From SiO₂ to Alkoxysilanes for the Synthesis of Useful Chemicals

Wahyu S. Putro, Vladimir Ya. Lee, Kazuhiko Sato, Jun-Chul Choi, and Norihisa Fukaya*

ABSTRACT: The transformation of silica (SiO₂) to useful chemicals is difficult to explore because of the strength of the Si–O bond and thermodynamic stability of the SiO₂ structure. The direct formation of alkoxysilanes from SiO₂ has been explored as an alternative to the carbothermal reduction (1900 °C) of SiO₂ to metallic silicon (Simet) followed by treatment with alcohols. The base-catalyzed depolymerization of SiO₂ with diols and mono-alcohols afforded cyclic silicon alkoxides and tetraalkoxysilanes, respectively. SiO₂ can also be converted to alkoxysilanes in the presence of organic carbonates, such as dimethyl carbonate. Alkoxysilanes can be further converted to useful chemicals, such as carbamates, organic carbonates, and chlorosilanes. An interesting and highly efficient pathway to the direct conversion of SiO₂ to alkoxysilanes has been discussed in detail along with the corresponding economic and environmental implications. The thermodynamic and kinetic aspects of SiO₂ transformations in the presence of alcohols are also discussed.

INTRODUCTION

Silicon, the second most abundant element in the earth’s crust (28%), is primarily bonded with oxygen and exists as silica (polymeric SiO₂) and metal silicates. These constitute more than 40% of the mineral content in the earth’s crust. However, despite its abundance, terrestrial life forms mainly consume carbon-based biomass compounds, whereas silicon remains an “accessory element”. Silicon compounds have limited impact due to the high strength of the Si–O bonds (~100 kcal/mol) and resonance delocalization across the Si–O–Si bonds, which impart considerable thermodynamic stability to the polymeric SiO₂ structure. In addition, silicon exists almost exclusively in the stable oxidation state of +4. Therefore, it is difficult to cleave the Si–O bonds and form Si–Si and Si–C bonds unless they are sterically stabilized.

To obtain molecular silicon derivatives for facile manipulation, silica is first reduced to metallic silicon (Siₖinet). Siₖinet is produced industrially in 70–90% yield by the carbothermal reduction of SiO₂ with carbonaceous reducing agents in an energy-intensive process (T = 1900 °C) (Figure 1). We have estimated that the carbothermal reduction of silica requires the energy of approximately 1.5 L of gasoline for the production of 1 kg of Siₖinet. This Siₖinet is subsequently reoxidized to Si derivatives containing Si in the +4 oxidation state in a direct synthesis to produce Si-containing materials, such as Me₅SiCl₆, HSiCl₅, SiCl₄, and Si(OR)₄ through chemical processes using MeCl, HCl, and ROH in the presence of Cu catalysts. These chemicals are widely used to fabricate materials of industrial importance, such as organosilicon products, semiconductor wafers, and ceramics. In particular, Me₅SiCl₆ (or Me₅SiCl₄–x) is used to synthesize polymethylsiloxane (PDMS), which is a typical Si-based polymer. The alternative “sand-to-Si” process has been proposed, which involves metallothermic reduction using pure Mg or Al metals at 600–650 °C. Simet has been recently obtained via metallothermic reduction at lower temperature (450 °C) using a Mg–Al alloy. All of these processes are prohibitively expensive and generate substantial amounts of byproducts. There are also issues related to the production of the associated metal or alloy-based reductants. Therefore, the direct formation of silicon compounds from silica through a nonredox process that precludes the production of Siₖinet and can be performed under milder conditions is a “grand challenge” for chemists.

