

Formation and Characterization of Monodisperse, Spherical Organo-Silica Powders from Organo-Alkoxysilane-Water System

Jae Young Choi, Chong Hee Kim,* and Do Kyung Kim*

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Taejeon 305-701, Korea

Monodisperse, spherical organo-silica powders were synthesized from an immiscible mixture of an aqueous NH_4OH solution and organo-alkoxysilanes, such as phenyl-trimethoxysilane (PTMS), methyltrimethoxysilane (MTMS), and methyltriethoxysilane (MTES). When the organo-alkoxysilanes were added to the aqueous NH_4OH solution with stirring, organo-alkoxysilane/water macroemulsions were formed because of the immiscibility of the aqueous NH_4OH solution and the organo-alkoxysilane. In the emulsion, organo-alkoxysilane droplets dissolved into the water phase through the droplet-water interface, and the organo-silica powder was formed by the hydrolysis and condensation of the organo-alkoxysilane. The powders were obtained reproducibly under broad concentrations of organo-alkoxysilanes; 0.3–1.5 mol/L for PTMS, 0.3–0.6 mol/L for MTMS, and MTES, with concentrations of ammonia between 0.0625 and 2.0 mol/L. According to the analysis of the solid-state MAS ^{29}Si NMR and the ^{13}C NMR analysis, the organo-silica powder did not contain any residual alkoxy groups, only carbon sources from nonhydrolyzable R groups: phenyl groups in PTMS, and methyl groups in MTMS and MTES.

I. Introduction

THE sol-gel process using metal alkoxides as starting materials has a high potential for preparing inorganic oxide ceramics. Tetraalkoxysilanes, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS), have been widely used to fabricate silica-related materials.¹⁻⁵ Recently, considerable attention has been paid to organo-alkoxysilanes as the raw material of organo-silica. A variety of organo-silicas, including powders,^{7,8,14} bulks,^{6,10-13} and fibers,⁹ have been obtained by the hydrolysis of organo-alkoxysilanes or mixtures of organo-alkoxysilanes and tetraalkoxysilanes. These organo-silica have been used for the studies of ceramics,⁶⁻¹³ colloids,¹⁴ and polymers.^{15,16}

For the synthesis of carbon or nitrogen-containing ceramics, the pyrolysis of organo-silica in an inert atmosphere gives silicon (oxy)carbides^{6-8,11,12} or carbon-containing glass composites,¹³ and the pyrolysis under ammonia or nitrogen leads to silicon oxynitrides¹⁰ or silicon oxynitride glasses.⁹

Several researchers showed that monodisperse and spherical β -SiC powders can be obtained by heating spherical organo-silica powder.^{7,8} According to their results, organo-silica powder was decomposed into a mixture of carbon and silica, and then the mixture formed β -SiC by carbothermal reduction un-

der an argon atmosphere. They also showed that the nonhydrolyzable R groups in organo-alkoxysilane acted as a carbon source.

During the study of the synthesis of SiC ceramics from organo-alkoxysilanes, we prepared monodispersed and spherical organo-silica powders from the immiscible mixture of an aqueous NH_4OH solution and organo-alkoxysilanes.¹⁷ Because water and silanes are immiscible, a mutual solvent, such as alcohol, is generally used as a homogenizing agent. A high concentration of water can cause phase separation to result in the formation of polydisperse and agglomerated powder. The concentration of water for the monodisperse silica powder produced by the SFB process using tetraethoxysilane is limited to a maximum of about 25 mol/L.³ Other alkoxides, such as titanium, zirconium, and aluminum alkoxides, which have higher reactivities than silanes, were used with much lower or stoichiometric levels of water in alcohol to produce controlled powders.^{9,21} A high content of water causes a too-rapid hydrolysis and condensation reactions, which does not allow control of the particle size, the size distribution, and the morphology.

