

From SiO<sub>2</sub> to Alkoxysilanes for the Synthesis of Useful Chemicals

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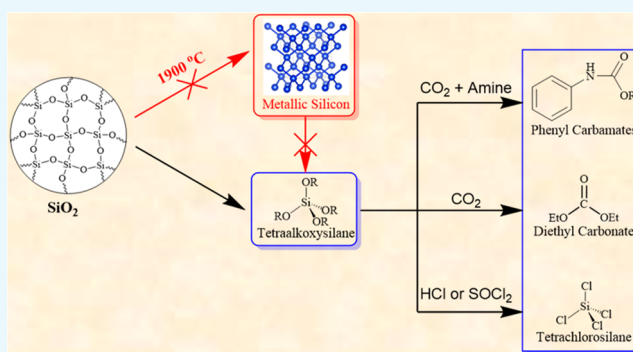
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**ABSTRACT:** The transformation of silica (SiO<sub>2</sub>) to useful chemicals is difficult to explore because of the strength of the Si–O bond and thermodynamic stability of the SiO<sub>2</sub> structure. The direct formation of alkoxysilanes from SiO<sub>2</sub> has been explored as an alternative to the carbothermal reduction (1900 °C) of SiO<sub>2</sub> to metallic silicon (Si<sub>met</sub>) followed by treatment with alcohols. The base-catalyzed depolymerization of SiO<sub>2</sub> with diols and monoalcohols afforded cyclic silicon alkoxides and tetraalkoxysilanes, respectively. SiO<sub>2</sub> 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 SiO<sub>2</sub> to alkoxysilanes has been discussed in detail along with the corresponding economic and environmental implications. The thermodynamic and kinetic aspects of SiO<sub>2</sub> 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 SiO<sub>2</sub>) and metal silicates. These constitute more than 40% of the mineral content in the earth's crust.<sup>1</sup> However, despite its abundance, terrestrial life forms mainly consume carbon-based biomass compounds, whereas silicon remains an "accessory element".<sup>2</sup> 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 SiO<sub>2</sub> structure.<sup>3</sup> In addition, silicon exists almost exclusively in the stable oxidation state of +4.<sup>4</sup> 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 (Si<sub>met</sub>).<sup>5</sup> Si<sub>met</sub> is produced industrially in 70–90% yield by the carbothermal reduction of SiO<sub>2</sub> with carbonaceous reducing agents in an energy-intensive process ( $T = 1900\text{ °C}$ ) (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 Si<sub>met</sub>.<sup>6</sup> This Si<sub>met</sub> is subsequently reoxidized to Si derivatives containing Si in the +4 oxidation state in a direct synthesis to produce Si-containing materials, such as Me<sub>2</sub>SiCl<sub>2</sub>, HSiCl<sub>3</sub>, SiCl<sub>4</sub>, and Si(OR)<sub>4</sub> through chemical processes using MeCl, HCl, and ROH in the presence of Cu catalysts.<sup>7</sup> These chemicals are widely used to fabricate materials of industrial importance, such as organosilicon products, semiconductor

wafers, and ceramics. In particular, Me<sub>2</sub>SiCl<sub>2</sub> (or Me<sub>x</sub>SiCl<sub>4-x</sub>) is used to synthesize polydimethylsiloxane (PDMS), which is a typical Si-based polymer.<sup>8</sup> The alternative "sand-to-Si" process has been proposed, which involves metallothermic reduction using pure Mg or Al metals at 600–650 °C.<sup>9a–c</sup> Si<sub>met</sub> has been recently obtained via metallothermic reduction at lower temperature (450 °C) using a Mg–Al alloy.<sup>9a,b</sup> 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 Si<sub>met</sub> and can be performed under milder conditions is a "grand challenge" for chemists.<sup>10</sup>

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, SiO<sub>2</sub> depolymerization using alcohols as reagents to generate alkoxysilanes can support the cause of sustainable chemistry.<sup>11</sup> In this review, discussions on the transformation of SiO<sub>2</sub> to alkoxysilanes have been organized into three sections, with particular emphasis on