A rational approach to overcoming these issues should rely on development of chemical methods that involve chemical transformation of renewable feedstock. Since alcohols can be produced from biomass in biorefineries, SiO₂ depolymerization using alcohols as reagents to generate alkoxysilanes can support the cause of sustainable chemistry. In this review, discussions on the transformation of SiO₂ to alkoxysilanes have been organized into three sections, with particular emphasis on...
recent reports on the direct synthesis of various alkoxysilanes from SiO$_2$ using alcohols and the application of alkoxysilanes in the synthesis of useful chemicals. The structures of the alkoxysilane products show a remarkable dependence on the
alcohols and catalysts used. Cyclic silicon alkoxides including tetra, penta, and hexacoordinate silicon compounds are produced from diols, and tetraalkoxysilanes (TROS) which are generated from monoalcohols (Figure 2). Thermodynamic studies, density functional theory (DFT) calculations, and technoeconomic and environmental assessments of the processes involved in the transformation of SiO$_2$ to alkoxysilanes provide general information that can facilitate the development of more effective processes with potential utility in industrial applications.

**SYNTHESIS OF CYCLIC SILICON ALKOXIDES FROM SiO$_2$ AND POLYOLS**

The chemistry of silicon is naturally dominated by its affinity for oxygen (oxophilicity), which is responsible for its tetrahedral configuration. Silicon alkoxides with coordination numbers exceeding 4 have been known since Rosenheim et al. synthesized hexacoordinate silicon compounds via the depolymerization of SiO$_2$ using catechol in the beginning of the 1930s. Since then, the synthesis and structural characterization of hypervalent silicon compounds, such as those containing penta-oxo and hexa-oxosilicon centers have elicited considerable interest. This section contains a literature survey related to the synthesis of cyclic silicon alkoxides, including hypervalent silicon compounds, via SiO$_2$ depolymerization.

The use of sterically hindered diols is key to the formation of spirocyclic alkoxysilanes. For example, the commercially available substrate 2-methyl-2,4-pentanediol has been used for the NaOH-catalyzed depolymerization of SiO$_2$ to produce one of the most stable spirocyclic alkoxysilanes, I (Figure 3, reaction 1). Laine and co-workers extended the synthesis of I using silica derived from various natural resources, such as rice hull ash (RHA) and diatomaceous earth (DE), achieving a 4–98% yield of I, depending on the surface area (SA). Strong alkali metal bases can be replaced by aminodiols to accelerate SiO$_2$ dissolution. The catalytic effects of SiO$_2$ dissolution are strongly influenced by the basicity of the aminodiols, which is responsible for the deprotonation of the alcohol solvents to form alkoxide. Alkoxides are the reactive species involved in SiO$_2$ dissolution. Using 2-amino-2-methyl-1,3-propanediol as the starting material, the aminospirosilicate II was produced at 160 °C under vacuum in the presence of triethylenetetramine (TETA) as an accelerator for the dissolution of SiO$_2$ (Figure 3, reaction 2). II was obtained in an overall yield of approximately 80% in 14 h using KOH as the cocatalyst and 24 h in the absence of KOH. In this case, fumed silica (SA ~ 280 m$^2$/g) proved to be more reactive than fused silica (SA ~ 182 m$^2$/g). A high-boiling aminodiol, such as triethanolamine (bp = 193 °C/5 mmHg, pK$_a$ = 6.35) is employed to depolymerize an equivalent amount of SiO$_2$ using ethylene glycol as the solvent, resulting in ~35% yield of the silatrane glycol III, when the reaction is performed at 200 °C for 3 h (Figure 3, reaction 3). The SiO$_2$ derived from RHA can also be depolymerized under ambient conditions in aqueous alcohol in the presence of R$_n$NOH (R = Me, CH$_2$CH$_2$OH) to exclusively form the choline octasilate [NR$_4$]$_4$[OSiO$_{1.5}$]$_8$ IV (Figure 3, reaction 4). The yield of IV increased with increasing water concentration, which indicated that water was essential to the formation of IV. According to the results of crystallographic studies, the crystal structure of IV contains 24 H$_2$O per octaanion or 3 H$_2$O per SiO$_{1.5}$ unit (SiO$_{1.5}$ unit implies that the ratio of the number of silicon and oxygen atoms in the siloxane cage is 2:3). These octasilate anions offer access to novel polyfunctional silsesquioxane platforms as precursors for polymers and many types of organic/inorganic hybrid composites.

