

## Catalytic Depolymerization

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

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**Abstract:** The direct depolymerization of  $\text{SiO}_2$  to distillable alkoxysilanes has been explored repeatedly without success for 85 years as an alternative to carbothermal reduction ( $1900^\circ\text{C}$ ) to  $\text{Si}_{\text{met}}$  followed by treatment with ROH. We report herein the base-catalyzed depolymerization of  $\text{SiO}_2$  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 ( $\text{EGH}_2$ ) react with silica sources, such as rice hull ash, in the presence of NaOH (10%) to form  $\text{H}_2\text{O}$  and distillable spirocyclic alkoxysilanes [bis(2-methyl-2,4-pentane-diolato) silicate, bis(2,2,4-trimethyl-1,3-pentane-diolato) 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-pentane-diolato) 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.

**R**HA is a by-product of rice production that is often produced coincidentally with electricity, whereby the energy derives from plant-fixed  $\text{CO}_2$ . 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 alkoxy-silanes 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 alkoxy-silanes 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,  $\text{SiO}_2$ ) 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.<sup>[1–5]</sup>

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 ( $534 \text{ kJ mol}^{-1}$ ) is one of the strongest found in nature. Thus, most silicon-containing compounds and materials are produced from  $\text{Si}_{\text{met}}$  (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);  $\text{Me}_2\text{SiCl}_2$  is a silicone/polysiloxane precursor].<sup>[6–10]</sup> The much higher purities required for photovoltaic-grade ( $\text{Si}_{\text{pv}}$ ) and electronics-grade silicon ( $\text{Si}_{\text{eg}}$ ) 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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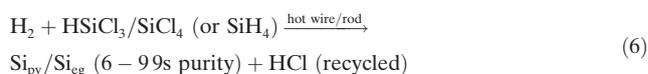
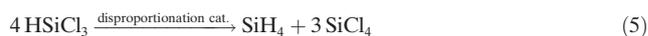
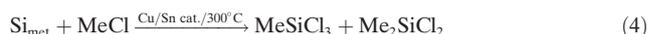
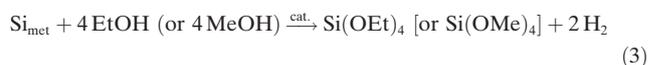
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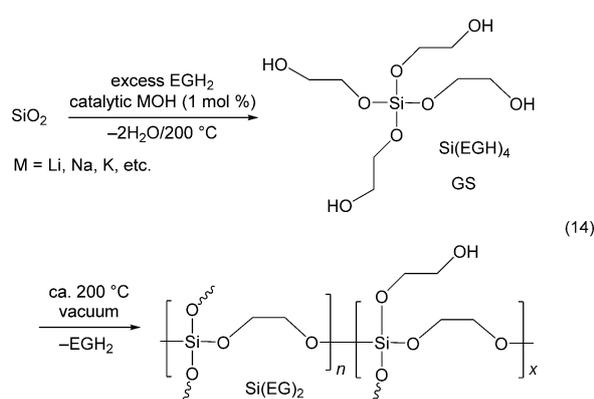
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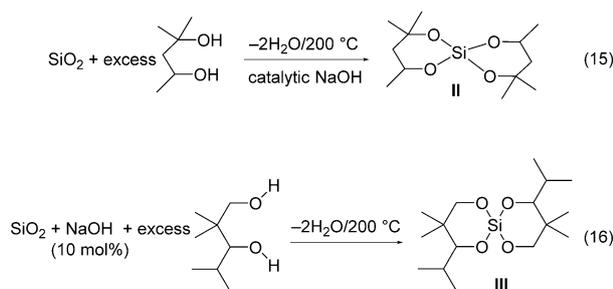






As a consequence, we sought other amorphous silica sources with high surface areas and identified rice hull ash (RHA) and diatomaceous earth (DE) as potential replacements for fumed silica.<sup>[26,27]</sup> RHA is produced in 250 kton per year quantities in the USA alone, is mostly amorphous, and offers specific surface areas (SSAs) of 20–85 m<sup>2</sup> g<sup>-1</sup>. 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.<sup>[28]</sup> 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 with > 95 wt % silica and with SSAs of approximately 230 m<sup>2</sup> g<sup>-1</sup>. DE is available from multiple sources with SSAs ranging from 1–70 m<sup>2</sup> g<sup>-1</sup> 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.<sup>[29,30]</sup> 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.<sup>[30]</sup> 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 (EGH<sub>2</sub>), 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 <sup>29</sup>Si 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.<sup>[25,30]</sup>

