Avoiding Carbothermal Reduction: Distillation of Alkoxyisilanes from Biogenic, Green, and Sustainable Sources

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Abstract: The direct depolymerization of SiO₂ to distillable alkoxyisilanes has been explored repeatedly without success for 85 years as an alternative to carbothermal reduction (1900° C to Si₅₆₆) followed by treatment with ROH. We report herein the base-catalyzed depolymerization of SiO₂ with diols to form distillable spirocyclic alkoxyisilanes and Si(OEt)₄. Thus, 2-methyl-2,4-pentanediol, 2,2,4-trimethyl-1,3-pentanediol, or ethylene glycol (EGH₂) react with silica sources, such as rice hull ash, in the presence of NaOH (10%) to form H₂O and distillable spirocyclic alkoxyisilanes [bis(2-methyl-2,4-pentanediolato) silicate, bis(2,2,4-trimethyl-1,3-pentanediolato) silicate or Si(eg)₄] polymer with 5–98% conversion, as governed by Eqs. (5) and (6) > 99.9999% pure which generate the by-product SiCl₄ (metallurgical grade, ca. 98% purity)), which is made by the carbothermal reduction of silica in a high-temperature capital-equipment- and energy-intensive process [see Eqs. (1–7); Me₂SiCl₃ is a silicone/polysiloxane precursor].

The much higher purities required for photovoltaic-grade (Si₅₆₆₆) and electronics-grade silicon (Si₅₆₆₆) necessitate additional processing steps, typically those of the Siemens process [Eqs. (5) and (6) 99,9999% pure which generate the by-product HCl (normally recycled).
Because all chlorosilanes and HCl gas are corrosive, toxic, and polluting, such production processes, including those used to produce fumed silica [Eq. (7)], require expensive and extensive safeguards, which add to the overall cost of the final products. Since Si$_{met}$ is a kinetic product (SiC is the thermodynamic product), its synthesis requires electric arc furnace processing at approximately 1900°C, thus adding to the overall cost even for the production of Si(OEt)$_4$ or Si(OME)$_4$. Likewise, precipitated silicas are most commonly made by the high-temperature fusion of sand with sodium carbonate, followed by dissolution and precipitation with H$_2$SO$_4$:

$$\text{SiO}_2 + \text{Na}_2\text{CO}_3 \xrightarrow{1500°C} \text{Na}_2\text{SiO}_3 + \text{CO}_2 \quad (8)$$

$$\text{Na}_2\text{SiO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{SiO}_2 + \text{H}_2\text{O} \quad (9)$$

As can be seen, each mole of Na$_2$SiO$_3$ produced releases one mole of CO$_2$ and requires one mole of H$_2$SO$_4$ to produce one mole of precipitated silica and one mole of Na$_2$SO$_4$, which must be disposed of. Thus the production of precipitated (ppt) silicas, such as those used as fillers in polymers (in tires, for example), as the abrasive in toothpaste, or in vacuum insulation panels, also requires high temperatures and generates unwanted by-products, in particular, CO$_2$ and Na$_2$SO$_4$. [11]

Reactions (1–7) begin with SiO$_2$, which is reduced to the metal (e.g. Si$_{met}$) and then reoxidized, often to some form of SiO$_2$, including fumed silica. This approach is illogical, and because all these processes are equipment- and energy-intensive, it is unreasonably costly. Beginning in the early 1930s, repeated attempts were made to develop low-temperature, low-cost methods of depolymerizing silica and thus alternate routes to silicon-containing compounds as well as precipitated silica. The establishment of such a process, as outlined in Equation (10), can be considered a “grand challenge” for silicon chemists. The ability to distill the resulting product should enable the direct production of silicon-containing materials of very high purity, including precipitated (ppt) SiO$_2$, directly from any silica source at low temperatures, thus greatly reducing energy costs, the carbon footprint, and the need for high capital-equipment investments. For example, high-purity ppt and colloidal silica are used in applications ranging from edible products (e.g. toothpaste) and polishing aids for planarizing silicon wafers to the production of high-purity silica for optical applications (lenses, gratings, photonic band gap materials) and the production of crucibles for growing electronics-grade silicon boules.[6–7,10]

