (diameter 28 mm) and heated to 420 °C. Molten phenol was added dropwise by means of a dropping funnel from the top of the tube and transported through the fixed bed by a stream of Ar. The product

Table 13. Reactions of Si^4 with ethanol in sealed tubes.

T [°C]	n (Si/EtOH)	$\text{HSi}(\text{OEt})_3$ [%]	$\text{Si}(\text{OEt})_4$ [%]	Side products [%]
150	1:3	78.17	6.64	15.19
250	1:3	63.74	2.20	33.05 ^[a]
300	1:3	65.38	33.49	1.12
200	1:8	70.49	15.68	13.83

[a] Mainly 1,3,5-triethoxycyclosiloxane. Product compositions were determined by using GC/MS analyses.

was collected in an ice-cooled flask at the bottom of the tube. Fractional distillation at 10^{-2} mbar and 225–235 °C yields $\text{Si}(\text{OPh})_4$ (m.p. 52–53 °C, ^{29}Si NMR $\delta = -101.89$ ppm). To confirm the formation of the reaction product, $\text{Si}(\text{OPh})_4$ was synthesized by the conversion of $\text{Si}(\text{OEt})_4$ with PhOH catalyzed by NaOEt ; the melting point and NMR spectra were identical.^[73]

Comparable reactions with oxide free Si^4 never yielded $\text{Si}(\text{OPh})_4$. The dark-brown-to-black color of Si^4 remained even at high temperatures. A high boiling product mixture (225–230 °C, 10^{-3} mbar) contained only polymeric material; no $\delta^{29}\text{Si}$ NMR signal could be detected for the product mixture.

From methoxysilanes to Si-methyl-substituted derivatives

According to Scheme 2 and based on our findings that especially samples of $\text{Si}^{4(\text{ox})}$ gave $\text{Si}(\text{OMe})_4$ upon reaction with methanol nearly quantitatively, thermolysis of methoxysilanes in the presence of Na looks attractive for the intermolecular introduction of methyl groups at a silicon center to give methylmethoxysilanes $\text{Me}_n\text{Si}(\text{OMe})_{4-n}$.^[59] Experimentally, $\text{Si}(\text{OMe})_4$ and $\text{MeSi}(\text{OMe})_3$ were reacted at 250 °C in sealed tubes with sodium in different molar ratios. After a reaction time of 20 h the liquid product mixtures were analyzed by using GC/MS. The results are listed in Table 14.

As can be seen from the Table 14, the conversion of tetramethoxysilane (molar ratio to Na corresponds to 1:1) gave a liquid product mixture that consists of compounds $\text{Me}_n\text{Si}(\text{OMe})_{4-n}$ with an overall methylation degree of about 75% ($n=1:36.7\%$; $n=2:27\%$; $n=3:11\%$), the products were identified by GC/MS measurements. Instead, from $\text{MeSi}(\text{OMe})_3$ only 12% of the di-

Table 14. Formation of methylmethoxysilanes $\text{Me}_n\text{Si}(\text{OMe})_{4-n}$ from precursors with $n=0$ and 1 (250 °C, 20 h)^[b].

Molar ratio methoxysilane/sodium	methoxysilane	A ^[a]	B ^[a]	C ^[a]	D ^[a]
1:1	$\text{MeSi}(\text{OMe})_3$	0.6	11.7	84.0	0.4
1:1	$\text{Si}(\text{OMe})_4$	11.0	27.0	36.7	25.3
3:1	$\text{MeSi}(\text{OMe})_3$	0.4	21.9	77.7	–
3:1	$\text{Si}(\text{OMe})_4$	2.2	3.2	10.9	83.6
10:1	$\text{MeSi}(\text{OMe})_3$	traces	traces	≈ 100	–
10:1	$\text{Si}(\text{OMe})_4$	traces	traces	traces	≈ 100

[a] Values given are in percent. A: Me_3SiOMe , B: $\text{Me}_2\text{Si}(\text{OMe})_2$, C: $\text{MeSi}(\text{OMe})_3$, D: $\text{Si}(\text{OMe})_4$. [b] For solid side product formation see the footnote of Table 7 and ref. [65]. Product compositions were determined by GC/MS analyses.

methyl derivative is formed, and most of the starting material remained unreacted. As expected, an increase of the molar amount of starting silane reduces silicon methylation drastically.

Exemplarily, the gas chromatogram of the tetramethoxysilane conversion into the methyl-substituted derivatives $\text{Me}_n\text{Si}(\text{OMe})_{4-n}$ is shown in Figure 1.

Conclusion

Amorphous silicon was synthesized in an experimentally simple way by treating tetrachloro- or tetrafluorosilane SiX_4 ($\text{X}=\text{Cl}, \text{F}$) with molten sodium metal in diglyme as the donor

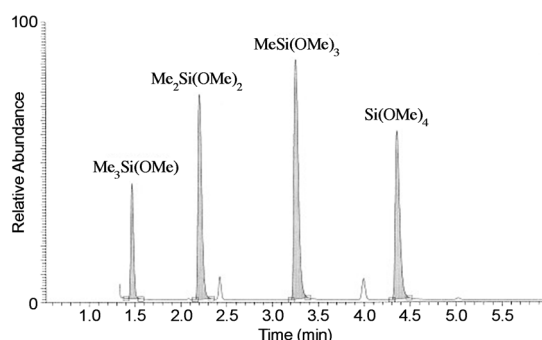


Figure 1. Product distribution in the liquid phase of the reaction of $\text{Si}(\text{OMe})_4$ with Na metal.

solvent or in high boiling apolar media (e.g., decane or toluene) to give either a brown or black amorphous solid, Si^3 and Si^4 , respectively, of high reactivity regarding oxidation to SiO_2 . For our reactivity studies we preferably used SiCl_4 to prepare the different Si samples because of the easier handling compared to gaseous SiF_4 . Separation of silicon from sodium chloride is possible but experimentally always difficult and combined with great losses of the silicon formed upon reduction. Thus, for reactions with suitable reaction partners NaCl is used as “solid solvent” to reduce and better control silicon reactivity. Interestingly, washing the brown amorphous silicon with water gives NaCl solutions with different pH values, depending on the molar amount of sodium used for SiCl_4 reduction. As demonstrated by a combination of PE- and MS spectroscopic investigations on the pyrolysis products of Si^3 , the surface of this material is obviously covered by chlorosilyl groups and solvent (diglyme) molecules. In addition, free sodium metal contaminates the amorphous powder mainly determining the high reactivity of that silicon, possibly including the spontaneous ignition at the open air. Therefore, we subsequently focused on reactivity studies on the black powder of Si^4 . The reactivity of the latter is strongly dependent from the reaction conditions used. Even small contaminations of basic sodium oxide or hydroxide, introduced by the sodium metal, dramatically change the reactivity of $\text{Si}^4_{(\text{ox})}$ compared to the base free Si^4 . These oxide/hydroxide contaminations often act as a catalyst, for example, in the reaction with alcohols to mainly give the tetraalkoxysilanes $\text{Si}(\text{OR})_4$ and releasing hydro-