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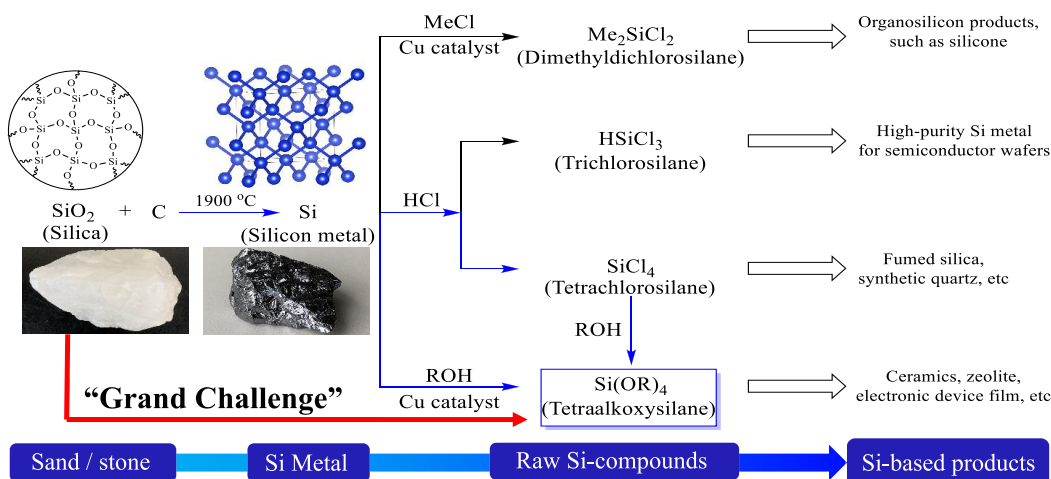


Figure 1. Transformation of  $\text{SiO}_2$  to various value-added chemicals.

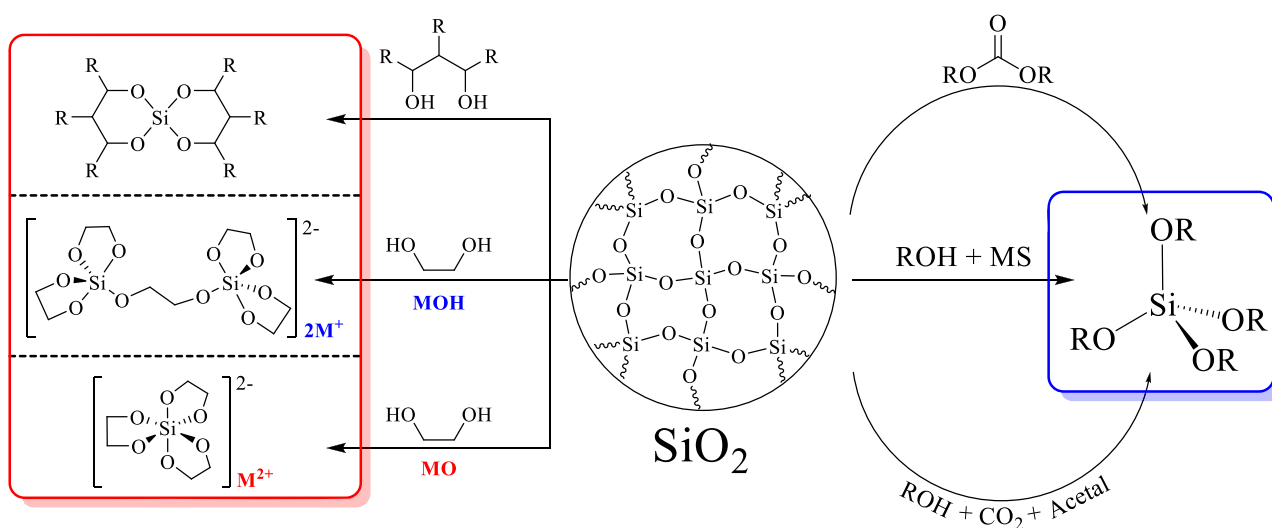


Figure 2. Formation of various alkoxy silanes from  $\text{SiO}_2$  and alcohols (MS = molecular sieves).

