Author Manuscript

Escaping Carbothermal Reduction. Distilling alkoxysilanes from biogenic, green and sustainable sources

Richard M. Laine,[1,3*] Joseph C. Furgal,[2] Phi Doan,[2] David Pan,[3] Vera Popova,[4] and Xingwen Zhang[5]

Departments of Materials Science and Engineering,[1] Chemistry[2] and Macromolecular Science and Engineering[3], University of Michigan, Ann Arbor, MI 48109-2136. Mayaterials Inc Ann Arbor, MI 48108.[4] Department of Chemistry, Harbin Institute of Technology, Harbin 150001, China.[5]

talsdad@umich.edu

Direct depolymerization of SiO_2 to distillable alkoxysilanes, $Si(OR)_4$ avoiding carbothermal reduction (1900°C) to Si_{met} followed by reaction with ROH to produce $Si(OR)_4$ has been explored repeatedly without success for 85 years. We report the first examples of base catalyzed depolymerization of SiO_2 using diols to form distillable spirocyclic alkoxysilanes and $Si(OEt)_4$. Thus, 2-methyl-2,4-pentanediol or 2,2,4-trimethyl-1,3-pentanediol or ethylene glycol (egH_2) react with multiple silica sources, e.g. rice hull ash (RHA, 85 m^2/g, 70 % SiO_2), with NaOH (10 %) to form H_2O, distillable spirocyclic alkoxysilanes [(2-methyl-2,4-pentanediolato)$_2$Si, (2,2,4-trimethyl-1,3-pentanediolato)$_2$Si] or $Si(eg)_2$ polymer at 5-98 % conversions governed by surface area/crystallinity. $Si(eg)_2$ or [(2-methyl-2,4-pentanediolato)$_2$Si react with EtOH and catalytic acid giving unoptimized 60 % $Si(OEt)_4$ yields providing inexpensive routes to high purity precipitated or fumed silica or compounds with single Si-C bonds.
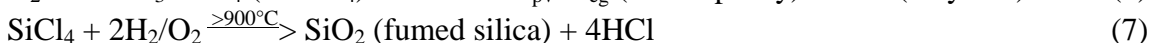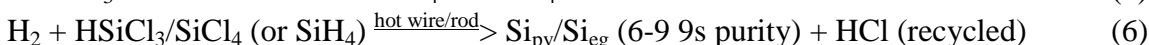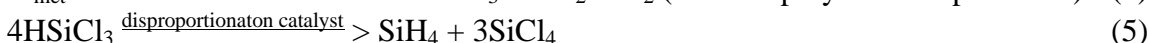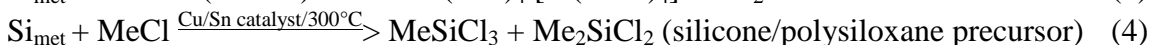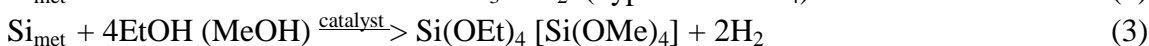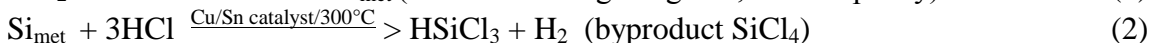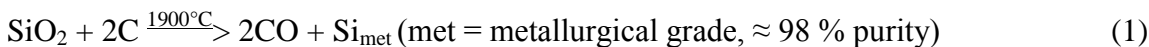
RHA is the byproduct of rice production often produced coincident with electricity where the energy derives from plant fixed CO_2. Thus, the above can be energy positive, sustainable, and offer low carbon footprints.

We report here the first examples of the direct, base catalyzed depolymerization of silica simply by reaction with low-cost, hindered diols producing spirocyclic alkoxysilanes that can be distilled, in high purity, directly from the reaction. This work represents 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. If we use the simple diol, ethylene glycol (antifreeze), we can first produce $Si(OCH_2CH_2OH)_4$, which on heating produces a polymer approximated as $Si(OCH_2CH_2O)_2$ that can then be mixed with EtOH and trace acid to produce $Si(OEt)_4$ in unoptimized yields of 60 %.

