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Abstract

A simple and practical method for direct synthesis of tetramethoxysilane (TMOS) from silica (SiO_2) and methanol was achieved using a base catalyst and acetal as a dehydrant under carbon dioxide (CO_2). The production of TMOS was strongly influenced by the kind of the acetal used, with 2,2-dimethoxypropane identified as the most effective dehydrant. We observed that the acetal used enabled the production of a high yield of dimethyl carbonate (DMC), which promoted the TMOS production. DMC is an intermediate product from the reaction of CO_2 and methanol, which supported the SiO_2 depolymerization process. When the reaction is conducted with 2,2-dimethoxypropane at 260 °C for 24 h, TMOS can be produced in up to 59% yield. For practical applications, the TMOS synthesis has been developed on a 250 mL and 1 L-scale reaction with constant yield (>50%) from various silica resources.

Keywords: Tetramethoxysilane, Silica, Natural resources

1. Introduction

Tetraalkoxysilanes (TROS) are important materials used to prepare various ceramics, zeolites, and synthetic pure silicas by the sol-gel process.[1] TROS are widely used as heat transfer media, electronic coolants, and protective silica films for electronic devices.[2] Research has also shown that TROS can be converted to $SiCl_4$, which is used as a raw material in the synthesis of polysilicon.[3, 4] In chemical industry, TROS is produced from SiO_2 through a multiple-step procedure. The SiO_2 is first reduced to metallic Si (Si_{met}) through an energy-intensive process. The Si_{met} is subsequently reacted with HCl followed by alcohols to obtain TROS. Alternatively, TROS can be produced by the direct reaction of Si_{met} with alcohols (Scheme 1.A).[5] This method is prohibitively expensive because it requires high-temperature conditions and a multiple-step reaction to obtain TROS. The direct synthesis of TROS from SiO_2 and alcohols would provide an ideal process and development of this method is considered as a "grand challenge" for chemists (Scheme 1.A).[6]

Rosenheim et al. initially reported the activation of SiO_2 by depolymerizing SiO_2 using catechol to generate hexacoordinated complexes (Scheme 1.B).[7] The synthesis of TMOS or TEOS could also be achieved by a reaction of alcohols (methanol or ethanol) with spirocyclic TROS prepared by the reaction of silica and diols, as reported by Laine et al (Scheme 1.C).[6, 8] Bailey et al. reported that TROS were isolated from dehydration of SiO_2

and alcohols by azeotropic distillation.[9] The synthesis of tetraethoxysilane (TEOS) by the reaction of calcium silicates and HCl/ethanol solution has been reported.[10] Another approach reported by Ono et al.[11] and Lewis et al.[12] involved the synthesis of TMOS from the reaction of silica with DMC in the presence of a base catalyst (Scheme 1.D). In this report, we demonstrated the TMOS production promoted by CO_2 rather than the use of stoichiometric DMC.
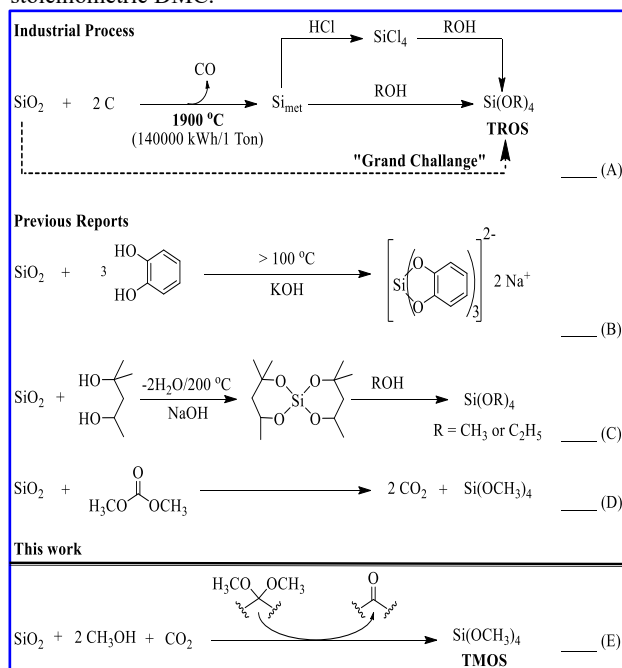
Scheme 1. Production of TROS from SiO_2.