In contrast to sterically hindered diols that transform SiO$_2$ to neutral spirocyclic alkoxysilanes, simple diols, such as ethylene glycol, can convert SiO$_2$ to anionic organosilicates, such as pentacoordinate and hexacoordinate silicate compounds. Pentacoordinate silicates V are prepared by the direct reaction of alkali metal hydroxides [MOH; M = Li, Na, K, Cs] with 1 equiv of SiO$_2$ in the presence of excess ethylene glycol (Figure 4, reaction 5), whereas VI can be synthesized using alkaline-earth metal oxides (MO; M = Ba, Ca, Mg) (Figure 4, reaction 6). The yields of V obtained using alkali metal hydroxides, such as LiOH, NaOH, KOH, and CsOH, are in the range of 60–95% after 1–2 h of reaction followed by purification. The dissolution rate observed in the presence of alkali metal hydroxides was reportedly 10 times higher than that in the presence of amines, suggesting a difference in the basic strengths of alkali metal hydroxides and amine bases.

**SYNTHESIS OF TROS FROM SiO$_2$**

TROS are promising raw materials that can be utilized to synthesize a variety of zeolites, ceramics, and inorganic—
organic nanocomposite films. Several simpler and more practical alternative methods for the synthesis of TROS from SiO2 have been proposed to replace the high-energy consuming processes that are applied in industries. For example, Laine et al. reported the synthesis of tetramethyl orthosilicate (TMOS) and tetraethyl orthosilicate (TEOS) from spirocyclic alkoxysilanes, which were prepared from SiO2 and diols, in the presence of MeOH and EtOH. The respective yields were 40 and 60% (Figure 5). Other reported methods for TEOS synthesis include the reaction of calcium silicate with HCl/EtOH, and the reaction of SiO2 and EtOH followed by azeotropic distillation.10b,c Recently, our group has developed a direct synthesis of TROS from SiO2 and alcohols.15 This approach promises because of its nontoxicity and the use of abundant alcohols. However, SiO2 is thermodynamically stable, and the H2O byproduct easily reacts with the TROS product to form oligomeric or polymeric SiO2. Therefore, molecular sieves (MS) were employed as dehydrating agents in the KOH-catalyzed direct synthesis of TROS from SiO2. To address the decomposition-related issues, we designed a system in which a reaction site and dehydrating vessel containing MS was arranged separately (Figure 6). The reaction was performed using simulator Pro/II.16a Compared to the conventional route, in which TEOS is produced from the reaction of SiO2 with ethanol or alternatively by the reaction of SiCl4 with ethanol,16b the proposed process leads to decreased production costs and markedly reduced greenhouse gas (GHG) emissions. The production cost and GHG emissions can be reduced by approximately 7 and 34%, respectively, by substituting the proposed process for the conventional one under optimum conditions. Despite its sensitivity toward utility cost related to the price of crude oil, the proposed synthetic technique is more sustainable and has potential for industrial application. In the direct synthesis of TEOS via the reaction between SiO2 and ethanol, the removal of water using dehydrating agents strongly influences the yields and economic and environmental implications.17 CaO was found to be the most effective dehydrating agent among various candidates, such as MS, CaCl2, MgSO4, and Na2SO4, which produced a TEOS yield of 76%. The feasibility of the designed process using CaO was evaluated in comparison with that using MS as the dehydrating agent and the conventional process. The evaluation results confirmed that the process involving CaO was more competitive economically and environmentally friendly, leading to reductions of 24 and 40% in the production cost and GHG emissions, respectively, compared to those of the conventional process. The process using CaO was found to be more competitive than that using MS. However, considering the cost of regenerating the dehydrating agent (MS are easier to regenerate than CaO), additional experiments are necessary for a conclusive estimation of the effectiveness of the dehydrating agent.