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 to fibers for textiles, to food packaging to major components in flat panel displays, etc. In contrast, silicon (as silica, SiO_2) lies just below carbon in the periodic chart, 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 to silicone rubbers to potential drug analogs.[1-4]
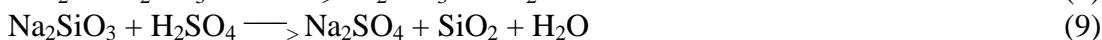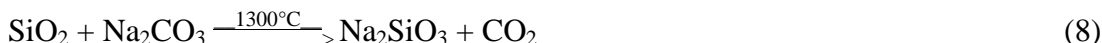
In part this problem arises because unlike carbon, silicon-silicon and silicon-carbon double bonds are very hard to synthesize unless sterically stabilized and hence are not easily polymerized using the same chemistries as used for carbon. In part this problem also arises because the silicon-oxygen bond (534 kJ/mol) is one of the strongest found in nature. Thus, most Si contain-

1

ing compounds and materials are produced from Si_{met}, which is made by carbothermal reduction of silica in a high temperature, capital equipment and energy intensive process; see reactions (1)-(7).[6-10] The much higher purities required for photovoltaic (Si_{pv}) and electronic (Si_{eg}) grade silicon require additional processing steps, typically those of the Siemens process, reactions (5) and (6), which generate byproduct HCl (normally recycled).

$$SiO_2 + 2C \xrightarrow{1900°C} 2CO + Si_{met} \text{ (met = metallurgical grade, } \approx 98\text{ \% purity)} \tag{1}$$
$$Si_{met} + 3HCl \xrightarrow{Cu/Sn\ catalyst/300°C} HSiCl_3 + H_2 \text{ (byproduct } SiCl_4) \tag{2}$$
$$Si_{met} + 4EtOH \text{ (MeOH)} \xrightarrow{catalyst} Si(OEt)_4 \text{ } [Si(OMe)_4] + 2H_2 \tag{3}$$
$$Si_{met} + MeCl \xrightarrow{Cu/Sn\ catalyst/300°C} MeSiCl_3 + Me_2SiCl_2 \text{ (silicone/polysiloxane precursor)} \tag{4}$$
$$4HSiCl_3 \xrightarrow{disproportionaton\ catalyst} SiH_4 + 3SiCl_4 \tag{5}$$
$$H_2 + HSiCl_3/SiCl_4 \text{ (or } SiH_4) \xrightarrow{hot\ wire/rod} Si_{pv}/Si_{eg} \text{ (6-9 9s purity)} + HCl \text{ (recycled)} \tag{6}$$
$$SiCl_4 + 2H_2/O_2 \xrightarrow{>900°C} SiO_2 \text{ (fumed silica)} + 4HCl \tag{7}$$

Nonetheless, because all chlorosilanes and HCl gas are corrosive, toxic and polluting, such production processes including those used to produce fumed silica (reaction 7) require expensive and extensive safeguards adding to the overall cost of the final products. Because Si_{met} is a kinetic product, where SiC is the thermodynamic product; its synthesis requires electric arc furnace processing at ≈ 1900 °C adding to the overall cost even for $Si(OEt)_4$ or $Si(OMe)_4$.

Likewise, precipitated silicas are most commonly made via high temperature fusion of sand with sodium carbonate followed by dissolution and precipitation with H_2SO_4:

$$SiO_2 + Na_2CO_3 \xrightarrow{1300°C} Na_2SiO_3 + CO_2 \tag{8}$$
$$Na_2SiO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + SiO_2 + H_2O \tag{9}$$

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 producing one mole of precipitated silica and one mole of Na_2SO_4, which must be disposed. Thus the production of precipitated (ppt) silicas such as used as filler in polymers (tires for example), as the abrasive in toothpaste, or in vacuum insulation panels also requires high temperatures and generates unwanted byproducts, especially CO_2 and Na_2SO_4.[11]

Reactions (1)-(7) begin with SiO_2, reduce it to the metal (e.g. Si_{met}) and then re-oxidize it; 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.
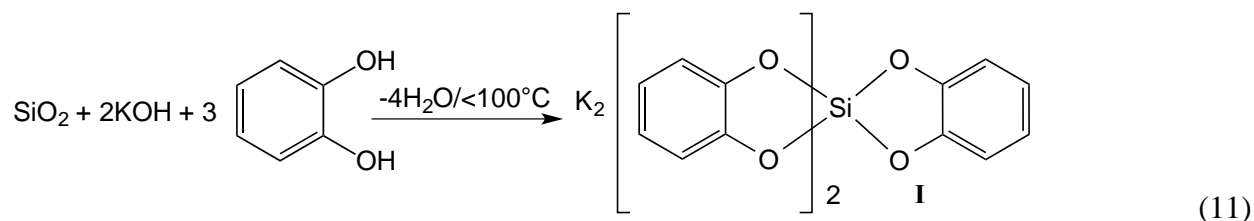
Thus, beginning in the early 1930's, repeated attempts were made to develop low temperature, low cost methods of depolymerizing silica thereby generating alternate routes to silicon containing compounds as well as precipitated silica. The success of such a process, as suggested by reaction (10) can be considered a "Grand Challenge" for silicon chemists. The idea of being

