

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

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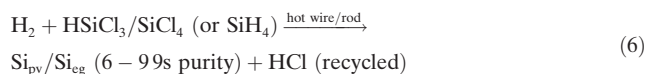
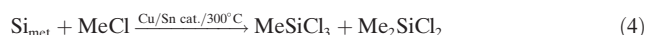
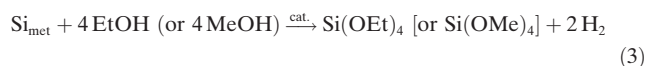
Abstract: The direct depolymerization of SiO_2 to distillable alkoxysilanes has been explored repeatedly without success for 85 years as an alternative to carbothermal reduction (1900°C) to Si_{met} followed by treatment with ROH. We report herein the base-catalyzed depolymerization of SiO_2 with diols to form distillable spirocyclic alkoxysilanes and $\text{Si}(\text{OEt})_4$. Thus, 2-methyl-2,4-pentanediol, 2,2,4-trimethyl-1,3-pentanediol, or ethylene glycol (EGH_2) react with silica sources, such as rice hull ash, in the presence of NaOH (10%) to form H_2O and distillable spirocyclic alkoxysilanes [bis(2-methyl-2,4-pentanediolato) silicate, bis(2,2,4-trimethyl-1,3-pentanediolato) silicate or $\text{Si}(\text{eg})_2$ polymer with 5–98% conversion, as governed by surface area/crystallinity. $\text{Si}(\text{eg})_2$ or bis(2-methyl-2,4-pentanediolato) silicate reacted with EtOH and catalytic acid to give $\text{Si}(\text{OEt})_4$ in 60% yield, thus providing inexpensive routes to high-purity precipitated or fumed silica and compounds with single Si–C bonds.

RHA is a by-product of rice production that is often produced coincidentally with electricity, whereby the energy derives from plant-fixed CO_2 . Thus, the production of RHA can be energy-positive, sustainable, and offers a low carbon footprint. We report herein the first examples of the direct, base-catalyzed depolymerization of silica simply by treatment with low-cost, hindered diols to produce spirocyclic alkoxysilanes that can be distilled, in high purity, directly from the reaction mixture. This process can be seen as the culmination of over 85 years of effort targeting the same or similar objectives. The resulting spirocyclic alkoxysilanes can be used to produce fumed, colloidal, or precipitated silica or as precursors to compounds containing Si–C bonds. When the

simple diol ethylene glycol (antifreeze) was used, we observed the initial production of $\text{Si}(\text{OCH}_2\text{CH}_2\text{OH})_4$, which on heating was converted into a polymer approximated as $\text{Si}(\text{OCH}_2\text{CH}_2\text{O})_2$; this polymer could be mixed with EtOH and a trace amount of an acid to produce $\text{Si}(\text{OEt})_4$ in 60% (unoptimized) yield.

Although coal and crude oil make up less than 0.01% of the Earth's crust, their utility to society is enormous given that they serve as the basis for much of the world's fuel, for most organic materials, ranging from plastic bags, food packaging, and fibers for textiles to major components in flat panel displays. In contrast, silicon (as silica, SiO_2) lies just below carbon in the periodic table, offers many chemical-bonding similarities, makes up more than 40% of the Earth's minerals, and yet has much less impact on our society, despite being important for applications ranging from solar cells and silicone rubbers to potential drug analogues.^[1–5]

One reason for the limited impact of silicon compounds is that silicon–silicon and silicon–carbon double bonds are very hard to synthesize unless they are stabilized sterically. Therefore, silicon compounds can not be polymerized readily by the methods used for carbon-based compounds. Another reason is that the silicon–oxygen bond (534 kJ mol^{-1}) is one of the strongest found in nature. Thus, most silicon-containing compounds and materials are produced from Si_{met} (met = 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); Me_2SiCl_2 is a silicone/polysiloxane precursor].^[6–10] The much higher purities required for photovoltaic-grade (Si_{pv}) and electronics-grade silicon (Si_{eg}) 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).



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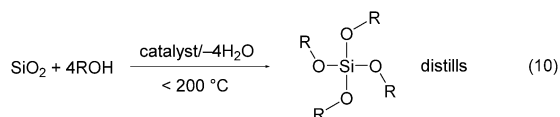
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Because all chlorosilanes and HCl gas are corrosive, toxic, and polluting, such production processes, including those used to produce fumed silica [Eq. (7)], require expensive and extensive safeguards, which add to the overall cost of the final products. 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 $\text{Si}(\text{OEt})_4$ or $\text{Si}(\text{OMe})_4$. Likewise, precipitated silicas are most commonly made by the high-temperature fusion of sand with sodium carbonate, followed by dissolution and precipitation with H_2SO_4 :



As can be seen, each mole of Na_2SiO_3 produced releases one mole of CO_2 and requires one mole of H_2SO_4 to produce one mole of precipitated silica and one mole of Na_2SO_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_2SO_4 .^[11]