We also extended the experiment using organic dehydrating agents, such as acetals, for the direct synthesis of TMOS from SiO2 in the presence of MeOH under CO2 pressure (Figure 7).18 CO2 is significant for promoting the TMOS yield. In the absence of CO2, the yield of TMOS was only 5%, whereas the incorporation of 0.8 MPa of CO2 resulted in a 47% yield (entry 1). Increasing the CO2 pressure to 2 MPa produced a 49% yield of TMOS when 2,2-dimethoxypropane was used as the dehydrating agent (entry 2). The use of excess acetal (25 mmol) significantly increased the TMOS yield to 83% (entry 3). Another acetal, 1,1-dimethoxyhexahexane, afforded a lower TMOS yield of 36% (entry 4). These results indicated that both CO2 and the acetal were important for optimizing the TMOS yield. As a dehydrating agent, the acetal was responsible for DMC (dimethyl carbonate) formation and accelerated TMOS production (Figure 7). The use of silica derived from various natural products afforded a TMOS yield of ∼40% (entries 5–7), demonstrating the potential application of natural SiO2 feedstocks in TMOS synthesis using acetals.

Computation of the thermodynamic parameters of silica depolymerization using alcohols, modeled on the alcoholysis of cyclic-[SiO(OH)]4 to Si(OH)3, 5,5-silaspirocycle, and 6,6-silaspirocycle was performed by Torgunrud et al.19 The reaction with methanol is never exergonic (in all media, the positive value of ΔG increases with

**Figure 5.** Synthesis of TROS from SiO2 using spirocyclic alkoxysilanes.

**Figure 6.** Direct synthesis of TROS from SiO2 and alcohols.
Figure 7. Synthesis of TMOS from SiO₂ and MeOH under CO₂ pressure using acetals as dehydrating agents and the plausible mechanism.

Figure 8. Calculated thermodynamic parameters for silica depolymerization by methanol, ethylene glycol, and 1,3-propanediol in different media.

*Calculated at the DFT/B3LYP/6-31+G* level of theory using the SM8 solvent correction model.
increasing temperature) because of its positive enthalpy and negative entropy values. However, positive entropies were obtained for the depolymerization reaction with ethylene glycol and 1,3-propanediol, indicating the existence of a temperature at which the reaction was exergonic. The thermoneutral temperature \( \Delta G_{\text{reaction}} = 0 \) for the reaction with ethylene glycol was 314 °C in the aqueous medium. The thermoneutral temperature for the reaction with 1,3-propanediol was considerably lower because of the higher stability of the 6,6-silaspirocyle versus that of the 5,5-silaspirocyle. In addition, the reaction with 1,3-propanediol was found to be exergonic at 100 °C and at temperatures exceeding 171 °C in aqueous and ethanolic media, respectively. Therefore, it is conceivable that chelating diols would form more thermodynamically stable alkylorthosilicates and behave as superior silica depolymerization agents because of the associated entropic benefits. Such a conclusion is in line with the earlier findings by Laine and co-workers.