$$SiO_2 + 4ROH \xrightarrow[< 200°C]{Catalyst/-2H_2O} \text{(silicate structure)} \text{ Distills} \tag{10}$$
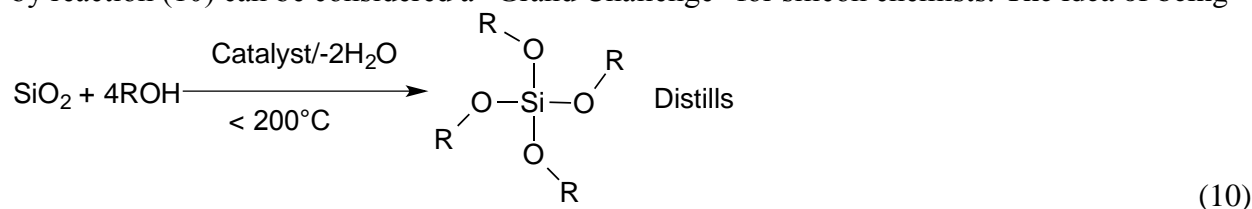
able to distill the resulting product should allow the direct production of very high purity silicon containing materials including precipitated (ppt) SiO_2 directly from any silica source at low temperatures greatly reducing energy costs and the need for high capital equipment investments. For example, high purity ppt and colloidal silica are used in applications ranging from edible prod-
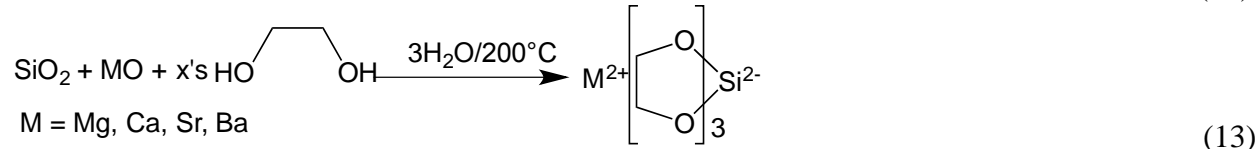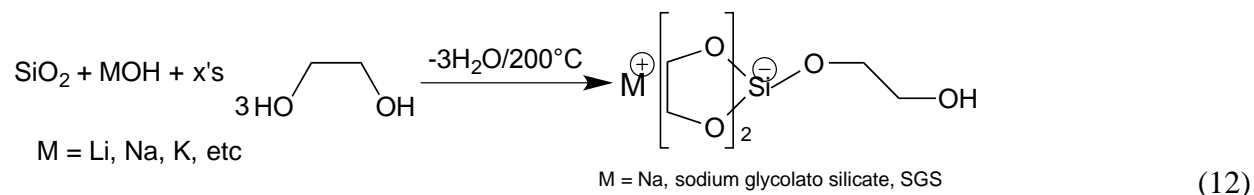
2

ucts (e.g. toothpaste) to polishing aids for planarizing silicon wafers to the production of high purity silica for optical applications (lenses, gratings, photonic band gap materials) to the production of crucibles for growing electronics grade silicon boules.[6,7,10]

Thus researchers beginning in 1931 with Rosenheim et al,[12] followed by Weiss et al (1961),[13] Frye (1964),[14] Boer and Flynn (1968),[15,16] Barnum (1970),[17,18] and Corriu (1986)[19] explored SiO_2 depolymerization. This work covers a wide range of SiO_2 feedstocks from amorphous silica to quartz powder, but most of these studies focused on some form of reaction (11) generating hexacoordinated triscatecholato Si, **I**.[12-19]

$$SiO_2 + 2KOH + 3 \quad \text{(catechol)} \quad \xrightarrow{-4H_2O/<100°C} \quad K_2 \quad \text{(structure)}_2 \quad \textbf{I} \tag{11}$$

The key to the success of this reaction is the fact 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 reacted 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 ≈ 330 g of catechol to produce 60 g of ppt SiO_2 and coincidentally 280 g of Na_2SO_4. This is quite unattractive; although no CO_2 would be produced.

