

Supporting Information

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

Richard M. Laine, Joseph C. Furgal, Phi Doan, David Pan, Vera Popova, and Xingwen Zhang*

ange_201506838_sm_miscellaneous_information.pdf

Supplemental Information

Table S1. Mass spectral, ^1H , ^{13}C and ^{29}Si NMR data.

Diol (bp°C) SiO ₂	EGH ₂ (197°)	HO(CH ₂) ₄ OH (235°)	2-methyl-2,4-pentanediol (197°)	2,2,4-trimethyl-1,3-pentanediol (232°)
Mass Spec. ^{††}	Si(glycoxy)₄ m/z [149], 80 % intensity ¹	Si(OROH)₄ m/z [205], 15 % intensity	II m/z [260], II = 15% -CH ₃ 245 100%	III m/z [316], III = 7 % 273 (-Me ₂ CH) I = 30%
^1H (δ)	Si(glycoxy)₄ ¹ CH ₂ O 3.74 CH ₂ OH 3.94	CH ₂ O 3.41, CH ₂ 1.45 Si(OROH)₄ CH ₂ O 3.70 CH ₂ 1.65	CHOH 4.20, CH ₂ 1.47, 1.64 CH ₃ 1.30, 1.24, 1.18 II CH ₂ O 4.30, CH ₂ 1.48-1.66 CH ₃ 1.28, 1.22, 1.18,	CHOH 3.7, CH ₂ OH, 3.32, CH 1.87 CH ₃ 0.73, 0.75, 0.95, III CHO 3.4, CH ₂ O, 3.20, CH 1.59 CH ₃ 0.87, 0.88, 0.97,
^{13}C (δ)	Si(glycoxy)₄ ¹ CH ₂ O 3.74 CH ₂ OH 3.94	CH ₂ O 62.55 CH ₂ 29.84 Si(OROH)₄ CH ₂ O 64.80 CH ₂ 31.99	C(Me) ₂ OH 71.56, C(H,Me)OH 65.64, CH ₂ 49.47 (CH ₃) ₂ 31.82, 27,71, CH ₃ 24.31 II C(Me) ₂ O 74.63, 74.38 C(H,Me)O 67.82, 67.60 CH ₂ 48.40, 48.32 (CH ₃) ₂ 32.20, 27.98 CH ₃ 24.17	CH ₂ OH, 83.11 CHOH 73.3, C 39.04, CH 29.08 CH ₃ 23.27, 19.66, 16.60, III CHO 82.52, CH ₂ O 69.17, C 40.80 CH 30.57 CH ₃ 23.11, 18.72, 15.16
^{29}Si (δ)	-82	-82	-82	-81.85

[†] 630 g RHA 75 wt % silica by TGA or 7.87 mol SiO₂, 7 l EGH₂, 10 mol % NaOH, 24 h distillation. ^{††} MALDI, EI, FABS ^{29}Si NMRs show GS is analogous to TEOS and **Si(OnBuOH)₄** peak, spirocyclic alkoxy silanes shifted. ^1H , ^{13}C NMRs suggest chirality in spirocyclic alkoxy silanes, likely a mixture of diastereomers.