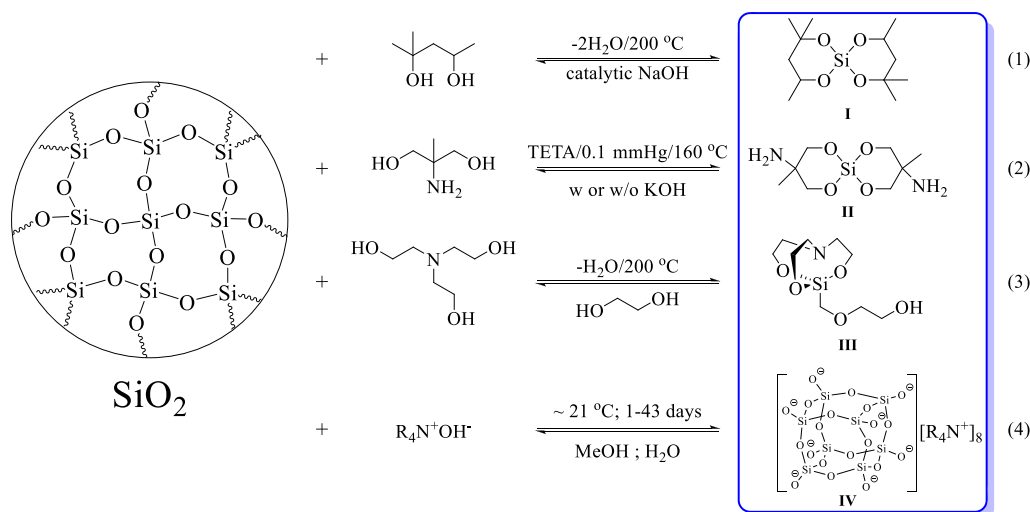
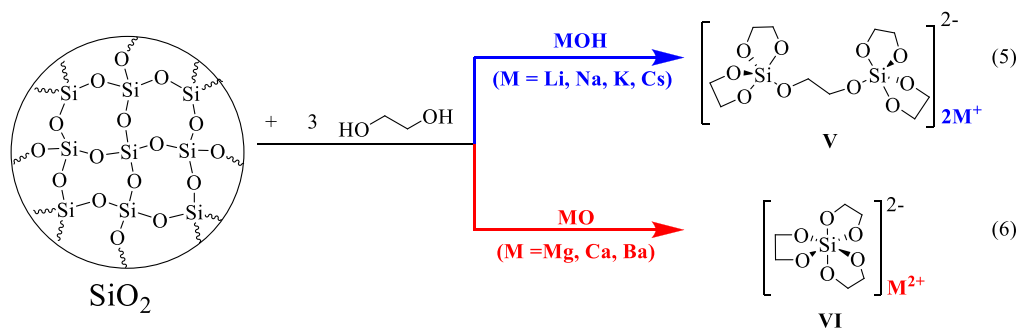


Figure 3. Direct synthesis of cyclic silicon alkoxydes from  $\text{SiO}_2$  and alcohols.

recent reports on the direct synthesis of various alkoxy silanes from  $\text{SiO}_2$  using alcohols and the application of alkoxy silanes

in the synthesis of useful chemicals. The structures of the alkoxy silane products show a remarkable dependence on the



**Figure 4.** Divergent synthesis of penta- and hexaalkoxysilicates from  $\text{SiO}_2$  and diols using alkali metal hydroxides and alkaline-earth metal oxides.

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  $\text{SiO}_2$  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 $\text{SiO}_2$ 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  $\text{SiO}_2$  using catechol in the beginning of the 1930s.<sup>12a</sup> 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.<sup>12b</sup> This section contains a literature survey related to the synthesis of cyclic silicon alkoxides, including hypervalent silicon compounds, via  $\text{SiO}_2$  depolymerization.

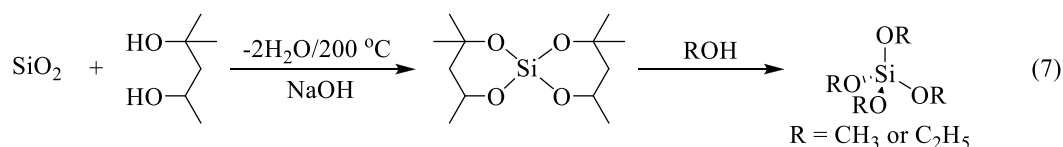
The use of sterically hindered diols is key to the formation of spirocyclic alkoxysilanes. For example, the commercially available substrate 2-methyl-2,4-pentanediol has been used for the NaOH-catalyzed depolymerization of  $\text{SiO}_2$  to produce one of the most stable spirocyclic alkoxysilanes, I (Figure 3, reaction 1).<sup>10a</sup> 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  $\text{SiO}_2$  dissolution. The catalytic effects of  $\text{SiO}_2$  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  $\text{SiO}_2$  dissolution. Using 2-amino-2-methyl-1,3-propanediol as the starting material, the aminospinosilicate II was produced at 160 °C under vacuum in the presence of triethylenetetramine (TETA) as an accelerator for the dissolution of  $\text{SiO}_2$  (Figure 3, reaction 2).<sup>13a</sup> 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  $\text{m}^2/\text{g}$ ) proved to be more reactive than fused silica (SA ~

182  $\text{m}^2/\text{g}$ ). A high-boiling aminodiol, such as triethanolamine (bp = 193 °C/5 mmHg,  $\text{p}K_b = 6.35$ ) is employed to depolymerize an equivalent amount of  $\text{SiO}_2$  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).<sup>13b</sup> The  $\text{SiO}_2$  derived from RHA can also be depolymerized under ambient conditions in aqueous alcohol in the presence of  $\text{R}_4\text{NOH}$  (R = Me,  $\text{CH}_2\text{CH}_2\text{OH}$ ) to exclusively form the choline octasilicate  $[\text{NR}_4]_8[\text{OSiO}_{1.5}]_8$  IV (Figure 3, reaction 4).<sup>13c,d</sup> 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  $\text{H}_2\text{O}$  per octaanion or 3  $\text{H}_2\text{O}$  per  $\text{SiO}_{1.5}$  unit ( $\text{SiO}_{1.5}$  unit implies that the ratio of the number of silicon and oxygen atoms in the siloxane cage is 2:3). These octasilicate anions offer access to novel polyfunctional silsesquioxane platforms as precursors for polymers and many types of organic/inorganic hybrid composites.<sup>13e,f</sup>