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

$$SiO_2 + MOH + x's \quad 3\ HO\text{—}OH \quad \xrightarrow{-3H_2O/200°C} \quad M^{\oplus} \quad \text{(structure)}_2 \text{—OH} \tag{12}$$

M = Li, Na, K, etc

M = Na, sodium glycolato silicate, SGS

$$SiO_2 + MO + x's\ HO\text{—}OH \quad \xrightarrow{3H_2O/200°C} \quad M^{2+} \quad \text{(structure)}_3 \tag{13}$$

M = Mg, Ca, Sr, Ba

The pentacoordinated silicate of reaction (12) provided the basis for Herreros et al to determine that this compound is the primary intermediate in the ethylene glycol mediated synthesis of silicalite zeolites.[22] Likewise, it allowed Kinrade et al to propose a mechanism whereby sugars form similar pentacoordinated silicates allowing plants to transport silica within the plant as the basis for biosilification processes.[23]

Still more recently, we were able to demonstrate that reaction (12) can be promoted catalytically using alkali base, reaction (14).[24,25] Our proof-of-principle studies were done with fumed silica (350 m^2/g), which defeats the overall objective of the "Grand Challenge;" however, these studies were important as they determined that: (1) reaction (14) is first order in base concentration and surface area; (2) the activation energy for the reaction is ≈ 60 kJ/mol; and (3) the reac-

3

tion is faster with amorphous rather than crystalline silica.[22] Unfortunately, glycoxysilane (GS) does not distill, it polymerizes to Si(eg)$_2$ on heating and is thus difficult to purify.

$$\text{(14)}$$
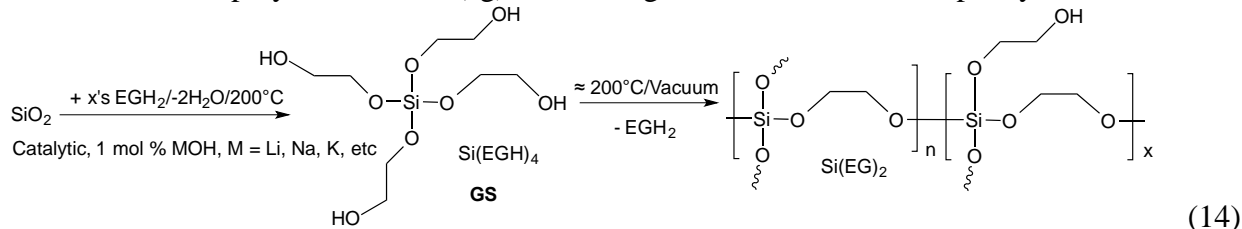
As a consequence we sought other amorphous silica sources with high surface areas identifying rice hull ash (RHA) and diatomaceous earth (DE) as potential reasonable replacements for fumed silica.[26,27] RHA is produced in 250k ton/yr quantities in the U.S. alone, is mostly amorphous and offers specific surface areas (SSAs) of 20-85 m^2/g. The samples used in our study are 70-90 wt % silica with 5-25 wt % carbon and 5 wt % minerals, removed easily by washing with dilute HCl.[28] We were also able to obtain a sample of rice hulls that had been ashed at $\geq$ 600 °C (A-RH) to produce a material > 95 wt % silica and with SSAs $\approx$ 230 m^2/g. DE is available from multiple sources with SSAs ranging from 1-70 m^2/g and is mostly amorphous.

We report here the first examples of base catalyzed synthesis of distillable spirocyclic alkoxysilanes directly from these biogenic silica sources. Sterically hindered diols are 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 as observed by Kemmitt and Milestone.[30] This and 2,2,4-trimethyl-1,3-pentanediol permit extension of reaction (14) to (15) and (16).
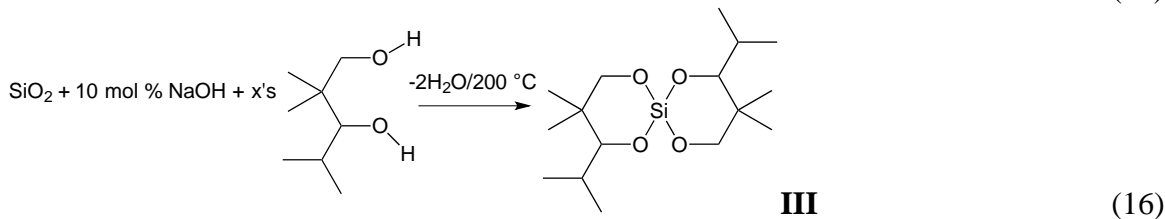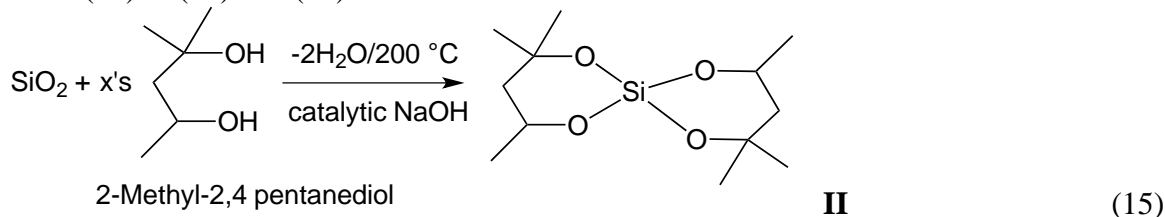
$$\text{(15)}$$