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 SiO<sub>2</sub> depolymerization with different diols.<sup>[a]</sup>

SiO <sub>2</sub>	SSA [m <sup>2</sup> g <sup>-1</sup> ]	EGH <sub>2</sub> (b.p. 197 °C)	HO(CH <sub>2</sub> ) <sub>4</sub> 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 % <sup>[b]</sup>	–	40 % <sup>[b]</sup>	–
DE	23	16 %	18 %	4 %	3 %
fumed SiO <sub>2</sub>	350	98 % <sup>[c]</sup>	98 % <sup>[c]</sup>	98 % <sup>[c]</sup>	98 % <sup>[c]</sup>
A-RH	230	–	–	60 %	–

[a] Standard reaction conditions: SiO<sub>2</sub> (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 SiO<sub>2</sub>), EGH<sub>2</sub> (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 SiO<sub>2</sub> 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 EGH<sub>2</sub>. 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 ( $85 \text{ m}^2 \text{ g}^{-1}$ ,  $7.87 \text{ mol SiO}_2$ ), NaOH (10 mol%), and  $\text{EGH}_2$  (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  $\text{SiO}_2$  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.<sup>[31]</sup>

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  $200^\circ\text{C}$  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 alkoxyxilanes 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 alkoxyxilane.

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 alkoxyxilanes synthesized by Frye undergo reversible ring-opening polymerization.<sup>[29]</sup>

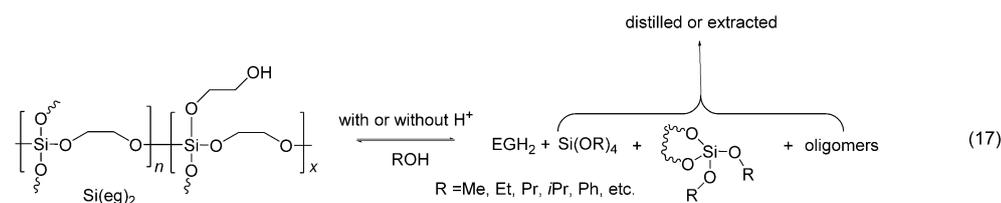
Although we could not isolate  $\text{Si}(\text{eg})_2$  as a spirocyclic alkoxyxilane, the highest-intensity ion peak at  $m/z$  149 in the EI mass spectrum of GS probably corresponds to the spirocyclic alkoxyxilane ( $\text{MW} = 148$  for  $^{28}\text{Si}$ ) and suggests that in the absence of a solvent this compound is stable. Furthermore, SGS can be isolated quantitatively from the stoichiometric reaction in Equation (12), and its crystal structure has been reported.<sup>[20]</sup> Thus, the pentacoordinated spirocyclic alkoxyxilane must be quite stable. Surprisingly, SGS is insoluble in EtOH ( $pK_a = 15.9$ ) but soluble in MeOH ( $pK_a = 15.5$ ), in which  $\text{EGH}_2$  ( $pK_a = 15.1$ ) is exchanged for MeOH.<sup>[20]</sup> Thus, SGS was originally recrystallized from MeOH with an excess of  $\text{EGH}_2$ . 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  $\text{EGH}_2$ , 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.