Previously, our group reported the direct synthesis of DMC from methanol and CO_2 using various dehydrating agents.[13-17] Accordingly, we expected that the catalytic synthesis of TMOS from SiO_2 and methanol could be achieved using this DMC production. As expected, the CO_2-mediated direct synthesis of TMOS from silica and methanol successfully proceeded and has been briefly communicated.[18,19] Herein, we describe the details and the application of this reaction to various natural silica resources.

2. Experimental

General. Silica (CARiACT Q-10) used as a starting material was supplied by Fuji Silysia Chemical Ltd. Silica (Wakogel 60N, 63-212 υm) used for scaling-up experiments was purchased from FUJIFILM Wako Pure Chemical Corporation. The surface area (BET), the average pore diameter (BJH), and pore volume (P/P0 = 0.99) were 261 m^2/g, 24.5 nm, and 1.19 cm^3/g, respectively. The silica was dried at 300 °C for 2 h prior to use. The other silica resources (Figure S1), such as rice hull, pampas grass, rice straw, and bamboo (Sasa) applied to this reaction system, were calcined at 500 ºC for 6 h to be the corresponding ashes. The 2,2-dimethoxypropane, 1,1-dimethoxycyclohexane, dimethoxydiphenylmethane, 1,1-dimethoxypropane, α,α-dimethoxytoluene, and dimethyl acetal were purchased from Tokyo Chemical Industry. The (1,1-dimethoxyethyl)benzene was purchased from Sigma-Aldrich. All chemicals were reagent grade and were used without further purification. Carbon dioxide (Showa Tansan, Kawasaki, purity > 99.99%) was used without further purification. Isothermal nitrogen adsorption/desorption measurement of SiO_2 was carried out at –196 °C on a BEL Japan BELSORP mini II. The SiO_2 content in the natural silica resources was determined using a Shimadzu EDX-800HS energy-dispersive X-ray fluorescence spectrometer (EDXRF) with accelerating voltage at 15 kV for Na-Sc and 50 kV for Ti-U element. The transformation of SiO_2 crystal structure due to calcination process was determined by x-ray diffraction (XRD) measurement. All volatile products were characterized by gas chromatography−mass spectrometry (GC-MS) using a Shimadzu GC-2010 connected to a GCMS-QP–2010 Plus mass spectrometer. The yield of products was determined by gas chromatography (GC) using a Shimadzu GC-2014 equipped with a flame ionization detector.

Reaction Procedure for Synthesis of TMOS. SiO_2 (0.18 g, 3.0 mmol), KOH (17 mg, 0.3 mmol), an acetal (6 mmol), and MeOH (7 ml) were added to a stainless-steel autoclave (20 cm^3 inner volume) at room temperature under a N_2 atmosphere. The autoclave was sealed and filled with CO_2. The initial pressure was adjusted to 2 MPa at 25 °C, and the autoclave was heated at 240 °C for 24 h. After cooling to room temperature, p-*tert*-butyltoluene (68 mg) was added to the mixture as an internal standard to determine the yield of products using GC.

Control Experiments for Mechanistic Studies. The reaction was performed at 240 °C for 24 h under the same procedure as the TMOS synthesis without SiO_2. After cooling to room temperature, p-*tert*-butyltoluene (68 mg) was added to the mixture as an internal standard to determine the amounts of DMC using GC analysis.

Scaling-up Synthesis of TMOS.
SiO_2 (30 or 150 mmol), KOH (3 or 15 mmol), acetal (60 or 300 mmol), and MeOH (70 or 350 ml) were added to a stainless-steel autoclave (200 or 1000 mL inner volume) at room temperature under a N_2 atmosphere. The autoclave was sealed and filled with CO_2. The initial pressure was adjusted to 0.8 MPa at 25 °C, and the autoclave was heated at 210 °C (internal temperature) for 24 h. The yield of TMOS was dtermied by GC analysis.