$$\text{(16)}$$

Table **1** records our *unoptimized* efforts to dissolve a set of biogenic and mineral silica sources using four diols ethylene glycol (EGH$_2$), 1,4-butane diol, 2-methyl-2,4-pentanediol and 2,2,4-trimethyl-1,3-pentanediol. The first two were not expected to form spirocyclic alkoxysilanes via base catalyzed silica dissolution whereas the latter two were likely candidates. Two more hindered diols were also tried, 2-methyl-1,3-propanediol and 1,3-butanediol that also gave spirocyclic alkoxysilanes that distilled over. We were not able to fully characterize these compounds because of their tendency to gel but ^{29}Si NMR gave peaks in the -62 to -65 and -70 to -73 ppm regions that we have previously associated with simple spirocyclic alkoxysilanes and ring opened polymer analogs.[25,30]

4

The silica sources explored included RHA, DE, celite (low surface area DE), vermiculite (iron magnesium aluminosilicate, ≈ 10-12 wt % silica), ashed rice hulls A-RH, and fumed silica. All materials except fumed silica, the high surface area A-RH and the large scale RHA experiment listed below were first boiled in dilute HCl (24 h, 5 wt %), washed with water, acetone and then oven dried (115°C, 24 h) prior to use. To eliminate basic components in the RHA that can also catalyze silica dissolution in the absence of added base.

The isolated products and undissolved silica samples were characterized by mass spectroscopy, multinuclear NMR, XRD, BET and TGA; Table S**1** and Figure S**1**.

With the exception of vermiculite, all of the sources are amorphous silica. In general, the amount of SiO_2 that dissolves for all sources relates to specific surface areas, SSAs and reaction temperatures. Vermiculite's low silicon content and crystallinity are likely at least partially responsible for its poor dissolution rates compared to the other silica sources.

Table 1. Percent SiO_2 depolymerization standard conditions; 0.3 mol SiO_2, 0.03 mol NaOH, 200 ml distilled at solvent boiling point as noted at atmospheric pressures, 4-8 h.[a]

Diol (bp°C) SiO_2	SSAs m^2/g	EGH_2 (197°)	$HO(CH_2)_4OH$ (235°)	2-methyl-2,4-pentanediol (197°)	2,2,4-trimethyl-1,3-pentanediol (232°)
Celite	1	12%	13 %	4%	1.5%
Vermiculite	4	2.5	3	3	--
RHA	26	20	23	24	12
RHA	85	40[T]		40[T]	
DE	23	16	18	4	3
Fumed SiO_2	350	98[+]	98[+]	98[+]	98[+]
A-RH	230			60	--

[a] 630 g RHA 75 wt % silica by TGA or 7.87 mol SiO_2, 7 l EGH_2, 10 mol % NaOH, 24 h distillation.

The depolymerization rates for 2-methyl-2,4-pentanediol (b.p. 200 °C) are slightly less than EGH_2. Mass spectral analysis suggests that the diol "cracks" producing isopropanol and acetone as the major product rather than the spirocycle **II.** Both DE and Celite likely have highly acidic sites that account for the observed cracking products. The ashed rice hulls give the second highest dissolution under standard conditions, as might be expected with SSAs of ≈ 230 m^2/g.

