doi:10.1246/cl.2012.280
Published on the web February 25, 2012

A Novel Sol–Gel Approach to Highly Condensed Silicas at Low Temperature

Yogesh R. Jorapur,[1,3] Norihiro Mizoshita,[2,3] Yoshifumi Maegawa,[2,3] Hiroki Nakagawa,[1]
Takeru Hasegawa,[1] Takao Tani,[2,3] Shinji Inagaki,*[2,3] and Toyoshi Shimada*[1,3]
[1]*Department of Chemical Engineering, Nara National College of Technology,*
22 Yata-cho, Yamatokoriyama, Nara 639-1080
[2]*Toyota Central R&D Laboratories, Inc., Nagakute, Aichi 480-1192*
[3]*Core Research for Evolutional Science and Technology (CREST),*
Japan Science and Technology Agency (JST), Kawaguchi, Saitama 332-0012

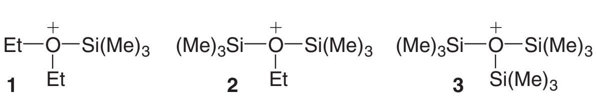
(Received December 26, 2011; CL-111231; E-mail: shimada@chem.nara-k.ac.jp)

We have discovered new Meerwein's reagent-catalyzed sol–gel polycondensations, which provide highly condensed silica Q^4 and biphenylene silica T^3 as amorphous gels with marginal silanols starting from TEOS and 4,4′-bis(triethoxysilyl)biphenyl (BTEBph), respectively. We propose a plausible pathway for this protocol with possible silyloxonium intermediates.

Since the first studies by Ebelman,[1] sol–gel processes have been used for the production of various functional materials.[2–4] To date, conventional sol–gel polycondensations have been carried out under acidic, basic, or neutral reaction conditions to yield silica via silanol intermediates, always providing silanol groups on the surface of the gels.[3] However, quite a few residual silanols in the gels sometimes result in functional deterioration due to hydrophilicity, local conductivity, and hydrogen bonding.[5] Thus, a more facile and efficient sol–gel technique under much milder conditions such as neutral media, low reaction temperature <100 °C, reaction time <24 h, and no cumbersome work-up to highly condensed silica still remains a challenge for chemists.[6]

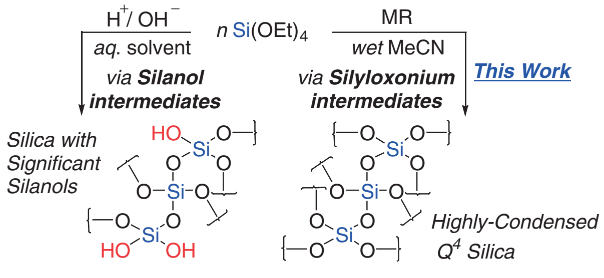
Two decades ago, Sakurai and Olah independently investigated silyloxonium intermediates (**1**–**3**, Figure 1).[7]

Although there have been few reports on the use of Meerwein's reagent[8] (MR, trialkyloxonium salts) in ring-opening polymerization[9] of cyclic ethers, to the best of our knowledge, there is no report of MR-catalyzed sol–gel process proceeding via silyloxonium intermediates. This prompted us to design a conceptually new sol–gel approach (Scheme 1). Herein we propose a novel MR-catalyzed sol–gel approach with a plausible pathway for Si–O–Si bond formation.



1 $\mathrm{Et{-}\underset{Et}{\overset{+}{O}}{-}Si(Me)_3}$ **2** $\mathrm{(Me)_3Si{-}\underset{Et}{\overset{+}{O}}{-}Si(Me)_3}$ **3** $\mathrm{(Me)_3Si{-}\underset{Si(Me)_3}{\overset{+}{O}}{-}Si(Me)_3}$

Figure 1. Previously reported silyloxonium intermediates.



Scheme 1. Traditional and proposed sol–gel polycondensations.