gen gas as byproduct. Therefore, the sodium metal has to be carefully pretreated prior to reduction of SiCl_4 . In particular, the simple alcoholysis of $\text{Si}^4_{(\text{ox})}$ qualifies this material for hydrogen storage producing this gas decentralized at any place for its use in, for example, fuel cells or as energy carrier admixed to natural gas. This application is even more attractive as tetraalkoxysilanes are technically produced on large scale for a wide field of different applications. That is why we carefully checked the silicon stability towards oxygen, air and moisture—just to learn more about the possibility of silicon storage under ambient conditions required for its use as hydrogen storage material. As can be seen from Table 2 and [Eq. (3)], such application of Si^3 and Si^4 might be possible, but the silicon has to be kept under an inert atmosphere.

With respect to the two most important silicon-based industrial processes, the Müller–Rochow–Direct Process for Me_2SiCl_2 production and the Siemens Process using trichlorosilane as precursor for the production of highly pure silicon, the reactivity of amorphous silicon towards chlorine-containing reaction partners was investigated. Both samples of Si^3 and Si^4 react with chlorine gas at comparably low temperatures such as 140 and 240 °C to give quantitative yields of SiCl_4 . For hydrogen chloride as reaction partner the temperatures are around 400 °C, but besides selective trichlorosilane generation also the production of di- and monochlorosilane is possible, which are technically important for, for example, silicon layer depositions and difficult to produce on alternative routes.^[74] Methylation of amorphous silicon by use of methyl chloride with and without a catalyst and promoters mainly results in formation of methyl-trichlorosilane. Obviously, we failed to reproduce the exact conditions required for the technically relevant Direct Process, because comparable reactions with Si^1 that is technically used to produce Me_2SiCl_2 gave the same result, but at much higher temperatures (600 vs. ≈ 400 °C). Regarding the broad technical use of the chlorosilanes $\text{Cl}_n\text{SiH}_{4-n}$ ($n=3,4$) and of $\text{Me}_n\text{SiCl}_{4-n}$ ($n=1,2,3$) on one hand and the toxicity and corrosivity of chlorine and chlorinating agents RCl ($\text{R}=\text{H}$, organo groups) on the other hand, a future replacement of chlorine at silicon by less reactive alternative functional groups is in the focus of industrial research. For that, the introduction of alkoxy- and acetoxy^[75] functionalities at silicon centers look very attractive. Due to its broad availability methanol is a versatile reaction partner for silicon: Tetramethoxysilane formation releases hydrogen gas for decentralized use, insertion into the $\text{MeO}-\text{H}$ bond gives H-substituted alkoxy silanes, preferably $\text{HSi}(\text{OMe})_3$, and the insertion into the carbon–oxygen bond of $\text{Me}-\text{OH}$ is supported by the formation of thermodynamically very stable silicon–oxygen bonds to give methyl-substituted alkoxy silanes, here preferably $\text{Me}_n\text{Si}(\text{OMe})_{4-n}$ ($n=1, 2$). Indeed, whereas reactions of “basic” Si^3 and of $\text{Si}^4_{(\text{ox})}$ with liquid methanol give the tetraalkoxysilane already at room temperature, the alcoholysis of Si^3 with methanol vapor gave methyltrimethoxysilane in more than 40% yield at elevated temperatures. Generally, the reactivity of Si^3 and $\text{Si}^4_{(\text{ox})}$ towards methanol strongly depends on the conditions: Whereas treatment with Si^4 at 230 °C and in paraffin oil as solvent gave $\text{HSi}(\text{OMe})_3$ in nearly 70% yield, higher temperatures with preheated MeOH vapor deliver

about 50% of the methyl-substituted alkoxy silane MeSi(OMe)₃. In fixed bed reactions, Si⁴ and MeOH yield nearly exclusively MeSi(OMe)₃ and Si(OMe)₄. The molar ratio mainly depends on the conditions; increasing temperatures result in an enhanced yield of MeSi(OMe)₃, the addition of CuCl as catalyst supports tetramethoxysilane formation. Instead, changing the "open reaction system" into reactions in sealed tubes under hydrogen atmosphere increase HSi(OMe)₃ formation up to yields of ≈85% at comparably low temperatures (150–200 °C). The addition of NH₄HF₂ as activator or of copper catalysts seems to support product formation. Summarizing our investigations, we identified reaction conditions that finally gave HSi(OMe)₃ in nearly 90% and Si(OMe)₄ in 100% yield with a silicon conversion of 100%. The methylmethoxysilanes Me_nSi(OMe)_{4-n} were isolated in yields of about 50% (*n* = 1) and up to 16% for *n* = 2, but at much lower silicon conversion ratios (20–50%). For optimization of silicon dimethylation we performed the thermolysis of tetramethoxysilane over molten sodium to give methylmethoxysilanes with an overall methylation of about 75% at 250 °C within 20 h reaction time. Noteworthy, reactions of metallic silicon Si¹ with methanol under comparable conditions completely failed in our hands, product formation was never detected and therefore demonstrates the broad versatility of amorphous silicon for production of technically relevant compounds and materials from cheap and easily accessible precursors.

Experimental Section

General remarks

Unless otherwise noted, all starting materials are commercially available (Fluka) and are used without further purification. The tetrahalosilanes SiX₄ (X = Cl, F) were a gift from Wacker-Chemie GmbH, Burghausen, Germany and Dow Corning Corp., Midland, USA. All reactions involving organometallic compounds were carried out under argon using standard Schlenk techniques.

¹H and ¹³C NMR spectra were measured on a Bruker AM 250 (250 MHz for ¹H and 62.9 MHz for ¹³C) spectrometer and ²⁹Si NMR spectra were measured on a Bruker DPX 250 (49.7 MHz) spectrometer with [D₂]chloroform as solvent at room temperature. Chemical shifts are reported in δ (in ppm) with reference relative to the CDCl₃ peak for ¹³C and TMS peak for ¹H and ²⁹Si.

MALDI-TOF-MS were recorded with a mass spectrometer FISIONS-Instruments VG ToF Spec. Matrices were: nH (*M_r* = 168.2), DHB (*M_r* = 154.12), ATT (*M_r* = 144.2), and Esc (*M_r* = 178.15).