Thus, following initial studies reported by Rosenheim et al. in 1931,[13] a number of researchers have previously explored SiO$_2$ depolymerization.[13–19] A wide range of SiO$_2$ feedstocks were used, from amorphous silica to quartz powder, but most of these studies focused on some form of the reaction depicted in Equation (11) to generate the hexacoordinated triscatecholato silicate I.[12–19]

$$\text{SiO}_2 + 2\text{KOH} + 3 \text{OH} \xrightarrow{>100°C} \text{K}_2\text{SiO}_3 + \text{H}_2\text{O} \quad (11)$$

The key to the success of this reaction is that silicon, unlike carbon, can form five and six bonds, and thus the original Si–O bond strength of tetrahedral silicon is diminished. Unfortunately, I cannot be distilled and is so stable that it is water-soluble and would have to be treated with H$_2$SO$_4$ to produce ppt SiO$_2$. From a practical perspective, this process, while offering a low-temperature route to ppt SiO$_2$, would require three moles of catechol per mole of ppt SiO$_2$ or about 330 g of catechol to produce 60 g of ppt SiO$_2$ and simultaneously 280 g of Na$_2$SO$_4$. These features are quite unattractive, although no CO$_2$ would be produced.

A search for a simpler reagent than catechol led us to try ethylene glycol to promote silica depolymerization according to Equations (12) and (13).[20,21] The depolymerization mechanism again builds on expansion of the coordination sphere around silicon.

$$\text{SiO}_2 + \text{MO} + 3 \text{H}_2\text{O} \underset{200°C}{\xrightarrow{\text{M} = \text{Li, Na, K, etc.}}} \text{M}_2\text{SiO}_3 + 2\text{H}_2\text{O} \quad (12)$$

$$\text{SiO}_2 + \text{MO} + \text{excess} \text{H}_2\text{O} \underset{3\text{H}_2\text{O} / 200°C}{\xrightarrow{\text{M} = \text{Mg, Ca, Sr, Ba}}} \text{M}_2\text{SiO}_3 \quad (13)$$

Herreros et al. deduced that the pentacoordinated silicate in Equation (12) is the primary intermediate in the ethylene glycol mediated synthesis of silicalite zeolites.[22] Likewise, Kinrade et al. proposed that the formation of similar pentacoordinated silicates by sugars allows plants to transport silica within the plant and thus forms the basis for biosilification processes.[23]

We were able to demonstrate that the reaction in Equation (12) can be promoted catalytically by an alkali base [Eq. (14)].[24,25] Our proof-of-principle studies were carried out with fumed silica (350 m$^2$ g$^{-1}$), which defeats the overall objective of the “grand challenge”. However, these studies were important, as they established that: 1) the reaction in Equation (14) is first order in the base concentration and surface area; 2) the activation energy for the reaction is approximately 60 kJ mol$^{-1}$; and 3) the reaction is faster with amorphous rather than crystalline silica.[22] Unfortunately, glycoxylsilane (GS) does not distill; instead, it polymerizes to Si(eg), on heating and is thus difficult to purify.
As a consequence, we sought other amorphous silica sources with high surface areas and identified rice hull ash (RHA) and diatomaceous earth (DE) as potential replacements for fumed silica.\cite{26,27} RHA is produced in 250 kton per year quantities in the USA alone, is mostly amorphous, and offers specific surface areas (SSAs) of 20–85 m²·g⁻¹. The samples used in our study contained 70–90 wt % silica with 5–25 wt % carbon and 5 wt % minerals, which could be removed readily by washing with dilute HCl.\cite{28} We were also able to obtain a sample of rice hulls that had been ashed at ≥600°C (A-RH) to produce a material with >95 wt % silica and with SSAs of approximately 230 m²·g⁻¹. DE is available from multiple sources with SSAs ranging from 1–70 m²·g⁻¹ and is mostly amorphous.

We report herein the first example of the base-catalyzed synthesis of distillable spirocyclic alkoxysilanes directly from these biogenic silica sources. The use of sterically hindered diols is key to the formation of spirocyclic alkoxysilanes.\cite{29,30} Of the commercially available hindered diols, 2-methyl-2,4-pentanediol, the hydrogenated product of 2,2,4-trimethyl-1,3-pentanediol and is mostly amorphous.