In contrast to sterically hindered diols that transform  $\text{SiO}_2$  to neutral spirocyclic alkoxysilanes, simple diols, such as ethylene glycol, can convert  $\text{SiO}_2$  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  $\text{SiO}_2$  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).<sup>14a–d</sup> 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.<sup>14a</sup> 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. Pentacoordinate silicon compounds are highly reactive and promising materials for the synthesis of silicone polymers, silicate glasses, and ceramics. The BaO-catalyzed transformation of  $\text{SiO}_2$  afforded the white microcrystalline product VI in ~90% yield.<sup>14d</sup> However, the yield of VI decreased when CaO or MgO was used instead of BaO due to the low reactivity of CaO or MgO toward ethylene glycol. It is plausible that a dication is necessary to stabilize the hexaalkoxysilicate product VI.

### ■ SYNTHESIS OF TROS FROM $\text{SiO}_2$

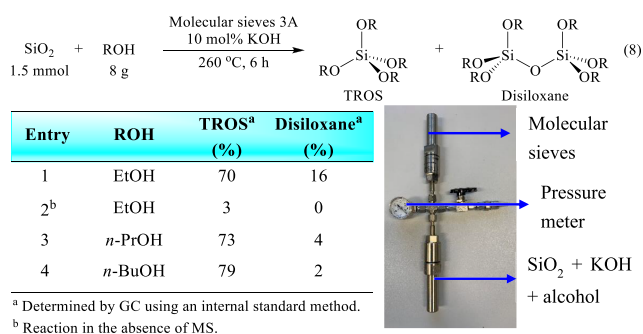
TROS are promising raw materials that can be utilized to synthesize a variety of zeolites, ceramics, and inorganic–



**Figure 5.** Synthesis of TROS from SiO<sub>2</sub> using spirocyclic alkoxyasilanes.

organic nanocomposite films. Several simpler and more practical alternative methods for the synthesis of TROS from SiO<sub>2</sub> 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 alkoxyasilanes, which were prepared from SiO<sub>2</sub> and diols, in the presence of MeOH and EtOH. The respective yields were 40 and 60% (Figure 5).<sup>10a</sup> Other reported methods for TEOS synthesis include the reaction of calcium silicate with HCl/EtOH, and the reaction of SiO<sub>2</sub> and EtOH followed by azeotropic distillation.<sup>10b,c</sup>

Recently, our group has developed a direct synthesis of TROS from SiO<sub>2</sub> and alcohols.<sup>15–19</sup> This method appears promising because of its nontoxicity and the use of abundant alcohols. However, SiO<sub>2</sub> is thermodynamically stable, and the H<sub>2</sub>O byproduct easily reacts with the TROS product to form oligomeric or polymeric SiO<sub>2</sub>. Therefore, molecular sieves (MS) were employed as dehydrating agents in the KOH-catalyzed direct synthesis of TROS from SiO<sub>2</sub>.<sup>15</sup> To address the decomposition-related issues, we designed a system in which a reaction site and dehydrating vessel containing MS were arranged separately (Figure 6). The reaction was



**Figure 6.** Direct synthesis of TROS from SiO<sub>2</sub> and alcohols.

performed at 260 °C, which enabled the evaporation of H<sub>2</sub>O and its adsorption by MS in an upper vessel. The 3 Å MS, with a pore diameter of ~0.3 nm, was the most effective at adsorbing water, resulting in the highest TEOS yield of ~70% (entry 1). In the absence of MS, the formation of TEOS almost leveled off, indicating the importance of the MS (entry 2). This system was also applied for the synthesis of tetrapropyl orthosilicate (TPrOS) and tetrabutyl orthosilicate (TBOS), generating 73 and 79% yields, respectively (entries 3 and 4). The large-scale experiment (10 times) afforded a 75% yield of TEOS, illustrating the potential utility of the developed method in industrial applications.