Preparation of dry solvents and reactants

n-Nonane, dodecylbenzene, *o*-xylene, and THF were heated at reflux over metallic sodium for at least five hours. The solvents were freshly distilled before use and stored under argon. *n*-Pentane was heated at reflux over sodium/potassium alloy for several hours. Par-

affin oil was heated at reflux over CaH₂ for at least five hours, filtered from solid residues (CaH₂ and Ca(OH)₂), and then distilled. The fraction boiling at temperatures below 350 °C was used as a solvent. Methanol was heated at reflux over metallic Mg for about eight hours and freshly distilled before use as reaction partner for amorphous silicon. Prepurified ethanol was dried by the addition of sodium metal (3 g per 1 L of EtOH) and heated at reflux for 3 h., then distilled, and stored under nitrogen atmosphere. Acetic acid was stirred over P₄O₁₀ for 24 h, then distilled, and stored under N₂. Phenol was heated to 120 °C in the presence of dry and active molecular sieve over 8–10 hrs.

Pretreatment of sodium metal

For the preparation of completely sodium oxide/hydroxide-free sodium samples, the thick oxide layer is cut off the commercial sodium pieces and the metal is transferred into a flask with isopropanol. Within about 5 min, the surfaces of the sodium pieces are cleaned by dissolving the oxide layer and conversion of some sodium into Na(OPr). Isopropanol and isopropanolate are removed by washing twice with dry THF or diethyl ether under an inert atmosphere. Afterwards the metal is transferred to the reaction vessel in a stream of protective gas and dried in vacuum. The amount of sodium is determined inside the reaction flask.

Reduction of tetrachlorosilane with sodium metal in diglyme

All reactions were conducted under exclusion of air and moisture and in an Ar protective atmosphere. Solvents were dried by commonly used methods and commercially available SiCl₄ purified by distillation prior to use. Performing the reaction according to Equation (1), diglyme containing solid sodium was heated to reflux. Rapid stirring then finely dispersed the molten sodium and SiCl₄ was added dropwise to the dispersion by means of a dropping funnel. The boiling temperature was controlled to stay above the melting point of Na. After the addition of SiCl₄ was completed, which took several hours, boiling was maintained until the boiling temperature remained constant. The reaction product was filtered from the liquid phase, washed twice with *n*-pentane, dried in vacuo, and finally isolated as a brown powder. Experimental details are given in Table 15.

Following the general procedure of silicon preparation, the amount of isolated product mixture "amorphous silicon/sodium chloride" was as follows: Run no. 1: 46.3 g; 2: 28.1 g; 3: 46.8 g; 4: 28.0 g; 5: 46.7 g; 6: 27.95 g; 7: 28.4 g; 8: 41.9 g.

Table 15. Series of reactions of SiCl₄ with sodium under varying conditions.

Run	Na[g]/[mol]	SiCl ₄ [mL] ^[a] /[mol] stoichiometric	introduced	Excess SiCl ₄ [%]	Diglyme [mL]	T [°C]	pH value (NaCl soln.)
1	16.43/0.71	20/0.17	25/0.22	25	170	103–162	neutral
2	9.86/0.43	12.14/0.11	15/0.13	21	90	114–162	basic
3	16.43/0.71	20/0.17	32/0.28	60	245	150	acidic
4	9.86/0.43	12.14/0.11	15/0.13	21	164	107–162	basic
5	16.43/0.71	20/0.17	32/0.28	60	250	98–162	acidic
6	9.86/0.43	12.14/0.11	15/0.13	21	200	112–161	basic
7	10.00/0.43	12.31/0.11	16/0.14	30	200	157	acidic
8	14.45/0.63	18/0.16	24/0.21	33	240	130–158	acidic

[a] For a complete consumption of sodium, tetrachlorosilane was added in excess.

In a similar procedure starting from 16.43 g Na (0.71 mol) and 18 g SiF₄ (0.17 mol), 34.5 g of a solid mixture Si/NaF was isolated (representative experiment).

Preparation of black amorphous silicon

The solvent toluene, *o*-xylene or nonane containing the sodium metal was heated to reflux under rapid stirring to generate a fine dispersion of the molten sodium. Freshly distilled SiCl₄ was injected with a syringe in portions of approximately 2 mL into the boiling dispersion. The boiling temperature of the mixture was indicated through an internal thermometer to prevent solidification of the sodium during the reaction. The introduced amount of SiCl₄ was completely consumed when the boiling temperature reaches the initial value again. Depending on the solvent, the reactant portion was consumed within a few minutes to a quarter of an hour. The reaction was finished as soon as the temperature did not rise back to the initial value but stood at a lower level for 1 h. After cooling to room temperature, the generated black powder was filtered from the inert medium by means of a Schlenk frit, washed twice with dry *n*-pentane, dried under vacuum, and stored under protective gas. In two representative experiments starting from 16.43 g Na (0.71 mol) and 28.9 g SiCl₄ (20 mL, 0.17 mol) (SiF₄: 18 g (0.17 mol)), 45.9 g of solid Si/NaCl (34.2 g Si/NaF) mixture were isolated and directly subjected to subsequent following reactions. To secure a complete sodium conversion, SiCl₄ or SiF₄ might be added in 10% excess.

Reduction of SiO₂ with Mg metal

For most methods of generating amorphous silicon reported in literature, non-crystallinity at inspection under a microscope is the only common definition of "amorphous". A method that is easy to reproduce in a laboratory on a comparatively large scale is the reduction of SiO₂ with Mg metal [Eq. (5)]. Supporting our reactivity studies on amorphous silicon against oxygen and air, for comparison reasons this material was included into our studies. It was basically prepared according to ref. [76] with some experimental modifications. These experiments are described below:



The vigorous reaction leads to initially molten and therefore, after cooling, crystalline silicon, but by addition of MgO to the reaction mixture the resulting temperatures can be limited to a level that allows the formation of an amorphous product.^[29b,76]

A mixture of SiO₂/Mg/MgO = 3:6:2 by molar amount is filled into a heat-resistant crucible and ignited by means of a sparkler. The resulting brown-to-grey powder (besides elemental silicon) consists of unreacted SiO₂, Mg and MgO, and often traces of Mg₂Si are detected during workup by the formation of self-igniting silanes. The powder is passed through a sieve and successively treated with diluted HCl, H₂SO₄, and HF. Each acid is washed from the product mixture with distilled water to neutral reaction before the next acid is applied. The dark-brown powder remaining after drying in air is the desired "amorphous" silicon. X-ray powder diffraction proves an at least partial crystalline habit of the grains. Applied SiO₂ sources used for Mg-reduction were ICN silica 32–63, 60 Å, quartz sand from Azerbaijan and sand from Sahara. Magnesium was used as turnings or as powder.