3. Results and Discussion

3.1 Acetal screening

The transformation of SiO_2 (3 mmol) to TMOS was carried out in a stainless-steel autoclave (20 mL) charged with methanol (7 mL), an acetal (6 mmol) as the dehydrant, and 10 mol% KOH as catalyst under 2 MPa of CO_2 (purged at room temperature) for 24 h reaction at 240 ºC. Yields of TMOS for the reactions with various acetals are shown in Figure 1. In the absence of CO_2 and acetals, under 2 MPa of Ar gas, only a small amount of TMOS

was observed (Entry 1). The finding that the CO_2-pressurized reaction promoted TMOS production indicates the imperative role of CO_2 in reaction system (Entry 2). The addition of 2,2-dimethoxypropane as a dehydrant significantly increased the TMOS yield to 57% (Entry 3). Other acetals including 1,1-dimethoxyethane (Entry 4), 1,1-dimethoxypropane (Entry 5), α,α-dimethoxytoluene (Entry 6), and dimethoxydiphenylmethane (Entry 7) were not effective in promoting the production of TMOS. The low product yield in the reaction with dimethoxydiphenylmethane as the dehydrant may be due to its low solubility in methanol. The reactions with 1,1-dimethoxycyclohexane and (1,1-dimethoxyethyl)benzene (Entries 8 and 9) improved the TMOS yields compared with other acetals (Entries 4-7). Therefore, 2,2-dimethoxypropane was selected as the most effective dehydrant for the reaction.

Figure 1. TMOS production with various acetals.

3.2 Mechanistic Studies

Figure 2. Correlation between TMOS yield and DMC production during the catalytic reaction.

As described above, both CO_2 and acetals play important roles in optimization of the TMOS yield. To clarify the roles, the generation of DMC was further scrutinized in a function of acetals without the use of silica. Our results demonstrated a linear correlation between the TMOS yield from SiO_2 and the amount of DMC generated in the absence of SiO_2 (Figure 2). The three acetals (i.e. 2,2-dimethoxypropane, 1,1-dimethoxycyclohexane, and (1,1-dimethoxyethyl)benzene) that promoted the highest TMOS yields produced higher DMC quantities compared with other acetals. These results strongly indicate that DMC plays an important role in accelerating the catalytic production of TMOS.
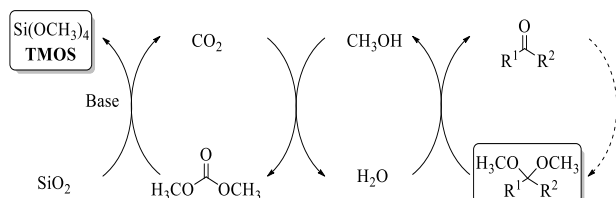
Figure 3. Schematic illustration of the present reaction system.

Based on the above findings, we propose a reaction mechanism involving the reaction of CO_2 and methanol to generate DMC with concomitant formation of H_2O (Figure 3). The reaction system is subsequently dehydrated by acetals to form ketone and methanol. In the final step, the *in situ* generated DMC promotes the catalytic depolymerization of SiO_2 to afford TMOS with regeneration of CO_2 (Figure 2. (b)). It is well known that DMC is effective for depolymerization[11] or de-oligomerization[20, 21] of silica-derived compounds in the presence of typical base catalysts. This work, however, demonstrated the promising prospect of direct synthesis of TMOS from silica and methanol in the absence of stoichiometric DMC.

3.3 Reaction optimization
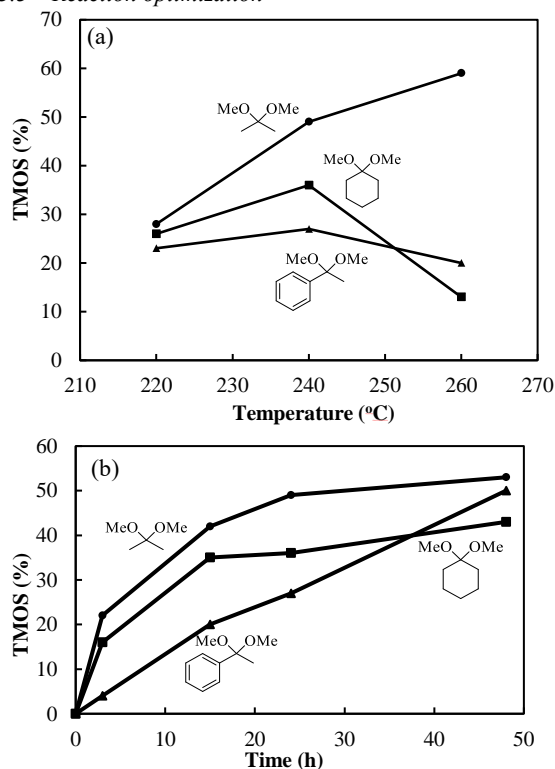
Figure 4. (a) The effect of temperature on TMOS formation using the three best acetals. (b) Profile of TMOS yield over time.