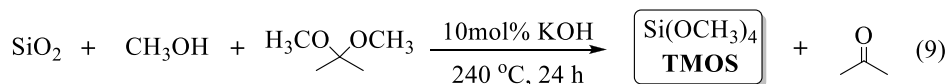
The technoeconomic and environmental assessment of the direct method for the synthesis of TEOS through the reaction between SiO<sub>2</sub> and ethanol in the presence of MS was performed using simulator Pro/II.<sup>16a</sup> Compared to the conventional route, in which TEOS is produced from the

reaction of Si<sub>met</sub> with ethanol or alternatively by the reaction of SiCl<sub>4</sub> with ethanol,<sup>16b</sup> 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 SiO<sub>2</sub> and ethanol, the removal of water using dehydrating agents strongly influences the yields and economic and environmental implications.<sup>17</sup> CaO was found to be the most effective dehydrating agent among various candidates, such as MS, CaCl<sub>2</sub>, MgSO<sub>4</sub>, and Na<sub>2</sub>SO<sub>4</sub>, 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 SiO<sub>2</sub> in the presence of MeOH under CO<sub>2</sub> pressure (Figure 7).<sup>18</sup> CO<sub>2</sub> is significant for promoting the TMOS yield. In the absence of CO<sub>2</sub>, the yield of TMOS was only 5%, whereas the incorporation of 0.8 MPa of CO<sub>2</sub> resulted in a 47% yield (entry 1). Increasing the CO<sub>2</sub> 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-dimethoxycyclohexane, afforded a lower TMOS yield of 36% (entry 4).<sup>19</sup> These results indicated that both CO<sub>2</sub> and the acetals 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 SiO<sub>2</sub> feedstocks in TMOS synthesis using acetals.

Computation of the thermodynamic parameters of silica depolymerization using alcohols, modeled on the alcoholysis of cyclic-[SiO(OH)<sub>2</sub>]<sub>4</sub> to Si(OMe)<sub>4</sub>, 5,5-silaspirocycle, and 6,6-silaspirocycle (Figure 8, reactions 10–12) was performed by Torgunrud et al.<sup>20</sup> The reaction with methanol is never exergonic (in all media, the positive value of ΔG increases with



Entry	SiO <sub>2</sub> source	CO <sub>2</sub> pressure (MPa)	Acetals (mmol)	TMOS Yield (%)
1	Synthetic SiO <sub>2</sub> <sup>a</sup>	0.8	2,2-dimethoxypropane (6 mmol)	47
2	Synthetic SiO <sub>2</sub> <sup>a</sup>	2	2,2-dimethoxypropane (6 mmol)	49
3	Synthetic SiO <sub>2</sub> <sup>a</sup>	2	2,2-dimethoxypropane (25 mmol)	83
4	Synthetic SiO <sub>2</sub> <sup>a</sup>	2	1,1-dimethoxycyclohexane (6 mmol)	36
5	Rice Hull Ash (RHA)	2	2,2-dimethoxypropane (6 mmol)	49
6	Pampas grass	2	2,2-dimethoxypropane (6 mmol)	40
7	Bamboo	2	2,2-dimethoxypropane (6 mmol)	44