The reaction is in all cases very fast and vigorous. No differences in the course of the reactions could be detected, independent of the types of starting materials. The reaction products were generally analyzed by X-ray powder diffraction, for one sample additionally

Table 16. Reduction of SiO₂ sources with Mg metal.

SiO ₂ source	Amount [g]	Mg	Amount [g]	MgO [g]	Yield [g]	Yield [%]	X-ray analysis
Si-1 silica	60.00	powder	38.00	27.00	10.68	38.10	pure Si
Si-2 silica	90.00	powder	72.00	40.50	18.53	44.10	pure Si
Si-3 silica	180.00	powder	144.00	81.00	23.21	–	pure Si
Si-4					3.47	–	Si, SiO ₂
Si-5 silica	35.90	powder	28.72	16.16	7.82	46.70	pure Si
Si-6 silica	35.90	turnings	28.72	16.16	5.92	35.30	Si, SiO ₂
Si-7 q-sand ^[a]	45.00	turnings	36.00	20.25	13.37	63.70	Si, SiO ₂
Si-8 Sahara	15.00	powder	12.00	6.75	4.90	70.00	Si, SiO ₂
Si-9 Sahara	15.00	powder	12.00	6.75	3.95	56.40	Si, SiO ₂
Si-10 Sahara	45.00	turnings	36.00	20.25	14.00	66.70	Si, SiO ₂

[a] q = Quartz sand from Azerbaijan

an EDX measurement for elementary analysis was conducted (Table 16).

Despite literature statements of yields larger than 90%, for our experiments 70% could hardly be reached. Especially during workup with HF product losses are inevitable.

With experiments Si-1 and Si-2 (Table 16), comparatively pure samples of silicon were generated. EDX analysis shows the following elemental content for Si-1 (atom%): Si, 90.60, O, 5.83; F, 2.10; Mg, 1.47. Si-3 and Si-4 are reaction products of the same experiment. The powder was divided into a coarse and a fine fraction by a sieve and the two fractions were handled separately. Si-3 contained no SiO₂.

The following experiments Si-5 and Si-6 (Table 16) used different sizes of Mg grains but identical amounts of starting materials. For Mg turnings, the yield was smaller and after workup, SiO₂ was detected in the product. In the final experiments, the silicon source was sand, which has a large grain size in comparison to the silica used before. Despite good overall yields, it was not possible to achieve products free of SiO₂. A SEM photograph of a sample of amorphous silicon is shown in the Supporting Information, Figure 4.

GC/MS-measurements and quantitative analyses

GC/MS spectra were recorded on a Thermo Quest Finnigan Quadrapol mass spectrometer Trace MS in combination with Trace GC 200 series on a RTX 200 column L 30 m ID 0.32 mm. As different compounds, in the present case alkoxy-silanes, show a compound specific mass spectroscopic fragmentation, for quantification of the percentage share in the composition of the product mixture corrections of the corresponding peak areas within the gas chromatogram are required. Exemplarily, a standard sample of the methoxy-silanes Me_nSi(OMe)_{4-n} (n = 0,1,2) and HSi(OMe)₃ was prepared in a molar ratio of 1:1:1:1 each. From this, and for four more diluted samples, GC/MS analyses were performed and from the corresponding peak areas the Response Factors were determined. For performance, all (i) integrals were added and the overall integral (I) is fixed to 100% for the complete sample. Due to the fact that the peak areas (FL_i) for each component in the mixture should be 1:1:1:1 for each methoxy-silane (Table 17) follows: FL₁·a = ΣI_i/i, FL₂·b = ΣI_i/I, FL₃·c = ΣI_i/I, FL₄·d = ΣI_i/I. From that the Response Factors **a**, **b**, **c**, and **d** can be calculated. The results are listed in Table 17.

Depending on the concentration of the samples investigated, the peak area for each compound was corrected with the corresponding Response Factor (correction factor). It is not surprising that the Response Factors for the methyl-substituted methoxy-silanes differ

Table 17. Response factors for GC/MS analyses of the diluted samples of the methoxysilanes.

Sample	HSi(OMe) ₃ a	Me ₂ Si(OMe) ₂ b	MeSi(OMe) ₃ c	Si(OMe) ₄ d
Standard	1.6777	1.0664	0.9001	0.7379
1. Dilution	1.7604	1.0621	0.8624	0.7514
2. Dilution	2.1072	1.0438	0.8233	0.7393
3. Dilution	2.6223	1.0160	0.7999	0.7224
4. Dilution	11.8841	0.9096	0.7288	0.6923

only in a small range, whereas those for trimethoxysilane show quite remarkable variations, especially with increasing dilution of the sample. In Tables 7 to 14 the corrected values for the product compositions are given. The same applies to the chlorosilanes in Tables 5 and 6 based on the corresponding standard mixtures.

Preparation of the catalysts CuCl and Cu₂O

Both catalysts were prepared according to ref. [77]. A copper(II) salt or a copper(I) salt, mixed with a copper(II) salt, was dissolved in concentrated hydrochloric acid at 70 °C. A reducing agent (NaHSO₃, Na₂S₂O₃, Na₂S₂O₅) was added to the hot solution to reduce Cu^{II} to Cu^I. During the reaction, a complex between CuCl and HCl was formed [Eq. (6)]:



Upon dilution of the resulting solution to pH 1–2, the unstable acid decomposes releasing HCl to give the white, only hardly soluble CuCl as a solid ($L_{\text{CuCl}} = 1.0 \times 10^{-6} \text{ mol}^2 \text{ L}^{-2}$). Cu₂O was yielded by neutralization of the copper(I) salt solution until a pH of 6.5–7 was reached. With increasing pH values, the black solid Cu₂O was precipitating. Both Cu^I solids were separated by filtration, washed with ethanol and diethyl ether, dried in vacuo, and stored under a nitrogen protective atmosphere.

Reactions of amorphous silicon with liquid alcohols and acetic acid

Portions of amorphous silicon/NaCl mixture (3–5 g, Si content ca. 12–20 mmol) were placed in a carefully dried and Ar-filled three-necked flask that was equipped with a magnetic stirrer and a dropping funnel. Under ice-cooling and stirring, 50 mL of the respective reactants were slowly added. After completion the reaction mixture was slowly warmed to room temperature and stirred until hydrogen release stopped. The reaction mixture was analyzed by using GC/MS and then heated at reflux until the reaction completely stopped. After filtration from remaining silicon and sodium chloride the products were distilled and characterized by using GC/MS and NMR spectroscopic methods.