Optimization studies evaluated the effects of temperature, acetal concentration, CO_2 pressure, reaction time, and base catalyst on the reaction. The temperature dependence and time profile of these three acetals providing the highest TMOS yields were investigated. Use of 1,1-dimethoxycyclohexane and (1,1-dimethoxyethyl)benzene at 240 °C gave the highest TMOS yields (36 and 27%, respectively) (Figure 4.(a)). The most effective acetal, 2,2-dimethoxypropane, produced TMOS in 49% yield at 240 °C. Elevating the temperature to 260 °C enhanced TMOS production up to 59%, but multiple unidentified by-products derived from the thermal decomposition of 2,2-dimethoxypropane (such as 2-methoxy propene, acetone, mesityl oxide, and others) were observed. The increase in TMOS yield up to 83% was also observed by increasing the amount of acetal to 25 mmol (Table S1). The conversion of SiO_2 also depends on CO_2 pressure. The TMOS yield increased with increasing CO_2 pressure, with a 49% yield of TMOS attained at 2 MPa CO_2 (Table S2).[19] The time profiles for the three best acetals were found to be similar (Figure 4. (b)). For the reaction with (1,1-dimethoxyethyl)benzene, the yield of TMOS steadily increased with increasing reaction time, with a yield of around 50% achieved at 48 h. This result is better than that of 1,1-dimethoxycyclohexane (43%) under the same conditions. A slightly higher yield of TMOS (53%) was reached when 2,2-dimethoxypropane was used in the reaction for 48 h, whereas prolonging the reaction time to 96 h did not improve the yield (59%) significantly.[19] Furthermore, hydroxides and carbonate salt catalysts significantly influenced the rate of TMOS synthesis (Figure S2). KOH was selected as the standard catalyst for further study. After identifying the optimal reaction conditions, this reaction system was applied to the depolymerization of SiO_2 from natural resources.

### 3.4 Application of various natural silica resources

Table 1. Synthesis of TMOS from natural silica substrates.

Entry	SiO_2 source	TMOS[a] (%)	Surface Area[b] /cm^2g^{-1}	Surface Area[c] /cm^2g^{-1}	SiO_2[d] / %
1	CARiACT Q-10	49	272	27	98
2	RHA-500	49	187	85	93
3	RHA-600	47	162	79	92
4	RHA-700	35	123	89	92
5	RHA-800	9	39	37	92
6	RHA-900	2	4	4	91
7	RHA-1000	1	1	1	91
8	Pampas grass-500	40	76	26	85
9	Rice straw-500	37	55	145	84
10	Bamboo-500	44	11	190	73

[a] Yield based on SiO_2. [b] Surface area (BET) before reaction. [c] Surface area (BET) after reaction. [d] SiO_2 content determined by EDXRF.[22,23]

Recent developments of ~~the~~ biomass refinery have mainly focused on carbon-based compounds.[24] The utilization of inorganic biomass based on silicon compounds is rarely reported. Silicon in the form of silica, SiO_2, makes up more than 40% of the earth's crust, but it is underutilized as resource.[25] Therefore, the production of fine chemicals from natural silica could be a sustainable process that offers a low carbon footprint.