<sup>a</sup> CARIACT Q-10

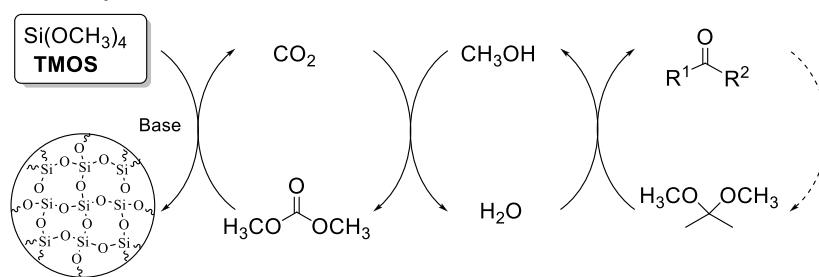
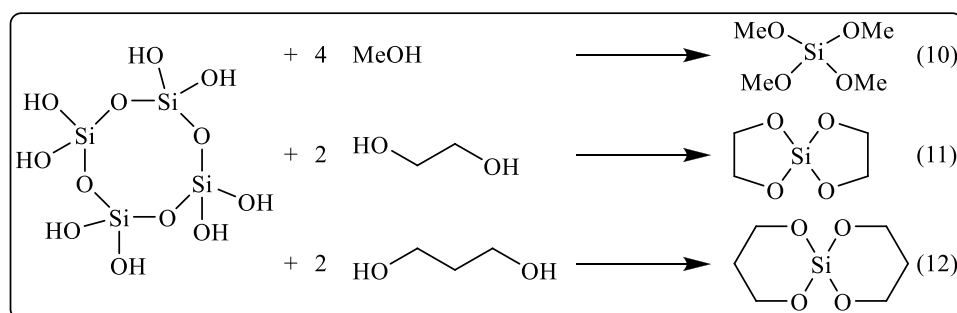
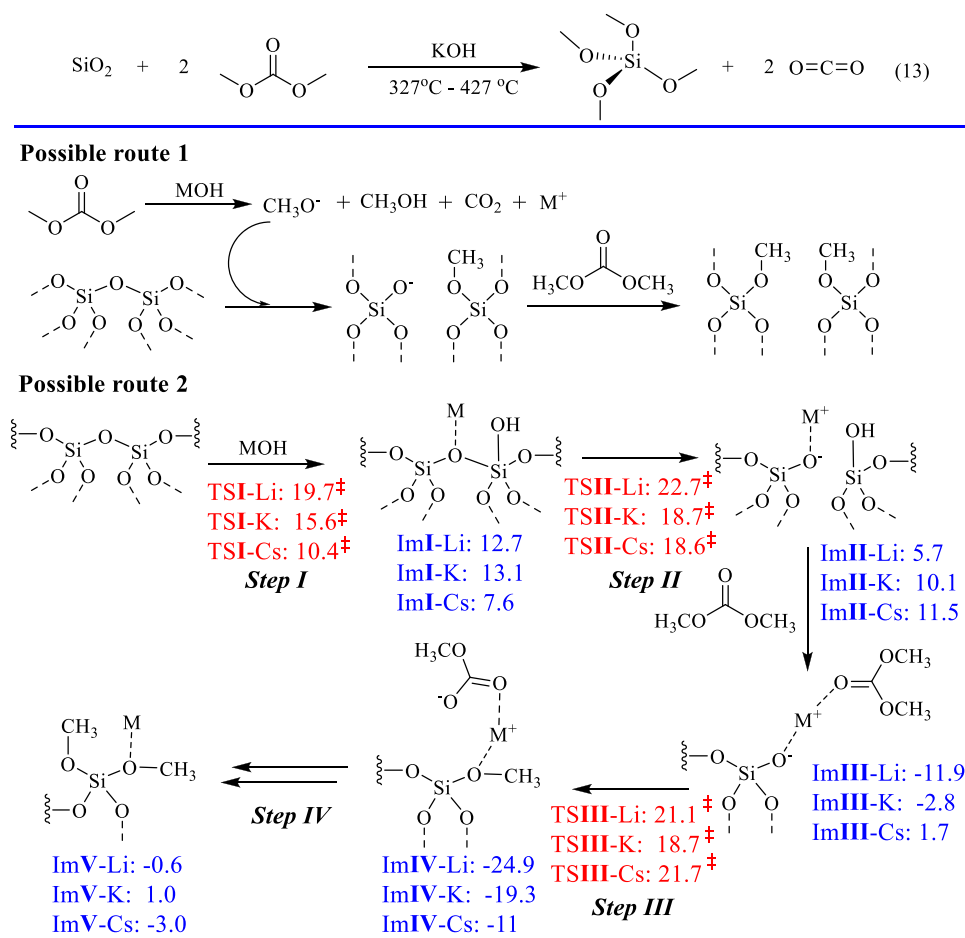


Figure 7. Synthesis of TMOS from SiO<sub>2</sub> and MeOH under CO<sub>2</sub> pressure using acetals as dehydrating agents and the plausible mechanism.



Alcohol	Medium	$\Delta H^a$ (kcal/mol)	$\Delta S^a$ (cal/mol·K)	$\Delta G_{298K}^a$ (kcal/mol)	$\Delta G_{373K}^a$ (kcal/mol)
Methanol	Vacuum	+6.3	-41.9	+18.8	+22.0
	Ethanol	+2.8	-46.6	+16.7	+20.2
	Water	+2.2	-45.4	+15.7	+19.1
Ethylene glycol	Vacuum	+28.4	+30.8	+19.2	+16.9
	Ethanol	+16.8	+26.4	+8.9	+6.9
	Water	+15.7	+26.8	+7.8	+5.7
1,3-propanediol	Vacuum	+21.3	+27.8	+13.0	+11.0
	Ethanol	+10.8	+24.3	+3.6	+1.7
	Water	+9.5	+25.4	+1.9	<b>-0.02</b>

Figure 8. Calculated thermodynamic parameters for silica depolymerization by methanol, ethylene glycol, and 1,3-propanediol in different media. <sup>a</sup>Calculated at the DFT/B3LYP/6-31+G\* level of theory using the SM8 solvent correction model.



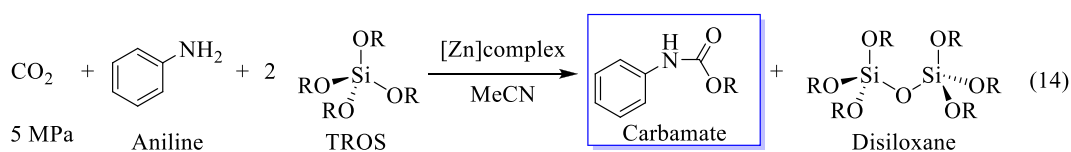
**Figure 9.** Direct synthesis of TMOS from SiO<sub>2</sub> and DMC (dimethyl carbonate): mechanistic studies.