We attempted to dissolve a set of biogenic and mineral silica sources by using four diols: ethylene glycol (EGH₂), 1,4-butandiol, 2-methyl-2,4-pentanediol, and 2,2,4-trimethyl-1,3-pentanediol (Table 1). The first two diols were not expected to form spirocyclic alkoxysilanes through base-catalyzed silica dissolution, whereas the latter two were likely candidates. Two other hindered diols were also tested, 2-methyl-1,3-propanediol and 1,3-butanediol, which also gave spirocyclic alkoxysilanes that distilled over. We were not able to fully characterize these compounds because of their tendency to gel; however, peaks were observed in their ²⁵Si NMR spectra in the ~62 to ~65 and ~70 to ~73 ppm regions, which we have previously associated with simple spirocyclic alkoxysilanes and ring-opened polymer analogues.\cite{25,30}

The silica sources explored included RHA, DE, Celite (low-surface-area DE), vermiculite (iron magnesium aluminosilicate, ca. 10–12 wt % silica), ashed rice hulls (A-RH), and fumed silica. All materials except fumed silica and the high-surface-area A-RH were first boiled in dilute HCl (24 h, 5 wt %), washed with water and acetone, and then oven dried.

![Diagram](image)

**Table 1: Percent SiO₂ depolymerization with different diols.**

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>SSA [m²·g⁻¹]</th>
<th>EGH₂ (b.p. 197°C)</th>
<th>HO(CH₂)₈OH (b.p. 235°C)</th>
<th>2-methyl-2,4-pentanediol (b.p. 197°C)</th>
<th>2,2,4-trimethyl-1,3-pentanediol (b.p. 232°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Celite</td>
<td>1</td>
<td>12%</td>
<td>13%</td>
<td>4%</td>
<td>1.5%</td>
</tr>
<tr>
<td>vermiculite</td>
<td>4</td>
<td>2.5%</td>
<td>3%</td>
<td>3%</td>
<td>–</td>
</tr>
<tr>
<td>RHA</td>
<td>26</td>
<td>20%</td>
<td>23%</td>
<td>24%</td>
<td>12%</td>
</tr>
<tr>
<td>RHA</td>
<td>85</td>
<td>40% [b]</td>
<td>–</td>
<td>40% [b]</td>
<td>–</td>
</tr>
<tr>
<td>DE</td>
<td>23</td>
<td>16%</td>
<td>18%</td>
<td>4%</td>
<td>3%</td>
</tr>
<tr>
<td>fumed SiO₂</td>
<td>350</td>
<td>98% [c]</td>
<td>98% [c]</td>
<td>98% [c]</td>
<td>98% [c]</td>
</tr>
<tr>
<td>A-RH</td>
<td>230</td>
<td>–</td>
<td>–</td>
<td>60%</td>
<td>–</td>
</tr>
</tbody>
</table>

- \[a\] Standard reaction conditions: SiO₂ (0.3 mol), NaOH (0.03 mol), 200 mL distilled at the boiling point of the solvent (as noted) at atmospheric pressure, 4–8 h.
- \[b\] The reaction was carried out with 630 g of RHA (75 wt % silica by TGA, or 7.87 mol SiO₂), EGH₂ (7 L), and NaOH (10 mol %); the distillation was continued for 24 h; see experimental details in the Supporting Information.

With the exception of vermiculite, all sources were amorphous silica. In general, the amount of SiO₂ that dissolved was related to the specific surface area of the source and the reaction temperature. The low silicon content and crystallinity of vermiculite were probably at least partially responsible for its poor dissolution rates as compared to those of the other silica sources.

The depolymerization rates for 2-methyl-2,4-pentanediol (b.p. 200°C) were slightly lower than for EGH₂. Mass spectral analysis suggests that the diol “cracks” to produce isopropenol and acetone as the major products rather than the spirocycle \(\text{II}\). Both DE and Celite probably have highly acidic sites that account for the observed cracking products. The
ashed rice hulls gave the second-highest degree of dissolution under standard conditions, as might be expected with SSAs of approximately 230 m² g⁻¹.

In one experiment with ethylene glycol, after dissolution, carbon-enriched RHA was filtered off, the liquid volume was reduced by vacuum evaporation, and the solution was cooled, thus causing sodium glycolato silicate [SGS, Eq. (12)] to precipitate. This SGS was recovered and recycled (see the Supporting Information) to catalytically dissolve the silica in RHA (26 m² g⁻¹) in a second reaction, thus enabling the dissolution of 24 wt % of the silica, which is essentially the same amount as that found in Table 1. In a second scaled experiment, a mixture of 630 g of RHA (85 m² g⁻¹, 7.87 mol SiO₂), NaOH (10 mol %), and EGH₂ (7 L) with a silica content of 75 wt % (as determined by TGA), gave (40 ± 3 %) silica dissolution after distillation for 20 h, as determined by TGA of the recovered RHA.