Reactions of amorphous silicon with gaseous reactants at different temperatures

A quartz tube with 1 m length and an inner diameter of 6 cm and divided into two halves by a glass frit or quartz wool was placed inside a vertical oven. The quartz tube was connected with a gas inlet from the bottom and a cooling trap at the top side. The latter was generally cooled to –116 °C. Amorphous silicon containing NaCl (3–5 g, 12–20 mmol Si content), either admixed with a catalyst or without, was placed on the frit or quartz wool. For reaction temperatures above room temperature, the oven and reactor were heated to the elevated temperatures required to perform the desired reaction for at least 30 min under an inert atmosphere (N₂ or

Ar) before the reaction was started. Afterwards the gaseous reactants ($\approx 20 \text{ L h}^{-1}$, for example, O₂, air, HCl, MeCl) were passed through the tube from the bottom of the reactor, and the reaction products were collected in the cooling trap on top. In general, the start of a reaction is visible by change of the silicon color, by silicon consumption and formation of a white fog containing the silicon-based products. Usually the reaction time was about 30 min. After completion, indicated by the white residue of solid NaCl, the reactor was cooled down and the cooling trap warmed to room temperature. The products were usually characterized by GC/MS analysis and NMR spectroscopic methods. In case of reactions with gaseous methanol, the alcohol was heated in a flask at the bottom of the quartz tube to the boiling point and the vapor then transferred into the reactor by a stream of argon ($\approx 10\text{--}12 \text{ L h}^{-1}$). After completion, the work up was as described before. For reactions with acetic acid and phenol, both compounds were dripped into the reaction zone from the top of the reactor from the dropping funnel. The products were collected in a flask at the bottom of the quartz tube and identified as before. Additionally, in some cases, a propeller stirrer was placed inside the quartz tube for agitation of the reaction mass.

Reactions of amorphous silicon in a “simple slurry phase reactor”

The amorphous silicon/NaCl mixture (3–5 g, Si content 10–20 mmol) and the catalyst (5 weight %, based on silicon) in a high boiling solvent ($\approx 70\text{--}90 \text{ mL}$ paraffin oil or dodecylbenzene) was added into a 250 mL three-necked flask, which was equipped with a reflux condenser, a dropping funnel, a magnetic stirrer, and a thermometer. Under stirring the suspension was heated to the required reaction temperature. After activation of the catalyst (30 min at the reaction temperature), methanol was slowly dripped in. After completion ($\approx 2 \text{ h}$) the mixture was heated at reflux at 230 °C for eight hours. Finally, the reaction products were distilled off and analyzed accordingly.

Reactions in an “alternative slurry phase reactor”

A 250 mL three-necked flask with a stirrer, thermometer, a Liebig condenser connected to a small Vigreux column, and a gas inlet tube was dried by heating in vacuo. Then, the amorphous silicon/NaCl mixture (10–15 g, silicon content 39–59 mmol), the catalyst (5 weight %) and paraffin oil (125 mL) were placed in the reactor and it was heated to the reaction temperature under vigorous stirring for about 30 min. Methanol vapor, diluted with a stream of Ar ($8\text{--}10 \text{ L h}^{-1}$) was introduced into the suspension through the gas inlet and the reaction products, including excess methanol, were immediately distilled off from the reaction mixture. After a reaction time of 3 h, the product mixture was analyzed by using GC/MS analysis and NMR spectroscopy. To preheat the methanol vapor to 150–200 °C, a separate flask was heated to 260 °C and connected with the slurry phase reactor by a heated glass tube ($\approx 200 \text{ °C}$). Methanol was dripped into the flask in small portions from a dropping funnel and evaporated instantaneously. After completion, the next portion was added. In total 200 mL of methanol were transferred into the slurry phase reactor within 5 h.

Reactions of amorphous silicon in sealed glass tubes

A glass ampoule (length 12 cm, diameter 2 cm) was heated and dried in vacuo and then filled with argon. The silicon/NaCl mixture (1–1.5 g, Si content 4–6 mmol), the catalyst (5 wt %, based on silicon) and, if applicable, the activator (5 wt %, based on reaction

mass) were filled in under a protecting atmosphere (N₂ or Ar) and mixed. The ampoule was cooled to -116 °C and the calculated amount of methanol was added. The mixture was cooled to -196 °C (liquid N₂) evacuated and sealed. After warming to room temperature, the ampoule was heated to the respective reaction temperature in an oven. After completion of the reaction the ampoule was opened under an Ar atmosphere and the product mixture was analyzed accordingly.

Quantitative determination of silicon residues after separation of products

After isolation of the reaction products, the solid residues were stirred in diluted KOH solution. Precipitated silica gel was washed with diluted HCl and water to separate from sodium chloride. Alternatively, the NaCl might be washed off with pure water from the solid residues. The remaining silica gel was dried at 115 °C and then heated to 900 °C until the weight remained constant. Based on the amount of starting material and the amount of silicon dioxide formed, the silicon consumption is calculated.

Thermolysis of methoxysilanes Me_nSi(OMe)_{4-n} (n = 0,1) in the presence of sodium

A glass ampoule was dried, evacuated and filled with Ar. The alkoxysilanes and sodium were filled in molar ratios given in Table 14. The reaction mixture was cooled to -196 °C, evacuated, and sealed. After warming to room temperature, the ampoule was heated to 250 °C for 20 h in an oven. Performing these reactions the sodium metal was covered with a white, waxy solid; evidently methylmethoxypolysiloxanes had been formed in a side reaction. After cooling to room temperature, the ampoule was opened under argon and the products were analyzed by using GC/MS and NMR spectroscopy.

Syntheses of selected products (SiCl₄, Me_nSiCl_{4-n} (n = 1,2), XSi(OMe)₃ (X = OMe, H, Me), Si(OEt)₄, and of Me₂Si(OMe)₂ are reported in the Supporting Information.