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-silaspirocyclic versus that of the 5,5-silaspirocyclic. 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.<sup>10a</sup>

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).<sup>21a–g</sup> Ono et al. reported the complete transformation of SiO<sub>2</sub> to TMOS in a fixed-bed flow reactor within 30 min at 327 °C by passing DMC at 96 kPa (43 mmol·h<sup>-1</sup>) in the presence of a KOH catalyst.<sup>21a</sup> The completion of the reaction between SiO<sub>2</sub> and diethyl carbonate (DEC) to form TEOS necessitates a higher temperature. One hundred percent SiO<sub>2</sub> 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<sub>2</sub> depolymerization. The SiO<sub>2</sub> present in RHA also reacts with DMC to afford a quantitative yield of TMOS at 388 °C, and an 80% yield of TEOS was obtained by reaction with DEC at 452 °C.<sup>21b</sup> This method demonstrates the promising prospect of using various natural SiO<sub>2</sub> 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<sub>2</sub>CO<sub>3</sub>, and CsF) as catalysts and found that the catalytic activity generally increases with the polarity of the metal halide salts.<sup>21c</sup> 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 alkoxy silanes to alkylalkoxy silanes (that is, conversion of the Si–O to the Si–C bond).<sup>21d,e</sup>

Two different pathways for SiO<sub>2</sub> activation were proposed by Ono et al. using gas chromatography.<sup>21f</sup> It is plausible that the surface SiO<sub>2</sub> was activated by the interaction with DMC. DMC initially interacted with the catalyst to form a reactive CH<sub>3</sub>O<sup>-</sup> species, which subsequently reacted with the surface SiO<sub>2</sub> (Figure 9, route 1). Once a reactive SiO<sub>2</sub> surface site containing SiO<sup>-</sup> is formed, it directly reacts with DMC to form an SiOCH<sub>3</sub> moiety and the cleavage of the Si–O–Si bonds is completed. The activation might also proceed through a direct interaction of SiO<sub>2</sub> 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



Entry	Si source	Amount (mmol)	T (°C)	t (h)	Yield of carbamate (%)
1	Si(OMe) <sub>4</sub> (TMOS)	2	150	24	84
2	Si(OEt) <sub>4</sub> (TEOS)	2	150	24	35
3	Si(OPr) <sub>4</sub> (TPrOS)	2	150	24	30
4	Si(OBu) <sub>4</sub> (TBOS)	2	150	24	32
5	Si(OBu) <sub>4</sub> (TBOS)	2	150	72	92
6	MeSi(OMe) <sub>3</sub>	2.67	150	24	60
7	Me <sub>2</sub> Si(OMe) <sub>2</sub>	4	150	24	40
8	Me <sub>3</sub> SiOMe	8	150	24	17

Figure 10. Carbamate synthesis from TROS, aniline, and CO<sub>2</sub> using Zn catalysts.

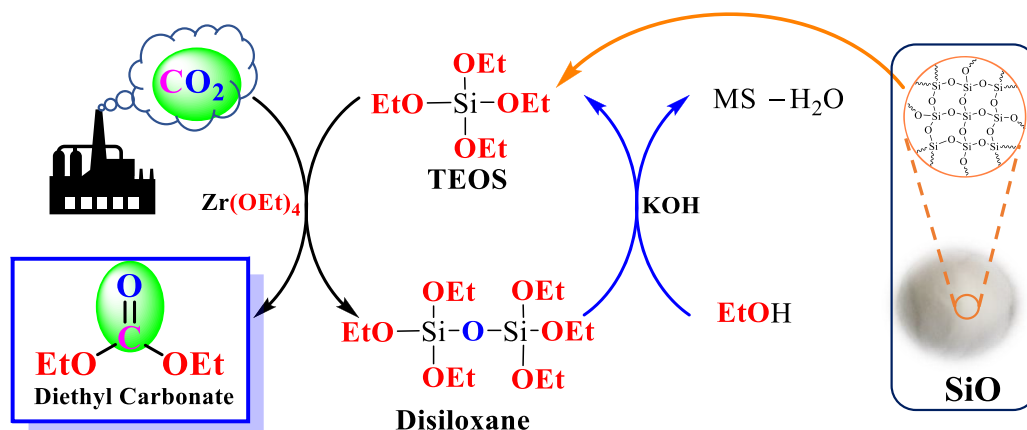


Figure 11. Synthesis of DEC using TEOS and CO<sub>2</sub> in the presence of Zr catalysts.

and DMC catalyzed by an alkali metal base through the MOH-activated SiO<sub>2</sub> pathway using DFT calculations.<sup>21g</sup> The results confirmed that the reaction typically proceeds through four mechanistic steps. Initially, the alkali metal base activates the Si–O bonds (step I) and cleaves them to form –SiO<sup>–</sup> and –SiOH (step II). The –SiO<sup>–</sup> moiety subsequently reacts with the methyl group of DMC to form an Si–OCH<sub>3</sub> 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 SiO<sub>2</sub> are replaced by two Si–OCH<sub>3</sub> to form a dimethoxysilyloxy (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 SiO<sub>2</sub> 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.