In one experiment with ethylene glycol after dissolution, carbon enriched RHA was filtered off and the liquid volume reduced by vacuum evaporation and the solution cooled causing sodium glycolato silicate (SGS, Reaction 12) to precipitate. This SGS was recovered and recycled (see experimental) to catalytically dissolve the silica in RHA (26 m^2/g) in a second reaction providing dissolution of 24 wt % essentially the same as found in Table **1**. In a second scaled experiment, 630 g of RHA (85 m^2/g, 7.87 mol SiO_2), 10 mol % NaOH, 7l of EGH_2 with a TGA determined 75 wt % silica content gave a 40±3 % silica dissolution after 20 h of distillation as determined by a TGA of the recovered RHA.

Vermiculite is a common aluminosilicate mineral with no free SiO_2 available for dissolution, yet some dissolution results. We have not characterized the product(s); although some alumina dissolution may occur concurrently given Al-EG complexes have been reported previously.[31]

The distillation of 2-methyl-2,4-pentanediol and **II** occur at nearly the same temperature making isolation and purification somewhat problematic. However, we were pleasantly surprised to find that both **II** and 2-methyl-2,4-pentanediol are hexane soluble with the diol also being water soluble. Hence simply washing hexane solutions of the recovered, distilled mixture *or the reaction filtrate* removes the diol *and leaves pure* **II**, which is easily recovered and can be re-

5

distilled at ≈ 200 °C to give much higher purities. Simple rotary evaporation leads to **II** as a liquid that slowly crystallizes on cooling.

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

Because $Si(OEt)_4$ (TEOS) and $Si(OMe)_4$ (TMOS) represent optimal products, we explored the use of **II** as a precursor to TEOS and TMOS finding it facile to effect unoptimized exchange (see experimental in SI) generating TEOS and TMOS in 65 and 40 % yields via acid catalyzed exchange. Next we explored the direct synthesis of TEOS from $Si(eg)_2$, reaction (14). We were able to successfully synthesize TEOS, reaction (17), in unoptimized yields of 55±3% using similar conditions. *Thus, we have now succeeded in meeting the "Grand Challenge," noted above.*

$$\text{(17)}$$
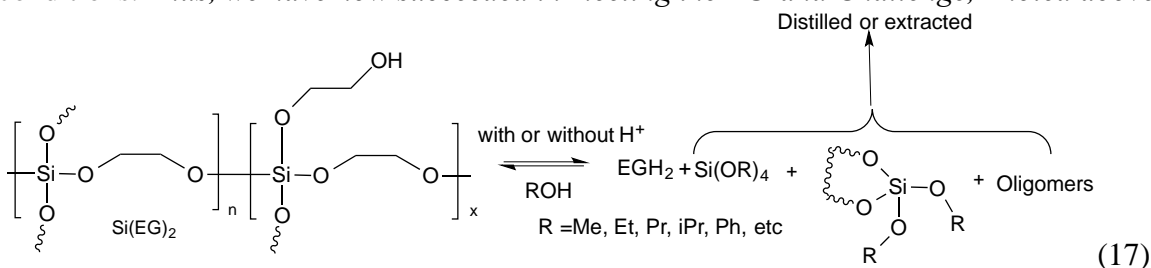
As noted in his original paper,[20] several of the spirocyclic alkoxysilanes synthesized by Frye undergo reversible ring opening polymerization. Although we cannot isolate $Si(eg)_2$ as a spirocyclic alkoxysilane, the EI mass spectrum of GS has as the highest intensity ion, m/z = 149 which likely corresponds to the spirocyclic alkoxysilane, M.W. = 148 for ^{28}Si and suggests that in the absence of solvent it is stable. A further point is that SGS can be isolated quantitatively from the stoichiometric reaction (12) and its crystal structure has been reported.[20] Thus, the pentacoordinated spirocyclic alkoxysilane must be quite stable. Surpisingly SGS is insoluble in EtOH (pKa = 15.9) but soluble in MeOH (pKa = 15.5) with exchange of MeOH for EGH_2 (pKa 15.1).[20] This was how SGS was originally recrystallized from MeOH with an excess of EGH_2. One might envision that $Si(eg)_2$ is then a mixed ring and ring-opened polymer. In excess EtOH or MeOH acid catalyzed elimination of ring-strain may drive partial replacement of EGH_2 whereas complete replacement occurs simply by displacement of the equilibrium towards TEOS and TMOS in excess EtOH or MeOH. The fact that the polymer itself is not soluble in EtOH or MeOH may also provide a second driving force for formation of TEOS and TMOS.

The next "Grand Challenge" will be to learn to form Si-C bonds without first having to produce silicon metal, per reaction (4), which we are able to do and will report elsewhere. In addition, we will also describe elsewhere the use of **II** or TEOS to produce fumed silica thereby escaping the entire Si_{met} to $SiCl_4$ route. See SI, and future reports.