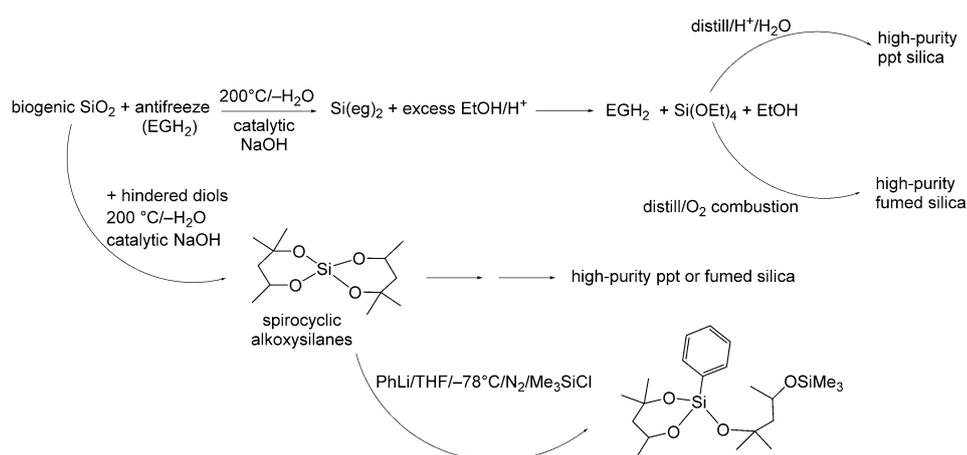
We have also successfully investigated the formation of Si-C bonds without first having to produce silicon metal [compare Eq. (4)]. Our results will be reported elsewhere, as well as the use of **II** or TEOS to produce fumed silica, thus avoiding the entire route from  $\text{Si}_{\text{met}}$  to  $\text{SiCl}_4$ .

In conclusion, we are now able to effect base-catalyzed depolymerization of silica to form readily isolated, distillable, spirocyclic alkoxyxilanes and/or TEOS without first carbothermally reducing  $\text{SiO}_2$  to Si metal. The spirocyclic alkoxyxilanes 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  $\text{CO}_2$  or  $\text{Na}_2\text{SO}_4$  by-products, thus making it a green, low carbon footprint,<sup>[32]</sup> low-temperature, and low-cost route to high-purity ppt  $\text{SiO}_2$ . 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.<sup>[32–34]</sup>

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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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- [1] T. Saga, *NPG Asia Mater.* **2010**, *2*, 96–102.
- [2] S. De Wolf, A. Descoedres, 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, New York, **2014**, ISBN: 978-1-118-46965-1.
- [5] G. A. Showell, J. S. Mills, *Drug Discovery Today* **2003**, *8*, 551–556.
- [6] “Silicon and Silicon Alloys, Chemical and Metallurgical”: V. Dosaj, M. Kroupa, R. Bitta in the Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, 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 Sci. Technol.* **1993**, *19*, 411.
- [9] M. Okamoto, E. Suzuki, Y. Ono, *J. Catal.* **1994**, *145*, 537–543.
- [10] Kirk-Othmer Encyclopedia of Chemical Technology, 5th ed., Vol. 22, **2007**, pp. 365–547.
- [11] “Silicon Compounds: Anthropogenic Silicas and Silicates”: J. Falcone in the Kirk-Othmer Encyclopedia of Chemical Technology, 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, 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] a) R. J. P. Corriu, J. C. Young, *Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rappaport), Wiley, Chichester, **1989**, chap. 20; b) R. J. P. Corriu, *Pure Appl. Chem.* **1988**, *60*, 99–106.
- [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. Ed. Engl.* **1993**, *32*, 287–289; *Angew. Chem.* **1993**, *105*, 283–285.
- [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, D. R. Treadwell, *J. Am. Chem. Soc.* **2000**, *122*, 10063–10072.
- [25] “Processable Oligomeric and Polymeric Precursors to Silicates Prepared Directly from SiO<sub>2</sub>, Ethylene Glycol and Base”: R. Bickmore, M. L. Hoppe, R. M. Laine in *Synthesis and Processing of Ceramics: Scientific Issues, Vol. 249 of Mater. Res. Soc. Symp. Proc.* (Eds.: W. E. Rhine, T. M. Shaw, R. J. Gottschall, Y. Chen), **1991**, pp. 107–110.
- [26] <http://www.enpowercorp.com/index.cfm?page=wadham>.
- [27] <http://www.bugging-out.com/mineinfo.htm> website for Diasource Inc.
- [28] “Low cost routes to high purity silicon and derivatives thereof”: R. M. Laine, D. J. Krug, J. C. Marchal, A. McColm, US Patent 8,475,758, 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] Patrick McDonnell, Agland Energy Services, Nicassio, CA, USA.
- [33] J. C. Marchal, D. J. Krug, P. McDonnell, R. M. Laine, *Green Chem.* **2015**, *17*, 3931–3940.
- [34] “Method of producing alkoxy silanes and precipitated silica from biogenic silicas”: R. M. Laine, J. C. Marchal, V. Popova, D. J. Krug, US Patent 8,916,122, published December 23, **2014**.

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