Our initial experiments with TEOS and 30 mol % of triethyloxonium tetrafluoroborate (Et_3OBF_4) in anhydrous acetonitrile (MeCN) at rt and then at 80 °C (Table 1, Entry 1) did not proceed to give the expected silica gel. Accidentally, we performed the same reaction in reagent grade MeCN under identical conditions (Entry 2). Astonishingly, the polycondensation proceeded successfully resulting in white precipitate, which was washed several times with MeCN and dried in vacuum to provide silica powder quantitatively. The obtained silica was then characterized using FT-IR and ^{29}Si MAS NMR. For comparison, gels were prepared by conventional sol–gel synthesis and characterized.

An intense signal was observed in the NMR spectrum for silica gels derived by MR-catalyzed synthesis (red line in Figure 2a, −113 ppm: denoted as Q^4 silicon species).[10] These results indicate that almost all the Si–OEt bonds are reacted to form Si–O–Si bonds, giving highly condensed (97%, see Supporting Information)[20] silica gels with marginal silanol groups. In contrast, conventional synthesis resulted in silica gels possessing a Q^3 silicon species in the NMR spectra (black line in Figure 2a). The FT-IR results showed almost no silanol groups for the silica gels derived by MR-catalyzed synthesis (red line in Figure 2b), which is in good agreement with the NMR results.

Table 1. Sol–gel polycondensation of TEOS in the presence of MR under various reaction conditions[a]

Entry	MR	Water /equiv	Yield /%[b]	Q^3:Q^4
1	Et_3OBF_4	—	NR	—
2[c]	Et_3OBF_4	0.18	>99	12:88
3	Et_3OBF_4	0.18	98	6:94
4	Et_3OBF_4	0.10	64	7:93
5	Et_3OBF_4	1.0	>99	5:95
6	Me_3OBF_4	0.18	>99	5:95

[a]All reactions were carried out on 200 mg reaction scale of TEOS and MR (0.3 equiv) in anhydrous MeCN (4.0 mL) at rt for 4 h and then at 80 °C for 12 h; NR: no reaction. [b]Isolated yield based on $(SiO_2)_n$ and mean of at least three runs. [c]Reagent grade MeCN was used.

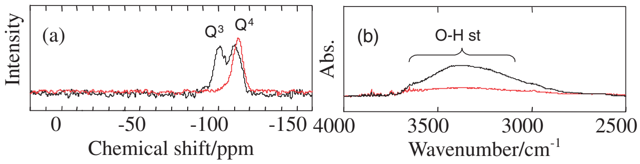
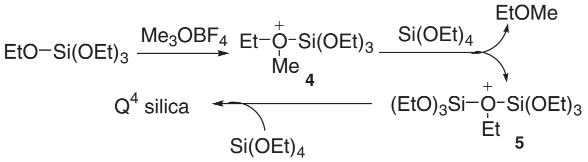


Figure 2. ^{29}Si MAS NMR (a) and FT-IR (ATR, b) spectra for the silica gels prepared by MR-catalyzed (red line) or conventional sol–gel synthesis (black line).



Scheme 2. Plausible pathway for MR-catalyzed sol–gel polycondensation of TEOS.

Additional experiments were performed for a thorough investigation by varying the mol % of water in anhydrous MeCN (Entries 3–5).[11] Entry 3 provided 98% silica with Q^4 content up to 94%. Polycondensation in the presence of trimethyloxonium tetrafluoroborate (Me_3OBF_4) also resulted in highly-condensed silica without altering the Q^4 content (Entry 6). Et_3OBF_4 is labile to hydrolysis with the formation of HBF_4. Thus, in order to ascertain any acid-catalyzed sol–gel polycondensation, we performed the reaction in the presence of 60 mol % of HBF_4 (45% solution in water). The polycondensation proceeded incompletely resulting in Q^2 and Q^3 together with Q^4 silicon species (see: SI).