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- [1] a) L. J. Gay-Lussac, L. J. Thenard, *Ann. Chim.* **1809**, 69, 204–220, p. 215; b) L. J. Gay-Lussac, L. J. Thenard, *Gilb. Ann.* **1809**, 32, 1–15, p. 11; c) L. J. Gay-Lussac, L. J. Thenard, *Recherches Phys. Chem. Paris* **1811**, 1, 313–314; d) L. J. Gay-Lussac, L. J. Thenard, *Recherches Phys. Chem. Paris* **1811**, 2, 1–73.
- [2] H. Davy, *Phil. Trans. R. Soc. Lond.* **1808**, 98, 333–370; *Phil. Trans. R. Soc. Lond.* **1809**, 99, 39–104.
- [3] J. J. Berzelius, *Ann. Physik Chem.* **1824**, 1, 204–205.
- [4] J. J. Berzelius, *Lehrbuch der Chemie, Vol. I*, (German translation by F. Wöhler), 3rd ed., Dresden–Leipzig **1833**, pp. 327–328.
- [5] H. Sainte-Claire Deville, *Comp. Rend.* **1855**, 40, 1034–1036.
- [6] H. Buff, F. Wöhler, *Liebigs Ann. Chem.* **1857**, 104, 94–109.
- [7] T. L. Phipson, *Proc. R. Soc. London* **1864**, 13, 217–218.
- [8] L. Gattermann, *Ber. Dtsch. Chem. Ges.* **1889**, 22, 186–197.
- [9] E. Vigouroux, *Comp. Rend.* **1895**, 120, 94–96.
- [10] E. Vigouroux, *Comp. Rend.* **1895**, 120, 1161–1164.

- [11] W. Hempel, v. Haasy, *Z. Anorg. Allg. Chem.* **1900**, 23, 32–42.
- [12] C. A. Winkler, *J. Prakt. Chem.* **1864**, 91, 193–208.
- [13] F. Roll, *Z. Anorg. Allg. Chem.* **1926**, 158, 343–348.
- [14] R. Schwarz, A. Köster, *Z. Anorg. Allg. Chem.* **1952**, 270, 2–15.
- [15] K. M. Sancier, US 4529576, **1985**.
- [16] a) A. Sanjurjo, S. Jose, US 4590043, **1986**; b) A. Sanjurjo, L. Nanis, K. Sancier, R. Bartlett, V. Kapur, *J. Electrochem. Soc.* **1981**, 128, 179–183; c) A. Sanjurjo, WO 83002443A1, **1983**.
- [17] a) A. F. Holleman, E. Wiberg, *Lehrbuch der Anorganischen Chemie*, 102 ed., de Gruyter, Berlin, **2007**, pp. 920 and 938; b) Although the term “amorphous” was initially used to describe a solid material that exhibited a powdery morphology without visible crystalline characteristics, today an amorphous solid can be characterized by the absence of the characteristic diffraction pattern in X-ray powder diffractograms. Such compounds in contrast to crystalline materials lack a long range order in their structures.
- [18] a) A. Sanfourche, *Comp. Rend.* **1929**, 188, 1672–1675; 189, 533–535; b) A. Sanfourche, *Comp. Rend.* **1934**, 199, 726–729.
- [19] a) J. J. Berzelius, *Pogg. Ann.* **1824**, 1, 169–230; *Ann. de Chim. et de Phys.* **1824**, 27, 2, 337–348; b) *Gmelins Handbuch der anorganischen Chemie, Silicium, Teil B*, 8th ed., Verlag Chemie, Weinheim, **1959**, p. 119; c) Y. Yamamoto, *Abstr. Rikwagaku-kenkyū-jo Ithō, Japan* **1940**, 13, 15–17.
- [20] a) W. Bernthaus, *Diss. Göttingen* **1910**, 1–74; b) *Gmelins Handbuch der anorganischen Chemie, Silicium, Teil B*, 8th ed., Verlag Chemie, Weinheim, **1959**, p. 117; c) E. Bonitz, *Angew. Chem. Int. Ed. Engl.* **1966**, 5, 462–469; *Angew. Chem.* **1966**, 78, 475–482; d) W. Manchot, H. Funk, *Z. Anorg. Allg. Chem.* **1922**, 120, 277–299.
- [21] a) E. Vigouroux, *Comp. Rend.* **1895**, 120, 367–370; b) H. Moissan, *Ann. d. Chim. et de Phys.* **1891**, 24, 6, 224–282.
- [22] E. Vigouroux, *Ann. de Chim. et de Phys.* **1897**, 12, 7, 5–74.
- [23] W. Manchot, K. Heinrich, H. Funk, *Ber. Dtsch. Chem. Ges.* **1921**, 54, 3107–3111.
- [24] a) C. Friedel, *Comp. Rend.* **1868**, 67, 98–101; b) R. Schwarz, A. Pflugmacher, *Ber. Dtsch. Chem. Ges.* **1942**, 75, 1062–1071.
- [25] H. Moissan, A. Stock, *Ber. Dtsch. Chem. Ges.* **1900**, 33, 2125–2131.
- [26] W. Blitz, *Ber. Berl. Akad.* **1938**, 99–110.
- [27] H. Küstner, H. Remy, *Phys. Z.* **1923**, 24, 25–29.
- [28] H. Moissan, F. Siemens, *Ber. Dtsch. Chem. Ges.* **1904**, 37, 2395–2397.
- [29] a) E. Wilke-Dörfurt, *Festschrift O. Wallach*, Göttingen **1909**, 671–684; b) *Gmelins Handbuch der anorganischen Chemie, Silicium, Teil B*, 8th ed., Verlag Chemie, Weinheim, **1959**, p. 119.
- [30] a) W. Manchot, *Z. Anorg. Allg. Chem.* **1922**, 124, 333–334; b) W. Manchot, H. Funk, *Ber. Dtsch. Chem. Ges.* **1930**, 63, 1441–1446.
- [31] C. Bedel, *Comp. Rend.* **1929**, 188, 1255–1275; 189, 180–182, 643–644.
- [32] a) Anonyme Veröff., *Met. Chem. Eng.* **1913**, 11, 102–103; b) *Gmelins Handbuch der anorganischen Chemie, Silicium, Teil B*, 8th ed., Verlag Chemie, Weinheim, **1959**, p. 120.
- [33] P. Urech, *Z. Anorg. Allg. Chem.* **1933**, 214, 111–112.
- [34] T. F. Banigan, *J. Ind. Eng. Chem.* **1922**, 14, 323.
- [35] a) W. Bernthaus, *Diss. Göttingen* **1910**, S. 1/74, 51; b) *Gmelins Handbuch der anorganischen Chemie, Silicium, Teil B*, 8th ed., Verlag Chemie, Weinheim, **1959**, p. 119.
- [36] a) E. Vigouroux, *Ann. de Chim. et de Phys.* **1897**, 12 (7), 5–153; b) *Gmelins Handbuch der anorganischen Chemie, Silicium, Teil B*, 8th ed., Verlag Chemie, Weinheim, **1959**, p. 121.
- [37] a) O. Ruff, W. Menzel, *Z. Anorg. Allg. Chem.* **1934**, 217, 85–92; b) O. Ruff, K. Stäuber, *Z. Anorg. Allg. Chem.* **1905**, 47, 190–202; c) H. Moissan, P. Lebeau, *Comp. Rend.* **1905**, 140, 1621–1626.
- [38] a) H. Moissan, P. Lebeau, *Bull. Soc. Chim. Fr.* **1902**, 27, 3, 230–236; b) L. M. Dubnikov, N. I. Zorin, *Žurnal obščej Chim. (Russ.)* **1947**, 17, 185–192.
- [39] E. B. R. Prideaux, C. B. Cox, *J. Chem. Soc.* **1928**, 1603–1607.
- [40] A. Besson, L. Fournier, *Comp. Rend.* **1909**, 148, 555–557.
- [41] W. C. Schumb, R. C. Young, *J. Am. Chem. Soc.* **1930**, 52, 1464–1469.
- [42] H. Moissan, *Ann. Chim. Phys.* **1885**, 6, 6, 433–467.
- [43] E. Berger, *Comp. Rend.* **1920**, 171, 29–32.
- [44] S. Nordschild, N. Auner, *Chem. Eur. J.* **2008**, 14, 3694–3702.
- [45] a) A. F. Holleman, E. Wiberg, *Lehrbuch der Anorganischen Chemie*, 102nd ed., de Gruyter, Berlin, **2007**, pp. 985, 988; b) E. G. Rochow, *J. Am. Chem. Soc.* **1945**, 67, 963–965.
- [46] D. Harwell, WO 0114250A2, **2001**.