Conclusions

We are now able to effect based catalyzed depolymerization of silica to form easily isolated, distillable, spirocyclic alkoxysilanes and/or TEOS without first carbothermally reducing SiO_2 to Si metal. Because the spirocyclic alkoxysilanes and TEOS/TMOS can be distilled to high purity and thereafter combusted or treated with water and trace acid thereby providing access to high purity ppt or fumed silica. If we only consider precipitated silica then our process *does not produce CO_2 or Na_2SO_4 by-products making it a green, low temperature, and low cost route to high purity ppt SiO_2.*

6

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 purities of 99.9999 % without further purification.[32-35]
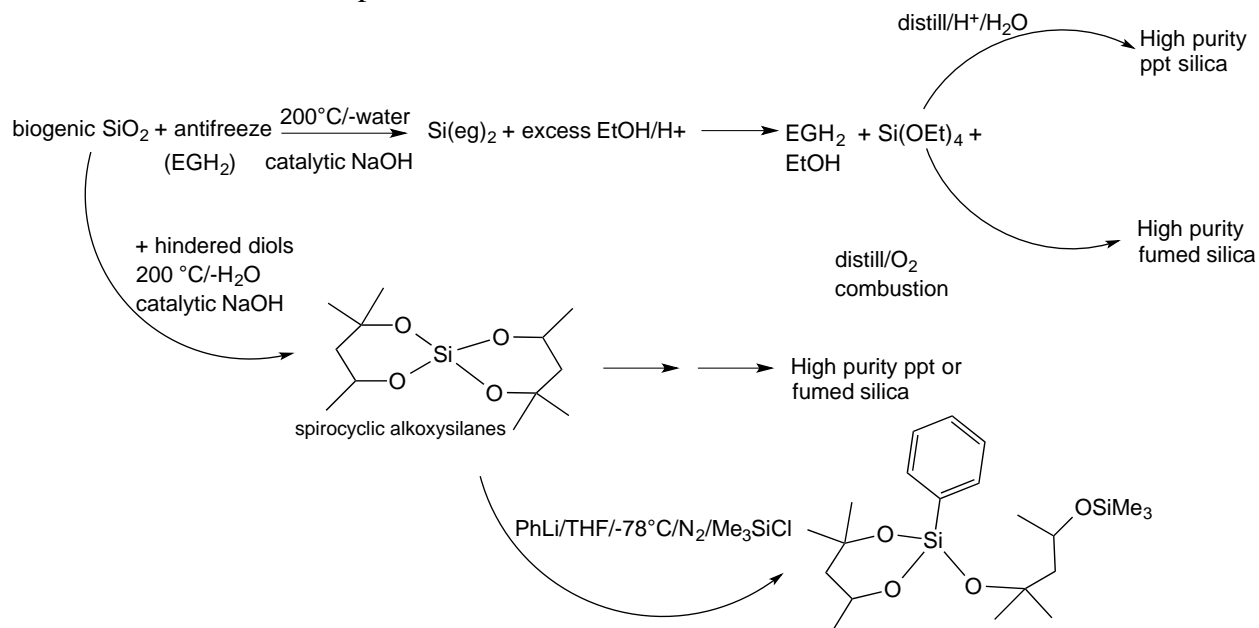

Figure 1. General scheme for converting biogenic silica directly to distillable alkoxysilanes and other products.