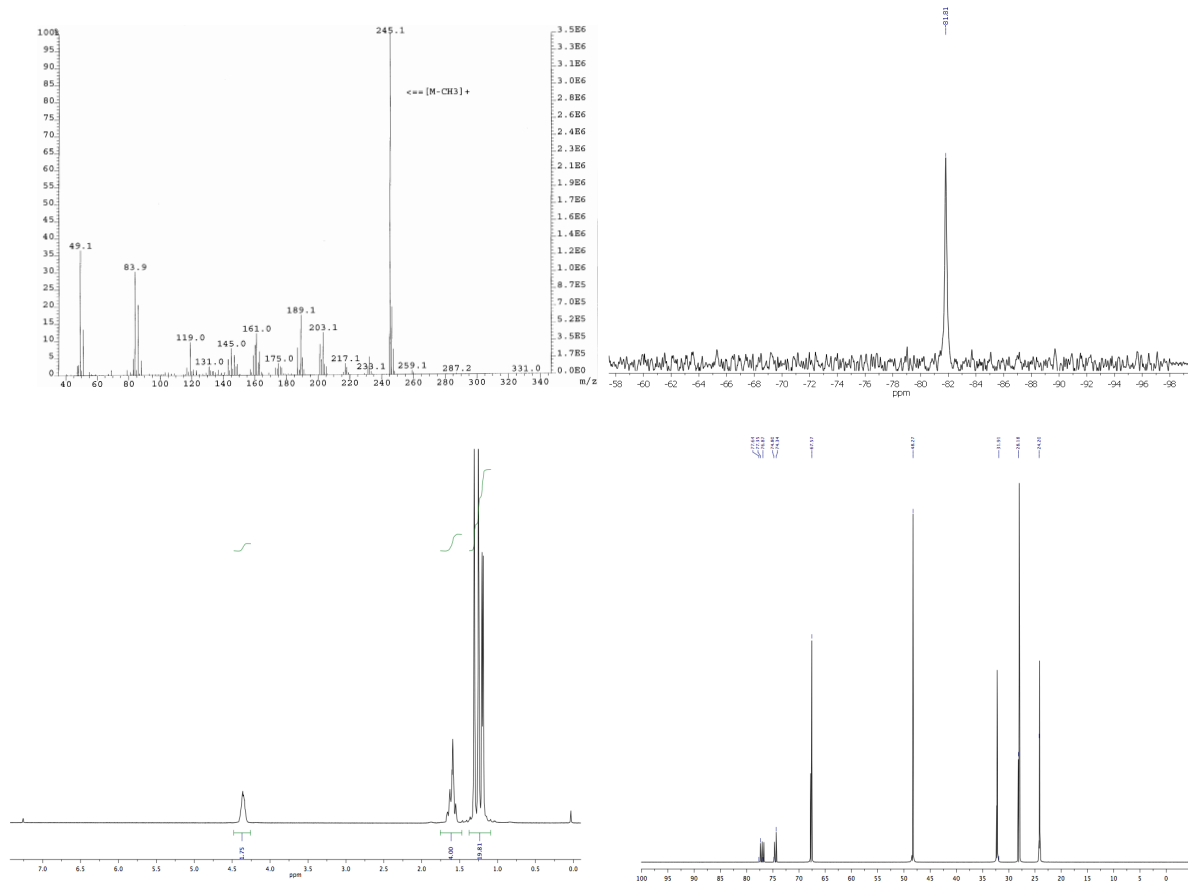


Figure S1. a. EI Mass spectrum of **II**, with M-CH₃ shown at 245.1 m/z and b. ²⁹Si NMR of **II**, c. ¹H NMR of **II**, d. ¹³C NMR of **II** all in CDCl₃.

Experimental

Materials. All chemicals and solvents were obtained from commercial suppliers and used without further purification. The ashed RH was received from the J. Cervantes group of the University of Guanajuato, Mexico.

General procedures. A standard dissolution reaction was established using 0.33 moles of silica (determined by TGA) mixed with 300 ml of diol and 0.03 moles of NaOH (1.33 g) and stirred to promote dissolution. Thereafter the solution is heated to 15 °C below the boiling point of the diol for 24 h to drive the reaction by removing water, typically 2-5 ml are collected; however, water is relatively soluble in all the diols at the volumes anticipated to form given complete dissolution and stoichiometric quantities were never collected at this juncture. After 24 h, the reaction was heated to distill out diol further driving the reaction. After 100 mL was collected, an additional 100 mL of diol was added and a second 100 mL distilled. For the EGH₂ and 1,4-butanediol, all of the dissolved silica remained in the reactor and was isolated by filtration and washing the recovered silica with EtOH.

Synthesis of spirocyclic alkoxy silane **II at scale using EGH₂ exchange.** 630 g of processed RHA (75 wt. % silica content, 7.87 moles of silica) was placed in a 12 L flask, equipped with a heating

mantle and a mechanical stirrer. 7 L of ethylene glycol (EGH₂) and catalyst (10 mol. % NaOH) was added and EGH₂ distillation started. Silica dissolution rates are seen in Table S2.

Table S2. Percent silica dissolved (by LOI) from processed RHA with 10 mol. % NaOH.