In addition to the previously mentioned methods using alcohols, direct synthesis of TROS from silica can also be realized by the reaction with dialkyl carbonates (Figure 9, reaction 13). Ono et al. reported the complete transformation of SiO\(_2\) to TMOS in a fixed-bed flow reactor within 30 min at 327 °C by passing DMC at 96 kPa (43 mmol·h\(^{-1}\)) in the presence of a KOH catalyst. The completion of the reaction between SiO\(_2\) and diethyl carbonate (DEC) to form TEOS necessitates a higher temperature. One hundred percent SiO\(_2\) conversion was observed at 427 °C in a 4 h reaction using the same catalyst and reaction system, which indicated the lower reactivity of DEC toward SiO\(_2\) depolymerization. The SiO\(_2\) present in RHA also reacts with DMC to a quantitative yield of TMOS at 388 °C, and an 80% yield of TEOS was obtained by reaction with DEC at 452 °C. This method demonstrates the promising prospect of using various natural SiO\(_2\) sources as feedstock for the production of tetraalkoxysilanes. In addition to alkali metal hydroxides, Suzuki, Ono, and co-workers screened alkali metal halides (KF, KCl, NaCl, Na\(_2\)CO\(_3\), and CsF) as catalysts and found that the catalytic activity generally increases with the polarity of the metal halide salts. The chemists from the General Electric Research Center also contributed to the field by screening many different mineral Si sources which enabled the transformation of alkoxysilanes to alkylalkoxysilanes (that is, conversion of the Si–O to the Si–C bond). Two different pathways for SiO\(_2\) activation were proposed by Ono et al. using gas chromatography. It is plausible that the surface SiO\(_2\) was activated by the interaction with DMC. DMC initially interacted with the catalyst to form a reactive CH\(_3\)O\(^-\) species, which subsequently reacted with the surface SiO\(_2\) (Figure 9, route 1). Once a reactive SiO\(_2\) surface site containing SiO\(^-\) is formed, it directly reacts with DMC to form an SiOCH\(_3\) moiety and the cleavage of the Si–O–Si bonds is completed. The activation might also proceed through a direct interaction of SiO\(_2\) with the alkali-base catalyst, which cleaves the Si–O–Si bonds (Figure 9, route 2). Herein, our group modeled the mechanistic details of the reaction between silica...
and DMC catalyzed by an alkali metal base through the MOH-activated SiO2 pathway using DFT calculations.21g The results confirmed that the reaction typically proceeds through four mechanistic steps. Initially, the alkali metal base catalyst activates the Si−O bonds (step I) and cleaves them to form −SiO− and −SiOH (step II). The −SiO− moiety subsequently reacts with the methyl group of DMC to form an Si−OCH3 fragment in step III, which is the rate-determining step. Finally, a methoxy group from DMC is transferred to the Si to produce a species in which the two Si−O bonds in SiO2 are replaced by two Si−OCH3 to form a dimethoxysilyloxide (step IV). The rate-determining step depends strongly on the nature of the cationic part of the alkali metal base catalysts, and the activation barrier height follows the order of LiOH > KOH > CsOH. LiOH was found to be the poorest alkali metal catalyst in terms of activating the SiO2 surface toward the reaction with DMC because of the formation of stable intermediate species in the rate-determining step, whereas CsOH was the most active catalyst, which is in line with previously reported experimental trends.

| Entry | Si source | Amount (mmol) | T (°C) | t (h) | Yield of carbamate (%) |
|-------|-----------|---------------|--------|-------|------------------------|
| 1     | Si(OMe)4 | 2             | 150    | 24    | 84                     |
| 2     | Si(OEt)4 | 2             | 150    | 24    | 35                     |
| 3     | Si(OPr)4 | 2             | 150    | 24    | 30                     |
| 4     | Si(OBu)4 | 2             | 150    | 24    | 32                     |
| 5     | Si(OBu)4 | 2             | 150    | 72    | 92                     |
| 6     | MeSi(OMe)3 | 2.67   | 150    | 24    | 60                     |
| 7     | Me2Si(OMe)2 | 4        | 150    | 24    | 40                     |
| 8     | Me2SiOMe  | 8           | 150    | 24    | 17                     |

Figure 10. Carbamate synthesis from TROS, aniline, and CO2 using Zn catalysts.

Figure 11. Synthesis of DEC using TEOS and CO2 in the presence of Zr catalysts.

### TETRAALKOXYSLANES FOR THE SYNTHESIS OF USEFUL CHEMICALS

In addition to being important to sol−gel chemistry, TMOS and TEOS are widely used in silicone sealants and the semiconductor industry. However, they have limited application in the synthesis of useful chemicals. Laine et al. reported the conversion of tetraalkoxy spiroxiloxanes synthesized from SiO2 and diols to diverse silicon-containing products through the nucleophilic attack of alkylolithium on the tetrahedral Si centers in the alkoxyxiloxanes.22a This group has also developed SiO2-derived silatrane and octasilane for the synthesis of polymer and ceramic precursors.22b By incorporating CO2, our group has reported a reaction system for the synthesis of carbamates and carbonates from the corresponding TROS.