- [47] Alternatively, the amorphous silicon can be completely separated from sodium chloride treating the latter at 1000 °C under high vacuum conditions (10^{-3} mbar). This is proven by powder diffractometry measurements and EDX analyses of different samples. Under these conditions, amorphous silicon slowly begins to crystallize (see the Supporting Information, Figures 2 and 3).^[14] Therefore, for our reactivity studies sodium chloride was generally not separated from silicon, instead, it was used as a "solid solvent" to reduce and therefore to better control the reactivity of the material against the respective reaction partners.
- [48] a) *Handbook of Chemical Vapor Deposition. Principles, Technology, and Applications (Materials Science and Process Technology Series)* (Ed.: H. O. Pierson), Noyes Publications, Berkshire, **1992**; b) *Surface and Thin Film Analysis. A Compendium of Principles, Instrumentation, and Applications* (eds: H. Bubert, H. Jenett), Wiley-VCH, Weinheim, **2002**; c) G. Wedler, *Lehrbuch der Physikalischen Chemie*, 3. Auflage, Verlag Chemie, Weinheim, **1987**; d) M. Henzler, W. Göpel, *Oberflächenphysik des Festkörpers* (Studienbücher Physik), 2. Auflage, Teubner Verlag, Stuttgart, **1994**; e) G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis*, Wiley, New York, **1994**; f) R. Pashley, M. Karaman, *Applied Colloid and Surface Chemistry*, Wiley, New York, **2004**; g) C. H. Bamford, C. F. H. Tipper, R. G. Compton, *Comprehensive Chemical Kinetics, Vol. 19 (Simple Processes at the Gas-Solid Interface)*, Elsevier, Amsterdam, **1984**.
- [49] a) A. Frost, *Oxidation von Chlorsilanen: Auf dem Weg zu Silanonen*, Diplomarbeit, J. W. Goethe-Universität Frankfurt a. M., **1999**; b) H. Bock, B. Solouki, *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 427–444; *Angew. Chem.* **1981**, *93*, 425–442; c) H. Bock, B. Solouki, G. Bert, T. Hirabayashi, S. Mohmand, P. Rosmus, *Nachr. Chem. Tech. Lab.* **1978**, *26*, 634–639; d) M. Kremer, *PE-spektroskopische Optimierung von Gas-Reaktionen*, Diplomarbeit, J. W. Goethe-Universität Frankfurt a. M., **1986**.
- [50] a) J. Elsner, *Gasphasen-Erzeugung und Reaktionen hochreaktiver Silicium-Fragmente*, Dissertation, J. W. Goethe-Universität Frankfurt a. M., **2004**; b) R. G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, New York, **1989**; c) W. Koch, M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, 2nd ed., Wiley-VCH, Weinheim, **2001**; d) H. Bock, *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 631–637; *Angew. Chem.* **1977**, *89*, 631–655; e) H. Bock, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1627–1650; *Angew. Chem.* **1989**, *101*, 1659–1682.
- [51] a) K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, S. Iwata, *Handbook of He(I) Photoelectron Spectra of Fundamental Organic Molecules*, Japan Scientific Societies Press, Tokyo/Halsted Press, New York, **1981**; b) *Gas phase ion energetics data in NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, P. J. Linstrom, W. G. Mallard, June **2005**, National Institute of Standards and Technology, Gaithersburg MD (<http://webbook.nist.gov/chemistry/>).
- [52] C. H. Choi, M. S. Gordon in *The Chemistry of Organic Silicon Compounds (The Chemistry of Functional Groups, Vol. 3)* (Eds.: Z. Rappoport, Y. Apeiloig) Wiley, Hoboken, **2001**, Chapter 15.
- [53] a) H. Neergaard Waltenburg, J. T. Yates, *Chem. Rev.* **1995**, *95*, 1589–1673; b) K. C. Pandey, T. Sakurai, H. D. Hagstrum, *Phys. Rev. B* **1977**, *16*, 3648–3651; c) H.-G. Yu, G. Nyman, *J. Chem. Phys.* **1999**, *111*, 6693–6704; d) R. Brückner, *Reaktionsmechanismen in der organischen Chemie. Organische Reaktionen, Stereochemie, moderne Synthesemethoden*, 3. Auflage, Elsevier Spektrum, München, **2004**.
- [54] a) L. N. Lewis, F. J. Schattenmann, T. M. Jordan, J. C. Carnachen, W. P. Flanagan, J. Wroneczynski, J. P. Lemmon, J. P. Anostario, M. A. Othan, *Inorg. Chem.* **2002**, *41*, 2608–2615; b) K. Winnacker, L. Küchler, *Chemische Technologie*, Band 6, 4. Auflage, **1982**, p. 833; c) S. Honda, S. Inaba, K. Koga, US 4752647, **1986**.
- [55] *Gmelins Handbuch der anorganischen Chemie, Silicium, Teil B*, 8th ed., Verlag Chemie, Weinheim, **1959**, pp. 185, 190.
- [56] a) U. Schubert, N. Hüsing, *Synthesis of Inorganic Materials*, 2nd revised and updated ed., Wiley-VCH, Weinheim, **2005**; b) C. J. Brinker, G. W. Scherer, *Sol-Gel-Science, The Physics and Chemistry of Sol-Gel-Processing*, Academic Press, Boston, **1990**; c) H. K. Schmidt, *Chemie in unserer Zeit*, **2001**, *35*, 176–184; d) W. Stöber, A. Fink, E. Bohn, *J. Colloid Interface Sci.* **1968**, *26*, 62–69.