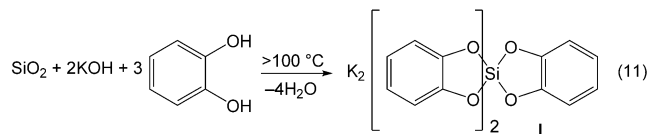
Reactions (1–7) begin with SiO_2 , which is reduced to the metal (e.g. Si_{met}) and then reoxidized, often to some form of SiO_2 , including fumed silica. This approach is illogical, and because all these processes are equipment- and energy-intensive, it is unreasonably costly. Beginning in the early 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]

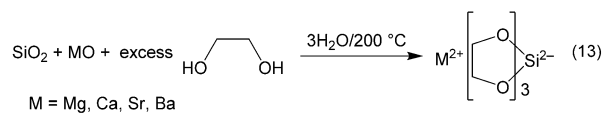
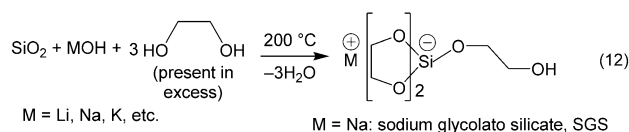
Thus, following initial studies reported by Rosenheim et al. in 1931,^[12] a number of researchers have previously explored SiO_2 depolymerization.^[13–19] A wide range of SiO_2 feedstocks were used, from amorphous silica to quartz

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]



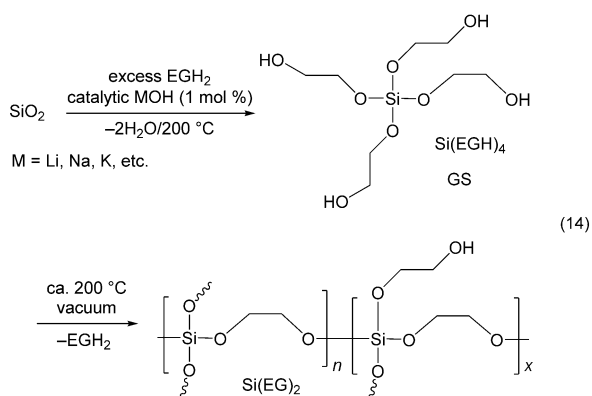
The key to the success of this reaction is that silicon, unlike carbon, can form five and six bonds, and thus the original Si–O bond strength of tetrahedral silicon is diminished. Unfortunately, **I** cannot be distilled and is so stable that it is water-soluble and would have to be treated with H_2SO_4 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_2SO_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.



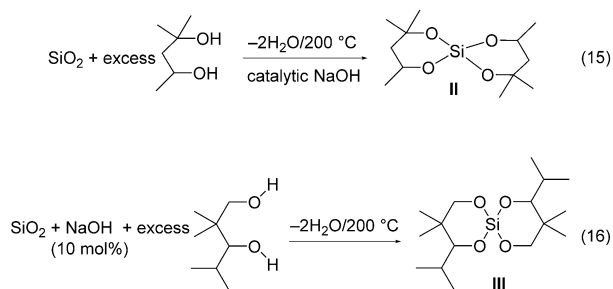
Herreros et al. deduced that the pentacoordinated silicate in Equation (12) is the primary intermediate in the ethylene glycol mediated synthesis of silicalite zeolites.^[22] Likewise, Kinrade et al. proposed that the formation of similar pentacoordinated silicates by sugars allows plants to transport 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 ($350 \text{ m}^2 \text{ g}^{-1}$), 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, glycoxysilane (GS) does not distill; instead, it polymerizes to $\text{Si}(\text{eg})_2$ 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.^[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.^[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 examples 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.^[29,30] Of the commercially available hindered diols, 2-methyl-2,4-pentanediol, the hydrogenated product of base-catalyzed acetone condensation, is the lowest cost diol available and forms some of the most stable spirocyclic alkoxysilanes, Kemmitt and Milestone.^[30] 2-Methyl-2,4-pentanediol and 2,2,4-trimethyl-1,3-pentanediol permit the extension of the reaction in Equation (14) to the formation of spirocyclic alkoxysilanes.



We attempted to dissolve a set of biogenic and mineral silica sources by using four diols: ethylene glycol (EGH₂), 1,4-butanediol, 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 ²⁹Si 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.^[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

Table 1: Percent SiO₂ depolymerization with different diols.^[a]

SiO ₂	SSA [m ² g ^{−1}]	EGH ₂ (b.p. 197 °C)	HO(CH ₂) ₄ OH (b.p. 235 °C)	2-methyl-2,4-pentanediol (b.p. 197 °C)	2,2,4-trimethyl-1,3-pentanediol (b.p. 232 °C)
Celite	1	12 %	13 %	4 %	1.5 %
vermiculite	4	2.5 %	3 %	3 %	–
RHA	26	20 %	23 %	24 %	12 %
RHA	85	40 % ^[b]		40 % ^[b]	
DE	23	16 %	18 %	4 %	3 %
fumed SiO ₂	350	98 % ^[c]	98 % ^[c]	98 % ^[c]	98 % ^[c]
A-RH	230			60 %	–

[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.