Vermiculite is a common aluminosilicate mineral with no free SiO₂ available for dissolution, yet some dissolution was observed. We have not characterized the product(s), although some alumina dissolution may occur concurrently, as Al–EG complexes have been reported previously.[31]

The distillation of 2-methyl-2,4-pentanediol and II occurred at nearly the same temperature, thus making isolation and purification somewhat problematic. However, we were pleasantly surprised to find that both II and 2-methyl-2,4-pentanediol are soluble in hexane; the diol is also water-soluble. Hence, simply washing hexane solutions of the recovered, distilled mixture or the reaction filtrate removed the diol and left pure II, which could be recovered readily and redistilled at about 200 °C to give a product with much higher purity. Simple rotary evaporation led to II as a liquid that slowly crystallized on cooling.

Compound III and the parent diol are also soluble in hexane, but the diol is not water-soluble; however, III could be isolated simply by washing with MeOH. Both spirocyclic alkoxysilanes could be distilled to higher purity. The formation of II and III are the first examples of the direct conversion of biogenic silica into a distillable alkoxysilane.

Because Si(OEt)₃, (TEOS) and Si(OMe)₃, (TMOS) represent optimal products, we explored the use of II as a precursor to TEOS and TMOS, and found it straightforward to generate TEOS and TMOS in 65 and 40 % (unoptimized) yield through acid-catalyzed exchange (see the Supporting Information). Next, we explored the direct synthesis of TEOS from Si(eg)₂, [Eq. (14)]. We were able to successfully synthesize TEOS [Eq. (17)] in (55 ± 3 %) (unoptimized) yield under similar conditions. Thus, we have now succeeded in meeting the “grand challenge” noted above.

Several of the spirocyclic alkoxysilanes synthesized by Frye undergo reversible ring-opening polymerization.[29] Although we could not isolate Si(eg)₂, as a spirocyclic alkoxysilane, the highest-intensity ion peak at m/z 149 in the EI mass spectrum of GS probably corresponds to the spirocyclic alkoxysilane (MW = 148 for ²⁸Si) and suggests that in the absence of a solvent this compound is stable. Furthermore, SGS can be isolated quantitatively from the stoichiometric reaction in Equation (12), and its crystal structure has been reported.[20] Thus, the pentacoordinated spirocyclic alkoxysilane must be quite stable. Surprisingly, SGS is insoluble in EtOH (pKₐ = 15.9) but soluble in MeOH (pKₐ = 15.5), in which EGH₂ (pKₐ = 15.1) is exchanged for MeOH.[20] Thus, SGS was originally recrystallized from MeOH with an excess of EGH₂. One might envision that Si(eg)₂ is then a mixed ring and ring-opened polymer. In the presence of excess EtOH or MeOH, acid-catalyzed elimination of ring strain may drive the partial replacement of EGH₂, whereas complete replacement occurs simply by displacement of the equilibrium towards TEOS and TMOS in the presence of excess EtOH or MeOH. The insolubility of the polymer itself in EtOH or MeOH may also provide a second driving force for the formation of TEOS and TMOS.

We have also successfully investigated the formation of Si–C bonds without first having to produce silicon metal [compare Eq. (4)]. Our results will be reported elsewhere, as well as the use of II or TEOS to produce fumed silica, thus avoiding the entire route from SiCl₄ to SiCl₉.

In conclusion, we are now able to effect base-catalyzed depolymerization of silica to form readily isolated, distillable, spirocyclic alkoxysilanes and/or TEOS without first carbothermally reducing SiO₂ to Si metal. The spirocyclic alkoxysilanes and TEOS/TMOS can be distilled to high purity and thereafter combusted or treated with water and trace acid to provide access to high-purity ppt or fumed silica (Scheme 1). If we only consider precipitated silica, then our process does not produce CO₂ or Na₂SO₄ by-products, thus making it a green, low carbon footprint,[32] low-temperature, and low-cost route to high-purity ppt SiO₂. Finally, the resulting carbon-enriched RHA, when treated with dilute HCl, provides a high-purity starting material for direct carbothermal reduction to produce silicon metal with 99.999 % purity without further purification.[33–34]

Acknowledgements

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Scheme 1. Direct conversion of biogenic silica into distillable alkoxysilanes and other products.