In the present study, we describe the formation behavior of monodisperse, spherical organo-silica powder from an immiscible mixture of an aqueous NH_4OH solution and organo-alkoxysilanes. The formation mechanism is discussed, and the chemical structure, particle size, and size distribution of the powder are characterized by NMR analysis and electron microscopy.

II. Experimental Procedure

(1) Preparation of Organo-Silica Powders from Organo-Alkoxysilanes

The organo-alkoxysilanes used in this work were phenyltrimethoxysilane (PTMS), methyltrimethoxysilane (MTMS), and methyltriethoxysilane (MTES) (Shin-Etsu Chemical, Tokyo, Japan), which were used as received without further purification. Ammonium hydroxide (EP grade, Junsei Chemical, Japan) with an ammonium concentration of 29 wt% was used as a catalyst. For the hydrolysis and condensation of organo-alkoxysilanes, distilled and deionized water with a resistance above 10 $\text{M}\Omega\cdot\text{cm}$ was used.

For the preparation of organo-silica powders, the necessary amounts of water and ammonium hydroxide were mixed with a magnetic stirrer in a 250-mL beaker and placed in a constant-temperature bath. After the solution came to 60°C, the organo-alkoxysilanes preheated to 60°C were poured into the solution while stirring at 600 rpm. The organo-silica powder was formed in the solution within a few seconds to minutes, and the solution was aged at room temperature for 2 h. The powders were separated from the solvent by centrifugal sedimentation at 10 000 rpm and dried under vacuum at 100°C for 10 h.

(2) Characterization

When the stirring was stopped, 10 s after the PTMS was poured into the aqueous NH_4OH solution, the solution separated into two phases (PTMS and aqueous NH_4OH solution),

C. F. Zukoski—contributing editor

Manuscript No. 191368. Received December 2, 1996; approved July 24, 1997. Supported by the Korea Science and Engineering Foundation (KOSEF) through the Center for Interface Science and Engineering Materials (CISEM).
*Member, American Ceramic Society.

and the organo-silica powder was not yet formed. A certain amount of each solution was taken out after the liquids were clearly separated. The reaction products in each solution were investigated by using liquid-state ^{29}Si and ^1H NMR spectroscopy (AM 300 spectrometer, Bruker, Billerica, MA). In the liquid-state ^1H NMR measurement, D_2O was used as a lock solvent. For the liquid-state ^{29}Si NMR measurement, tetramethylsilane (TMS) was used as a reference, chloroform (CDCl_3) as a lock solvent, and chromium acetylacetonate ($\text{Cr}(\text{acac})_3$) as a nonpolar paramagnetic relaxation agent. A 5-mm NMR tube with a solution of TMS and $\text{Cr}(\text{acac})_3$ in CDCl_3 was inserted coaxially into the 12-mm sample tube to serve as a standard.

Particle size, size distribution, and shape of the powders were determined by scanning electron microscopy (SEM). Three hundred particles were measured for each sample.

To characterize the chemical structural of the organo-silica powders, solid-state cross polarization/magic-angle spinning (CP/MAS) ^{13}C NMR and solid-state magic-angle spinning (MAS) ^{29}Si NMR spectroscopy were used. The spectra were measured at room temperature in a Bruker AM 300 spectrometer with a Bruker solid-state accessory. For the solid-state CP/MAS ^{13}C spectra, T^1 of 1.4 s, a 90° pulse, a 1.75-s delay between pulses, and a contact time of 3.0 ms were used during the data acquisition, and a spinning speed of 4000 Hz was employed. Solid-state MAS ^{29}Si spectra were obtained at 4000 Hz, a delay of 30 s between pulses, and a 90° pulse. A small amount of $\text{Cr}(\text{acac})_3$ was used as a nonpolar paramagnetic relaxation agent.