- [57] G. Wheeler, *Alkoxysilanes and the Consolidation of Stone*, The Getty Conservation Institute, Los Angeles, **2005**.
- [58] F. J. Schattenmann, W. V. Ligon, P. Donahue, H. Grade, K. Abatto, *Organometallics* **2004**, *23*, 6202–6204.
- [59] a) J. W. Ryan, *J. Am. Chem. Soc.* **1962**, *84*, 4730–4734; b) D. L. Kleyer, J. L. Speier, EP 0430272A2, **1991**.
- [60] *Gmelins Handbuch der anorganischen Chemie, Silicium, Teil B*, 8th ed., Verlag Chemie, Weinheim, **1959**, pp. 329–332.
- [61] W. Noll, *Chemie und Technologie der Silicone*, 2. Auflage, Verlag Chemie, Weinheim, **1968**, pp. 60–63.
- [62] L. N. Lewis, F. J. Schattenmann, T. M. Jordan, K. Abatto, J. C. Carnahan, W. P. Flanagan, R. J. Wroczynski, J. P. Lemmon, J. M. Anostario, M. A. Othon, W. V. Ligon, P. Donahue, H. Grade, J. P. Ray, K. P. Davis, D. Rohr Jr., S. Buddle in the proceedings of *Silicon for the Chemical Industry VI* **2002**, Trondheim, pp. 103–114.
- [63] M. A. Brook, *Silicon in Organic, Organometallic and Polymer Chemistry*, Wiley, **2000**, pp. 401–421.
- [64] A. F. Holleman, E. Wiberg, *Lehrbuch der Anorganischen Chemie*, 102nd ed., de Gruyter, Berlin, **2007**, p. 947.
- [65] a) K. M. Lewis, R. N. Eng, H. Yu, S. R. Cromer, D. L. Bailey, F. D. Mendicino, T. E. Childress, J. S. Ritscher, R. L. Ocheltree in the proceedings of *Silicon for the Chemical Industry V* **2000**, Trondheim, pp. 151–169; b) K. M. Lewis, C.-L. O'Young, A. T. Mereigh, S. R. Cromer, R. N. Eng, J. S. Ritscher in the proceedings of *Silicon for the Chemical Industry VI*, **2002**, Trondheim, pp. 243–263; c) J. S. Ritscher in the proceedings of *Silicon for the Chemical Industry IV* **1998**, Trondheim, pp. 265–273; d) F. D. Mendicino, H. E. Bartrug, D. J. Boley, P. J. Burns, T. E. Childress, P. J. Collins, N. G. Delong, H. D. Furbee, J. E. Goldsmith, K. W. Hartman, L. G. Hawkins, T. L. Hays, J. W. Heintzman, M. A. Hershman, M. C. Houston, T. G. Hurley, C. S. Knoop, J. P. Kuch, S. Magri, E. E. Malson, W. D. Mercer, S. Miller, L. G. Moody, J. L. McIntyre, S. W. Nichols, R. L. Ocheltree, P. H. Paugh, R. L. Pirolo, M. R. Powell, T. A. Reed, J. S. Ritscher, C. L. Schilling, J. W. Smith, B. A. Snider, D. M. Wilcox, and J. T. Williams in the proceedings for *Silicon for the Chemical Industry IV* **1998**, Trondheim, pp. 275–294; e) C. L. Schilling, M. P. Bowman, P. J. Burns, T. Childress, F. D. Mendicino, R. E. Sheridan, S. M. Turner, W. T. Young, E. M. Graban, E. E. Malson, J. I. McIntyre, M. R. Powell, K. W. Hartman, S. Magri, G. Trotta in the proceedings for *Silicon for the Chemical Industry IV* **1998**, Trondheim, pp. 295–306; f) K. M. Lewis, H. Yu, R. N. Eng, T. E. Childress, F. D. Mendicino, T. A. Reed in the proceedings for *Silicon for the Chemical Industry IV* **1998**, Trondheim, pp. 307–327.
- [66] a) F. J. Schattenmann, EP 1236731A1, **2001**; b) F. J. Schattenmann, WO 01/77120A1, **2001**; c) F. J. Schattenmann, WO 02/14327A1, **2002**.
- [67] Y. Yamada, K. Harada, Nagoya, US 526047, **1993**.
- [68] F. D. Mendicino, US 4762939, **1988**.
- [69] a) B. T. Nguyen, J. L. Speier, US 19910709056, **1992**; b) B. T. Nguyen, J. L. Speier, US 5177234, **1993**.
- [70] a) K. M. Lewis, H. Yu, R. N. Eng, S. R. Cromer, C.-L. O'Young, A. T. Mereigh, US 2001-265153, **2002**; b) K. M. Lewis, R. N. Eng, S. R. Cromer, C.-L. O'Young, A. T. Mereigh, US 2001–265154, **2002**; c) K. M. Lewis, H. Yu, US 5728858, **1998**.
- [71] a) M. Okamoto, H. Abe, Y. Kusama, E. Susuki, Y. Ono, *J. Organomet. Chem.* **2000**, *616*, 74–79; b) H. Wada, Y. Kasori, S. Sasaki, K. Sakamoto, JP 86–171367 19860721, **1988**; c) H. Wada, Y. Kasori, S. Sasaki, K. Sakamoto, JP 86–128316 19860603, **1987**.
- [72] A. Brand, US 2002-0010354 A1, **2002**.
- [73] J. Kuis, H. I. Waterman, *Research Commun., Suppl. to Research* **1955**, *8*, 2.
- [74] A. F. Holleman, E. Wiberg in *Lehrbuch der Anorganischen Chemie*, 102nd ed., de Gruyter, Berlin, **2007**, p. 938.
- [75] Reactions of $\text{Si}^{\text{IV}}_{(\text{ox})}$ with acetic acid gives $\text{Si}(\text{O}(\text{OCH}_3))_4$, nearly quantitatively and at room temperature. Reactions of Si^{IV} with acetic acid do not occur, even with the boiling acid. That means the reaction is base catalyzed.
- [76] *Gmelins Handbuch der anorganischen Chemie, Silicium, Teil B*, 8th ed., Verlag Chemie, Weinheim, **1959**, pp. 2–3.
- [77] I.-B. Jeong, Y.-S. Kim, B.-Y. Lee, Y.-H. Kim, B.-S. Jeong M. S. Lee, US 2004–0221685A1.

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