In this context, we extended the direct synthesis of TMOS using silica derived from various natural resources, such as rice hull, pampas grass, rice straw and bamboo (Sasa).[26] These silica-rich waste coproducts of agricultural industries have the potential to provide a silica-based commodity. The raw materials were calcined at various temperatures (500–1000 °C) prior to use to eliminate basic components that could inhibit the reaction. The SiO_2 contents of rice hull ash (RHA), pampas grass, rice straw and bamboo (Sasa) determined by EDXRF were > 90%, 85%, 84%, and 73%, respectively. The surface areas of these pre-treated materials were determined by N_2 adsorption–desorption isotherms (using the BET method), as shown in Table 1. Notably, the surface area of RHAs decreased with increasing calcination temperature and after the reaction (Entries 2–7). Based on x-ray diffraction (XRD) results, the amorphous SiO_2 from RHA was transformed to the α-cristobalite crystalline phase (JCPDS 39-1425)[24] after being annealed to > 900 °C (Figure 5). These changes due to calcined treatment are further reflected in the observed reactivity. The RHA samples with higher surface areas afforded higher TMOS yields, and the higher crystallinity resulting from higher calcination temperatures produced lower TMOS yields (Entries 2–7). Low surface area rice straw-500 and bamboo-500, however, generated high TMOS yields (37% and 44%, respectively) due to the increased surface area during the reaction, which was confirmed by the surface area of recovered SiO_2 after the reaction (Entries 9 and 10). Low surface area and high crystallinity were presumably responsible for poor dissolution rates which lowered the depolymerization velocity. This methodology provides an alternative pathway for TROS synthesis from the carbothermal reduction (1900 °C) to Si_{met} followed by ROH treatment.
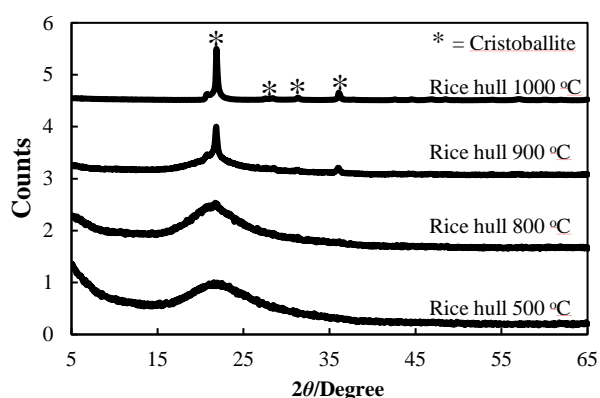
Figure 5. XRD pattern of RHAs with various calcination temperatures.

3.5 Results of scaling-up synthesis of TMOS
Table 2. Scaling-up of TMOS Synthesis

Entry	SiO₂ source	Reactor /mL	SiO₂ /mmol	CO₂[b] /MPa	TMOS[c] / %
1	Wakogel	200	30	0.1	33
2	Wakogel	200	30	0.4	49
3	Wakogel	200	30	0.8	52
4[a]	Wakogel	200	30	0.8	2
5	Wakogel	1000	150	0.8	63
6	RHA-500	1000	150	0.8	69

[a] Ar gas was used instead of CO_2. [b] Intial pressure at 25 °C.
[c] Yield based on SiO_2.

Although our work has demonstrated the promising prospect for direct synthesis of TMOS using silica from natural resources, further investigation is necessary to evaluate their feasibility in large-scale application. In this study, scale-up experiments were systematically carried out in 200 mL and 1 L batch reactor scale. For 200 mL-scale synthesis, Wakogel was used as SiO_2 source under various CO_2 initial pressures (Entries 1-4). Obviously, the TMOS yield increased steadily with increasing CO_2 pressure, and reaction at 0.8 MPa yielded TMOS 52% (Entry 3). The presence of CO_2 is, again, crucial for TMOS synthesis, since in the reaction under Ar, TMOS yield drastically dropped to 2% (Entry 4). Finally, synthesis of TMOS was carried out in 1 L batch reactor using Wakogel and RHA-500 as SiO_2 source (Entries 5 and 6). Increasing the synthesis scale to 1 L showed no depletion of TMOS yield, as the TMOS yield can be achieved to 63% and 69% using Wakogel and RHA-500, respectively (Entries 5,6).

4. Conclusion
A simple and practical method to synthesize TMOS *via* a direct transformation of silica with methanol was achieved using a base catalyst and organic dehydrating agents. The kind of the dehydrating agent was crucial factor in the production of TMOS, with 2,2-dimethoxypropane identified as the best dehydrant for optimal TMOS yields. In fact, we found that the TMOS yield was directly proportional to DMC generation. We proposed that the TMOS production was promoted by CO_2 arising from the *in-situ* generation of DMC, which enhanced the depolymerization rate of SiO_2. Therefore, this reaction system not only demonstrates the potential application of SiO_2 feedstock but also introduces a new synthetic approach for the application of CO_2 as a benign catalyst.

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