Time, h	Silica Dissolution
6	28.2 %
12	31.7 %
18	35.4 %
24*	37.1 %

*When 37.1 % silica dissolution was reached, the reaction was converted to synthesize spirocyclic alkoxyasilane **II** (SP).

Spirocyclic alkoxyasilane **II** (SP) reaction

Then, 3.5 L of 2-methyl, 2,4-pentanediol (hexylene glycol, HG) was then added and SP distillation commenced. SP was distilled out (~ 3 L) and collected, and then worked up [addition of hexane (3 L) and water (3x 1 L) washing steps]. After addition of hexane, the solution formed two immiscible layers (diol and hexane) that were separated prior the washing steps. Then the hexane layer (containing the SP product) was washed with water three times, dried over sodium sulfate and collected. In the final step the hexane was removed on a rotary evaporator to yield the product (spirocyclic alkoxyasilane **II**) giving ~ 507 g **II** (~ 67 % yield).

The remaining RHA was washed with ethanol and filtered off and analyzed by TGA-DTA, Figure S2. TGA-DTA of RHA showed 43 wt. % silica content.

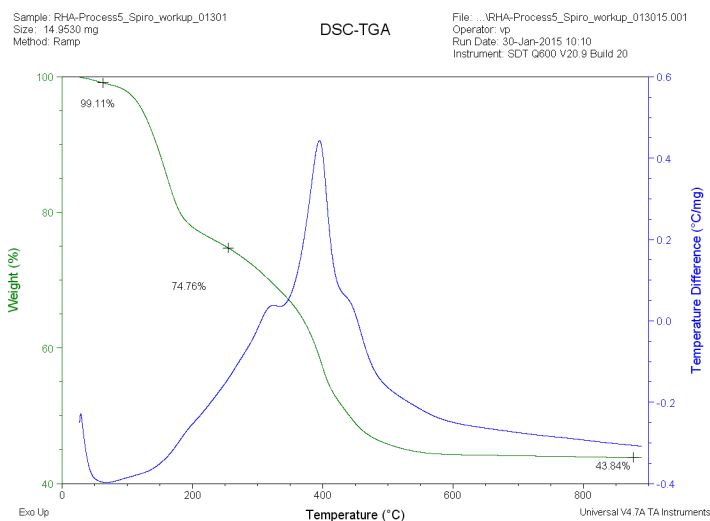


Figure S2. TGA-DTA of RHA after the work-up of SP.

Synthesis of spirocyclic alkoxyasilane **III**. To a 500 mL 2-neck round bottom flask with mechanical stirrer and distillation apparatus under N₂ is added 0.33 moles of silica (i.e. fumed silica), 200 g of 2,2,4-trimethyl-1,3-pentanediol and 0.03 moles of NaOH (1.33 g) and stirred to promote dissolution. Thereafter the solution is heated to 15 °C below the boiling point of the diol or (~215 °C) for 24 h to drive the reaction by removing water. At this point, all of the silica has dissolved. After 24 h, 200 mL of MeOH was added to the reactor flask to dissolve the formed gel, a mixture of spirocyclic alkoxyasilane **III** and diol. The spirocyclic alkoxyasilane **III** is extracted

by washing the solution (MeOH + reactor) with hexanes (3x 150 mL), then the combined hexanes layers are washed 3x 100 mL of MeOH. The hexanes mixture is then dried over Na₂SO₄, filtered and solvent removed by rotary evaporation. 76 g isolated spirocyclic alkoxy silane **III** at 73% isolated yield.

Recycle of SGS.^{2,3} To a 1000 ml round bottom flask, equipped with a distillation condenser and magnetic stirring and kept under N₂ were placed 60 g (0.9 moles of silica) of RHA (26 m²/g, twice acid milled, neutralized with ammonium hydroxide, dried at 70°C for a week) with 500 mL of ethylene glycol. The solution was heated to distill 250 mL of over 5 h to remove residual water. To this was added a solution of 0.072 moles of SGS (16.74 g or 8 mol % of the silica) dissolved in 250 mL of ethylene glycol. The initial TGA of this sample showed a ceramic weight of 1.56%. The theoretical ceramic weight from the SGS in solution is 1.54%. In total there is 58.3 g of SiO₂ in the system (4.3 g of it coming from the dissolved SGS and therefore not in the form of SiO₂) and the equivalent of 2.23 g of Na₂O equivalents. Fresh EGH₂ was added regularly to keep the reaction volume constant. Samples were taken at 11/17/23 h, filtered then analyzed by TGA-DTA resulting in dissolution of 20, 23 and 27 wt %. This is the same as the initial study.