## ■ TETRAALKOXYSIANES FOR THE SYNTHESIS OF USEFUL CHEMICALS

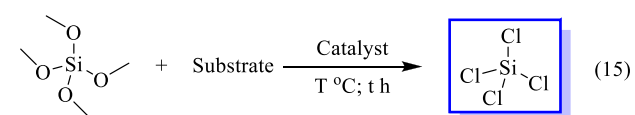
In addition to being important to sol–gel chemistry, TMOS and TEOS are widely used in silicone sealants and the semiconductor industry. However, they have limited application in the synthesis of useful chemicals. Laine et al. reported the conversion of tetraalkoxy spiroloxanes synthesized from SiO<sub>2</sub> and diols to diverse silicon-containing products through the nucleophilic attack of alkyllithium on the tetrahedral Si centers in the alkoxyloxanes.<sup>22a</sup> This group has also developed SiO<sub>2</sub>-derived silatrane and octasilane for the synthesis of polymer and ceramic precursors.<sup>22b–d</sup> By incorporating CO<sub>2</sub>, 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 CO<sub>2</sub>, aniline, and TROS with a Zn complex catalyst (Figure 10, reaction 14).<sup>23a</sup> 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 alkoxy silanes 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 carbamates is thus established, which is useful in the synthesis of polyurethane and medicinal and agricultural chemicals. Compared to conventional methods (phosgenation method or reductive carbonylation of nitroaromatics),<sup>23b</sup> 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 CO<sub>2</sub> as substrates.<sup>24</sup> In the presence of Zr(OEt)<sub>4</sub> 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 CO<sub>2</sub>. As mentioned previously, TEOS was successfully synthesized from SiO<sub>2</sub> through the direct depolymerization of SiO<sub>2</sub> 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 (SiCl<sub>4</sub>) through the reaction between TROS and gaseous HCl or SOCl<sub>2</sub> as a chloride source has been reported (Figure 12).<sup>25a,b</sup> Traditionally, the production of



Substrate	Catalyst	Solvent	T (°C)	t (h)	Yield of SiCl <sub>4</sub> (%)
HCl	LiCl	MeCN	90	6	99
	ZnCl <sub>2</sub>	MeCN	90	6	31
	FeCl <sub>3</sub>	MeCN	90	6	50
	HMPA	MeCN	0	6	86
SOCl <sub>2</sub>	HMPA	DMF	90	3	85
	Bu <sub>4</sub> NCl	DMF	90	3	99
	Me <sub>4</sub> NCl	DMF	90	3	99
	Bu <sub>4</sub> NBr	DMF	90	3	99

**Figure 12.** Catalytic chlorination of TMOS with Cl-containing substrates (HCl and SOCl<sub>2</sub>).

SiCl<sub>4</sub> has been based on the chlorination of Si<sub>met</sub> with methyl chloride (the Rochow–Muller process) or HCl. Although these methods are robust, they rely on the carbothermal reduction of SiO<sub>2</sub> to Si<sub>met</sub>. Similar to the alternative low-energy methods for synthesizing TROS from SiO<sub>2</sub>, the direct synthesis of SiCl<sub>4</sub> via the chlorination of TROS has been reported. An exclusive yield of SiCl<sub>4</sub> was achieved by employing a LiCl catalyst (among other Lewis acid catalysts) in the reaction between TMOS and HCl using acetonitrile (MeCN) as an

MeOH trap and/or a solvent.<sup>25a</sup> Upon using a Lewis base catalyst, for example, hexamethyl phosphoramide (HMPA), an 86% yield of SiCl<sub>4</sub> was obtained at 0 °C. HMPA was effective at catalyzing the chlorination of TMOS in the presence of SOCl<sub>2</sub> (as a replacement for corrosive HCl) in DMF at 90 °C, producing an 85% yield of SiCl<sub>4</sub>.<sup>25b</sup> Other Lewis bases, such as Bu<sub>4</sub>NCl, Me<sub>4</sub>NCl, and Bu<sub>4</sub>NBr were effective in generating an exclusive yield of SiCl<sub>4</sub>, which is used as a raw material in the synthesis of high-purity polysilicon and silica.

## CONCLUSION

Silica is one of the most significant minerals on Earth. However, the production of useful Si-based chemicals from SiO<sub>2</sub> 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 SiO<sub>2</sub>. Integrating catalysis and innovative technology will facilitate more efficient exploitation of the SiO<sub>2</sub> 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

The authors declare no competing financial interest.



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