(115 °C, 24 h) prior to use to eliminate basic components that could also catalyze silica dissolution in the absence of added base; however, this procedure was not used for the large-scale RHA experiment described below. The isolated products and undissolved silica samples were characterized by mass spectroscopy, multinuclear NMR spectroscopy, XRD, BET surface-area measurement, and thermogravimetric analysis (TGA; see Table S1 and Figure S1 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 isopropanol and acetone as the major products rather than the spirocycle **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 $230 \text{ m}^2 \text{ g}^{-1}$.

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 ($26 \text{ m}^2 \text{ g}^{-1}$) 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 ($85 \text{ m}^2 \text{ g}^{-1}$, 7.87 mol SiO_2), NaOH (10 mol %), and EGH_2 (7 L) with a silica content of 75 wt % (as determined by TGA), gave $(40 \pm 3) \%$ silica dissolution after distillation for 20 h, as determined by TGA of the recovered RHA.

Vermiculite is a common aluminosilicate mineral with no free SiO_2 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 $\text{Si}(\text{OEt})_4$ (TEOS) and $\text{Si}(\text{OMe})_4$ (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 $\text{Si}(\text{eg})_2$ [Eq. (14)]. We were able to successfully synthesize TEOS [Eq. (17)] in $(55 \pm 3) \%$ (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]

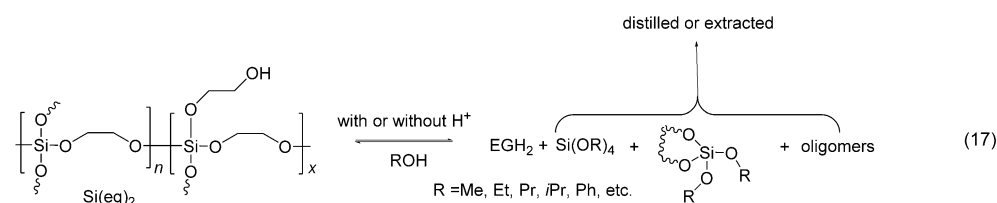
Although we could not isolate $\text{Si}(\text{eg})_2$ as a spirocyclic alkoxysilane, the highest-intensity ion peak at m/z 149 in the EI mass spectrum of GS probably corresponds to the spirocyclic alkoxysilane ($\text{MW} = 148$ for ^{28}Si) and suggests that in the absence of a solvent this compound 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 ($\text{p}K_a = 15.9$) but soluble in MeOH ($\text{p}K_a = 15.5$), in which EGH_2 ($\text{p}K_a = 15.1$) is exchanged for MeOH.^[20] Thus, SGS was originally recrystallized from MeOH with an excess of EGH_2 . One might envision that $\text{Si}(\text{eg})_2$ 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 EGH_2 , 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.

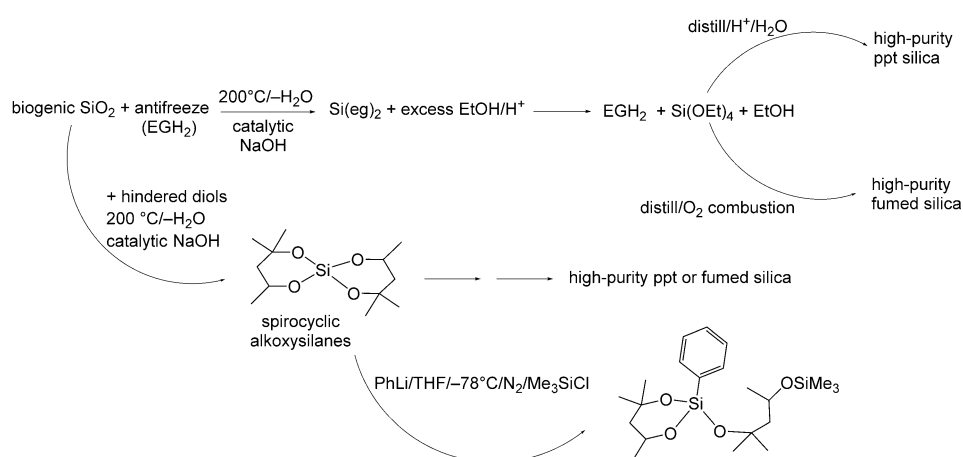
We have also successfully investigated the formation of Si-C bonds without first having to produce silicon metal [compare Eq. (4)]. Our results will be reported elsewhere, as well as the use of **II** or TEOS to produce fumed silica, thus avoiding the entire route from Si_{met} to SiCl_4 .

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 SiO_2 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 CO_2 or Na_2SO_4 by-products, thus making it a green, low carbon footprint,^[32] low-temperature, and low-cost route to high-purity ppt SiO_2 . 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 99.9999% purity without further purification.^[32–34]

Acknowledgements

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

Keywords: depolymerization · materials science · silicon · sustainable chemistry

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