References

1. T. Saga, *NPG Asia Mater*. **2010**, *2,* 96-102.
2. S. DeWolf, A. Descoeudres, Z. C. Holman, C. Ballif, *Green* **2012**, *2*, 7-24.
3. S.C. Shit, P. Shah, *Natl. Acad. Sci. Lett*. **2013**, *36*, 355-365.
4. Concise Encyclopedia of High Performance Silicones, Eds. A. Tiwari, M. D. Soucek, Wiley 2014, ISBN: 978-1-118-46965-1.
5. G. A. Showell and J. S. Mills, *Drug Discovery Today* **2003**, *8*, 551-556.
6. Silicon and Silicon Alloys, Chemicals and Metallurgical, V. Dosaj, M. Kroupa, R. Bitta in Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc. online.
7. H. Kawamoto, K. Okuwada, *Sci. Tech. Trends Quarterly Rev.* **2007**, *24*, 38-50.
8. A. Gurav, T. Kodas, T. Pluym, Y. Xiong, "Aerosol processing of materials" Aerosol Sci. Tech., **19**, 411 (1993).
9. M. Okamoto , E. Suzuki , Y. Ono, *J. Catalysis* **1994**, *145,* 537–543.
10. Kirk-Othmer Encyclopedia of Chemical Tech., 5th Ed. Vol. **22**, pp 365-547 (2007).
11. J. Falcone, Silicon Compounds: Anthropogenic Silicas and Silicates," Kirk-Othmer Encyclopedia of Chemical Tech. DOI: 10.1002/0471238961.1925142006011203.a01.pub22005.
12. A. Rosenheim, B. Raibmann, G. Schendel, *Z. Anorg, Chem.*, **1931**, *196*, 160-176.
13. V. A. Weiss, G. Reiff, and A. Weiss, *Z. Anorg. Allg. Chem*. **1961**, *311*, 151-179.
14. C. L. Frye, *J. Am. Chem. Soc.* **1964**, *86*, 3170-3171.
15. F.P Boer, J.J. Flynn, J.W. Turley, *J. Am. Chem. Soc.* **1968**, *90*, 6973-6977.
16. J.J. Flynn, F.P. Boer, *J. Am. Chem. Soc.* **1969***, 91*, 5756-5761.
17. D.W. Barnum, *Inorg. Chem.* **1970**, *9*, 1942-1943.
18. D.W. Barnum, *Inorg. Chem.* **1972**, *11* 1424-1429.
19. R.J. P Corriu, J.C. Young, Chemistry of Organic Silicon Compounds, S. Patai, Z. Rappaport, eds. Ch. 20, Wiley, Chichester, 1989. b. R.J.P. Corriu, *Pure and Appl. Chem.* **1988**, *60*, 99-106.

7

20. R.M. Laine, K.Y. Blohowiak, T.R. Robinson, M.L. Hoppe, P. Nardi, J. Kampf, J. Uhm, *Nature* **1991**, *353*, 642-644.
21. M.L. Hoppe, R.M. Laine, J. Kampf, M.S. Gordon, L.W. Burggraf, *Angew. Chem. Int*. **1993**, *32*, 287-289.
22. B. Herreros, S. W. Carr, J. Klinowski, Science, **1994**, *263* 1585-1587.
23. S. D. Kinrade, J. W. Del Nin, A. S. Schach, T. A. Sloan, K. L. Wilson, C. T. G. Knight, *Science* **1999**, *285*, 1542-1545.
24. H. Cheng, R. Tamaki, R. M. Laine, F. Babonneau, Y. Chujo, and D. R. Treadwell, *J. Am. Chem. Soc*. **2000**, *122,* 10063-10072.
25. C.R. Bickmore, M.L. Hoppe, R.M. Laine, "Processable Oligomeric and Polymeric Precursors to Silicates Prepared Directly from SiO_2, Ethylene Glycol and Base." in Synthesis and Processing of Ceramics: Scientific Issues, Mat. Res. Soc. Symp. Proc.; Rhine, W. E.; Shaw, T. M.; Gottschall, R. J.; Chen, Y. **1991**, *249*, 107-110.
26. http://www.enpowercorp.com/index.cfm?page=wadham
27. http://www.bugging-out.com/mineinfo.htm website for Diasource Inc.
28. R.M. Laine, D. J. Krug, J. C. Marchal, A. McColm, "Low cost routes to high purity silicon and derivatives thereof," U.S. Patent 8475758 July 2, 2013.
29. C. L. Frye, J. Org. Chem. **1983**, *22*, 2496-2499.
30. T. Kemmitt, N. B. Milestone, *Aust. J. Chem.,* **1995**, *48*, 93-102.
31. B. Herreros , T. L. Barr, J. Klinowski, *J. Phys. Chem.* **1994**, *98*, 738-741.
32. Mr. Patrick McDonnell, Agland Energy Services, Nicassio, CA, USA.
33. R.M. Laine, D. J. Krug, J. C. Marchal, A. McColm "Low cost routes to high purity silicon and derivatives thereof, Application number: U.S. Patent 8,475,758, July 2, 2013
34. J. C. Marchal, D. J. Krug, P. McDonnell, R. M. Laine, Green Chemistry **2015**, 17, 3931–3940.
35. R. M. Laine, J. C. Marchal, V. Popova, D. J. Krug "Method of producing alkoxysilanes and precipitated silica from biogenic silicas U. S. Patent 8,916,122 published Dec 23, 2014.

8