A simple catalytic synthesis of carbamates is achieved by the reaction of CO2, aniline, and TROS with a Zn complex catalyst (Figure 10, reaction 14).23a Upon using 1,10-phenanthroline as a ligand and TMOS as a methoxy source, the carbamate was selectively obtained in 84% yield (entry 1). Expanding the scope of the catalytic reaction with TROS containing longer alkyl groups, such as TEOS, TPrOS, and TBOS, afforded lower yields of the carbamate products (entries 2–4). Extending the reaction time to 72 h increased the yield remarkably to 92%,
indicating that TROS species containing longer chains required longer reaction times (entry 5). Studies on the relationship between the reactivity and number of alkoxy groups in alkoxysilanes showed that the yield of carbamates gradually decreased with a decrease in the number of alkoxy groups (entries 1 and 6–8), underlining the importance of the latter for carbamate synthesis. An efficient synthetic route to carbanates is thus established, which is useful in the synthesis of polyurethane and medicinal and agricultural chemicals. Compared to conventional methods (phosgenation method or reductive carboxylation of nitroaromatics),23b the above-discussed approach has the advantages of low toxicity and easy handling.

An improved sustainable synthesis of DEC has been reported using TEOS and CO2 as substrates.24 In the presence of Zr(OR)4 catalysts, the maximum yield of DEC was ∼50% at 180 °C. No improvement in the yield was observed upon extending the reaction time from 15 to 40 h due to equilibration. The reverse reaction between disiloxane and DEC led to the recovery of the starting TEOS and CO2. As mentioned previously, TEOS was successfully synthesized from SiO2 through the direct depolymerization of SiO2 using a base catalyst. Hence, the depolymerization of the disiloxane byproduct was performed using the same reaction system as that used for the regeneration of TEOS. In the presence of the KOH catalyst, ethanol, and MS, the disiloxane was reconverted to TEOS in 74% yield. A combination of these cyclic protocols enables the waste-free synthesis of DEC, which is used as a fuel additive and in electrolyte batteries, using regenerable TEOS (Figure 11).

The development of improved and energy-efficient routes to synthesize chlorosilanes (SiCl4) through the reaction between TROS and gaseous HCl or SOCl2 as a chloride source has been reported (Figure 12).25a,b Traditionally, the production of SiCl4 via the chlorination of TMOS has been reported (Figure 12).25a,b Traditionally, the production of SiCl4 via the chlorination of TMOS in the presence of SOCl2 or HCl has been reported. In the presence of SiO2, the yield of SiCl4 was 99% at 90 °C. However, the production of useful Si-based chemicals from SiO2 necessitates the highly expensive carbothermal reduction process. Therefore, a high demand exists for elegant, cost-effective methods for the production of various Si derivatives from SiO2. Integrating catalysis and innovative technology will facilitate more efficient exploitation of the SiO2 present in natural resources. For example, a KOH catalyst combined with a CaO dehydrating agent is more economically and environmentally competitive, reducing the cost and GHG emissions by 24 and 40%, respectively, compared with the traditional method for producing TEOS.

The development of a state-of-the-art alternative method to generate various silicon compounds must also include economic and environmental considerations to implement the concept of sustainable chemistry. Consequently, only those processes that require a low-energy input and employ environmentally friendly reagents have the potential for industrial use.

**CONCLUSION**

Silica is one of the most significant minerals on Earth. However, the production of useful Si-based chemicals from SiO2 necessitates the highly expensive carbothermal reduction process. Therefore, a high demand exists for elegant, cost-effective methods for the production of various Si derivatives from SiO2. Integrating catalysis and innovative technology will facilitate more efficient exploitation of the SiO2 present in natural resources. For example, a KOH catalyst combined with a CaO dehydrating agent is more economically and environmentally competitive, reducing the cost and GHG emissions by 24 and 40%, respectively, compared with the traditional method for producing TEOS. The development of a state-of-the-art alternative method to generate various silicon compounds must also include economic and environmental considerations to implement the concept of sustainable chemistry. Consequently, only those processes that require a low-energy input and employ environmentally friendly reagents have the potential for industrial use.

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**Notes**

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