During the course of our studies on the MR-catalyzed sol–gel process, Asefa et al. reported the use of Et_3OBF_4 for the fluorination of mesoporous silicas.[12] In accordance with his and previous reports by Sakurai[7a] and Olah,[7b,7c] we propose that during the initial stage of polycondensation, Et_3OBF_4 dissociates into Et^+, Et_2O, and BF_4^-.[13] Formation of BF_4^- raised a question about the ≡Si–F containing species in the obtained silica. Consequently, ^{19}F MAS NMR was measured, which showed a sharp peak at −150 ppm (assigned for BF_4^-) and a broad peak ranging from −140 to −150 ppm (assigned for ≡Si–F). These results suggest that nucleophilic fluorination[14] to the Si center occurred to some extent in the course of the condensation reaction with TEOS. Furthermore, ion chromatography analysis data for the silica sample showed a residual fluoride content of 1.1 mass % (SI).

In order to elucidate the plausible reaction mechanism, we next performed additional reaction of TEOS (1.0 equiv) with Me_3OBF_4 (0.3 equiv) using an NMR tube with J Young valve (see SI). The formation of EtOMe observed by ^1H NMR indicates the presence of silyloxonium intermediate **4**.[7a,15,16] Moreover, we observed two new quartets at 4.0 and 4.54 ppm corresponding to $-CH_2$ protons adjacent to $-CH_3$ groups at 1.27 and 1.45 ppm, respectively. As there is no previous report and no NMR evidence regarding such intermediates, we speculate that these two quartets correspond to silyloxonium intermediates. On the basis of these findings, we propose a plausible reaction pathway in Scheme 2.

As we discussed, Me_3OBF_4 dissociates into Me^+ which presumably alkylate the –OEt group of TEOS to form silyloxonium **4**. According to reports by Asefa[12] and Maier,[17] nucleophilic attack by F^- at the Si center likely results in a hypervalent silicon intermediate that stretches and weakens the Si–OEt bonds. At a later stage, silyloxonium **5** will also likely be generated with an additional mol of TEOS. Independent reports by Sakurai[7a] and Olah[7b,7c] on the detection of silyloxoniums **1**–**3** (Figure 1) support our claim for proposed silyloxoniums **4** and **5**. In addition to the above reports, Charpentier also recently observed the presence of a silyloxonium in the polycondensation of TMOS.[18] Furthermore, our protocol need 10–18 mol % of water in dry MeCN[19] however, role of water is unclear at this stage. We speculate that the use of water may possibly help in either solubilizing the oxonium salts or in shifting the equilibrium from silyloxonium intermediate **5** to carry forward further condensation of TEOS.

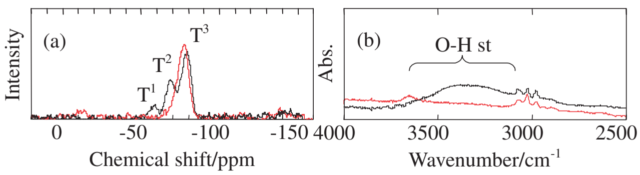


Figure 3. ^{29}Si MAS NMR (a) and FT-IR (ATR, b) spectra for biphenylylene silica prepared by MR-catalyzed (red line) or conventional sol–gel synthesis (black line).

After achieving highly-condensed silica gels from TEOS using MR, we extended our idea to generate organosilica gels. BTEBPh as a model compound successfully provided highly condensed amorphous biphenylylene silica in 94% yield in the presence of Me_3OBF_4 (Figures 3 and SI[20]).

We thank Kyoto Advanced Nanotechnology Network for generous support.