Spirocyclic alkoxy silane:phenyllithium reaction. To a flame dried and argon purged 100 mL Schlenk flask was added 2.5 g (10 mmol) of **II** and magnetic stir bar. The flask was then evacuated under vacuum 3 times and purged with argon. The flask was then cooled to -78 °C (dry ice/acetone bath for 10 min under argon. Then 75 mL of dry argon purged diethyl ether was added to the reaction and allowed to cool for another 10 min. Then 10 mmol of Phenyl-lithium solution in diethylether was added dropwise by syringe to the reaction mixture, at which time the reaction became a yellow color. The reaction was run till the yellow color subsided and was then quenched with excess Me₃SiCl or MeI and allowed to stir cold for >30 min before warming to room temperature. The reaction was then worked up by a quick water wash (2x 10 mL) to remove salts and then dried over MgSO₄. The reaction was then filtered through Celite to remove salts and solvent removed in-vacuo. A clear semi-viscous oil was obtained.⁴

Conversion of **II** or **GS** to TEOS. To a flame dried 500 mL r/b flask equipped with magnetic stirrer under N₂ was added ~25 mL of activated 4 Å molecular sieves, 10 g (0.038 mol) of Si(2-methyl-2,4-pentanediolato)₂ (**II**) or 10 g (0.036 mol) of Si(EGH)₄, and 400 mL of anhydrous ethanol. The reaction is allowed to stir for 1 h before adding of 2.5 mL (0.015 mol) of TFA. The reaction continues to stir at ambient for 24 h before the sieves are removed along with small amounts of ppt silica. Hexanes, 400 mL, are added and washed with water to remove TFA and diol. Before drying over Na₂SO₄. Removal of solvent in-vacuo provides Si(OEt)₄ as determined by GPC and EI-MS (m/z = 208.1), typical yield 5.2 g, 65%.

Conversion of **II** to TMOS To a flame dried 500 mL round bottom flask equipped with magnetic stirrer under N₂ were added ~25 mL of activated 4 Å molecular sieves, 10 g (0.038 mol) of Si(2-methyl-2,4-pentanediolato)₂ (**II**), and 200 mL of dry methanol and 200 mL of dry hexanes (an immiscible mixture). The reaction mixture was stirred for 1 h, then 2.5 mL (0.015 mol) TFA was added and the reaction was stirred an additional 24 h at ambient. The hexane layer was removed, washed with water then dried. Hexanes were removed in-vacuo, resulting in a colorless oil of Si(OMe)₄ as determined by GPC and EI-MS (m/z = 153.1), crude yield 3 g, 52%.

Conversion of **II** to Precipitated Silicas. To a 250 mL round bottom flask equipped with magnetic stirrer were added 10 g (0.038 mol) of Si(2-methyl-2,4-pentanediolato)₂ (**II**), 50 mL of 200 proof ethanol, 4 mL of H₂O and 2 mL of 12N HCl. The reaction was stirred at room temperature for 24 h, then resulting in a transparent colloidal dispersion of silica particles. Alternately, it was neutralized with Na₂CO₃ to produce precipitated silica.

Analytical studies using multinuclear NMR, mass spectroscopy, and thermal gravimetric analysis were conducted using standard methods.^{1,5}

References

1. H. Cheng, R. Tamaki, R. M. Laine, F. Babonneau, Y. Chujo, and D. R. Treadwell, *J. Am. Chem. Soc.* **2000**, *122*, 10063-10072.
2. R. M. Laine, J. C. Marchal, V. Popova, D. J. Krug "Method of producing alkoxy silanes and precipitated silica from biogenic silicas U. S. Patent 8,916,122 published Dec 23, 2014.
3. 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
4. J.C. Furgal, R.M. Laine, Manuscript in Preparation
5. J.C. Furgal, J.H. Jung, T. Goodson III, R.M. Laine, *J. Am. Chem. Soc.* **2013**, *135*, 12259.