References and Notes

1 J. J. Ebelman, *Ann. Chim. Phys.* **1846**, *16*, 129.
2 M. A. Brook, *Silicon in Organic, Organometallic, and Polymer Chemistry*, John Wiley & Sons, Inc., New York, **2000**, Chap. 10.
3 a) R. C. Mehrotra, *J. Non-Cryst. Solids* **1988**, *100*, 1. b) C. J. Brinker, G. W. Scherer, *Sol–Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press, New York, **1990**. c) K. J. Shea, D. A. Loy, *Acc. Chem. Res.* **2001**, *34*, 707; For nonhydrolytic sol–gel, see: L. Bourget, R. J. P. Corriu, D. Leclercq, P. H. Mutin, A. Vioux, *J. Non-Cryst. Solids* **1998**, *242*, 81.
4 a) T. Shimada, K. Aoki, Y. Shinoda, T. Nakamura, N. Tokunaga, S. Inagaki, T. Hayashi, *J. Am. Chem. Soc.* **2003**, *125*, 4688. b) K. Aoki, T. Shimada, T. Hayashi, *Tetrahedron: Asymmetry* **2004**, *15*, 1771. c) M. P. Kapoor, S. Inagaki, S. Ikeda, K. Kakiuchi, M. Suda, T. Shimada, *J. Am. Chem. Soc.* **2005**, *127*, 8174.
5 a) W. K. Jozwiak, I. G. D. Lana, R. Fiedorow, *J. Catal.* **1990**, *121*, 183. b) P. Ugliengo, V. Saunders, E. Garrone, *J. Phys. Chem.* **1990**, *94*, 2260. c) K. Su, D. R. Bujalski, K. Eguchi, G. V. Gordon, D.-L. Ou, P. Chevalier, S. Hu, R. P. Boisvert, *Chem. Mater.* **2005**, *17*, 2520. d) N. Thakar, T. J. Schildhauer, W. Buijs, F. Kapteijn, J. A. Moulijn, *J. Catal.* **2007**, *248*, 249.
6 a) A. D. Irwin, J. S. Holmgren, J. Jonas, *Mater. Lett.* **1987**, *6*, 25. b) W. K. Pang, I. M. Low, J. V. Hanna, *J. Aust. Ceram. Soc.* **2009**, *45*, 39.
7 For mono-, di-, and trisilyloxonium intermediates, see: a) M. Kira, T. Hino, H. Sakurai, *J. Am. Chem. Soc.* **1992**, *114*, 6697. b) G. A. Olah, X.-Y. Li, Q. Wang, G. Rasul, G. K. S. Prakash, *J. Am. Chem. Soc.* **1995**, *117*, 8962. c) G. A. Olah, H. Doggweiler, J. D. Felberg, S. Frohlich, *J. Org. Chem.* **1985**, *50*, 4847.
8 H. Meerwein, *Org. Synth.* **1966**, *46*, 113.
9 Y. Kawakami, Y. Yamashita, *Macromolecules* **1979**, *12*, 399.
10 Powder XRD reveals amorphous architecture without any periodicity. The sample has a BET surface area of 109.3 $m^2 g^{-1}$ (SI).
11 For experimental procedure, ^{29}Si and ^{19}F MAS NMR, see: SI.
12 C. T. Duncan, A. V. Biradar, S. Rangan, R. E. Mishler, II, T. Asefa, *Chem. Mater.* **2010**, *22*, 4950.
13 G. A. Olah, H. Doggweiler, J. D. Felberg, *J. Org. Chem.* **1984**, *49*, 2112.
14 a) K. Tamao, T. Hayashi, Y. Ito, M. Shiro, *J. Am. Chem. Soc.* **1990**, *112*, 2422. b) O. Farooq, G. V. D. Tiers, *J. Org. Chem.* **1994**, *59*, 2122.
15 D. D. Eley, D. F. Monk, C. H. Rochester, *J. Chem. Soc., Perkin Trans. 2* **1976**, 1292.
16 Diethylsilyloxonium has been detected by ^1H NMR in methylene chloride-d_2. For details, see: ref. 7a.
17 For hypervalent silicon species, see: I. C. Tilgner, P. Fischer, F. M. Bohnen, H. Rehage, W. F. Maier, *Microporous Mater.* **1995**, *5*, 77.
18 P. A. Charpentier, X. Li, R. Sui, *Langmuir* **2009**, *25*, 3748.
19 For the reactions of MeCN with Me^+, see: J. E. Gordon, G. C. Turrell, *J. Org. Chem.* **1959**, *24*, 269.
20 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.