III. Results and Discussion

(1) Formation of Organo-Silica Powders

Figure 1 shows schematics of the formation of organo-silica powders. When organo-alkoxysilane was added to the aqueous NH_4OH solution, the organo-alkoxysilane (silane phase) and the aqueous NH_4OH solution (water phase) separated into two phases (Fig. 1(A)). Stirring of the mixture formed the macroemulsion where the silane phase was dispersed as droplets of the size of a few millimeters in the water phase (Fig. 1(B)). After a few seconds to minutes, the size of the silane droplets became smaller and the water phase turbid white to show that organo-silica powder started to form in the water phase. With further stirring, the silane droplets finally disappeared. The turbid time depended on the reagent concentration and was shorter at higher concentrations of organo-alkoxysilane and ammonia. Figure 2 shows the variation of the turbid time with the concentration of organo-alkoxysilanes.

Figure 3 shows SEM photographs of organo-silica powders prepared from various organo-alkoxysilanes. The powders were monodisperse and spherical. The average particle size and the standard deviation of the organo-silica powders increased with increasing concentration of the organo-alkoxysilanes (Fig. 4). Monodisperse powders were produced at concentrations of 0.3–0.6 mol/L MTMS and MTES. In the case of PTMS, its monodispersity was maintained up to as high as 2.0 mol/L silane concentration, where the volume ratio of aqueous NH_4OH solution to PTMS is 2.2:1. The concentration of ammonia was varied from 0.0625 to 2.0 mol/L for the synthesis of the powder in the preliminary experiment. There was no visible effect of ammonia concentration on the monodispersity of the powder, but the mean particle size decreased slightly with increase of the ammonia concentration. The powders were obtained reproducibly in all of the experimental conditions.

When the stirring was stopped prior to the formation of the powder after the pouring of the PTMS to the aqueous NH_4OH solution, the mixture separated clearly into two phases of water and silane as shown in Fig. 1(A). Each water and silane solution was poured into test tubes. Some portion of each solution was analyzed by liquid-state ^1H and ^{29}Si NMR spectroscopy. While alcohol and silane were detected in the water solution,

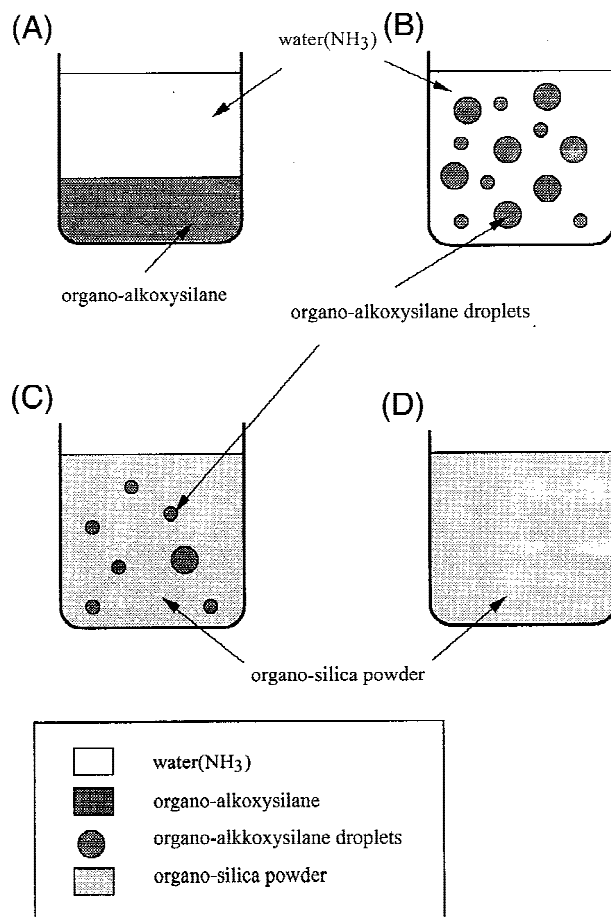


Fig. 1. Schematic showing the formation of organo-silica powder in the mixture of aqueous NH_4OH solution and organo-alkoxysilane.

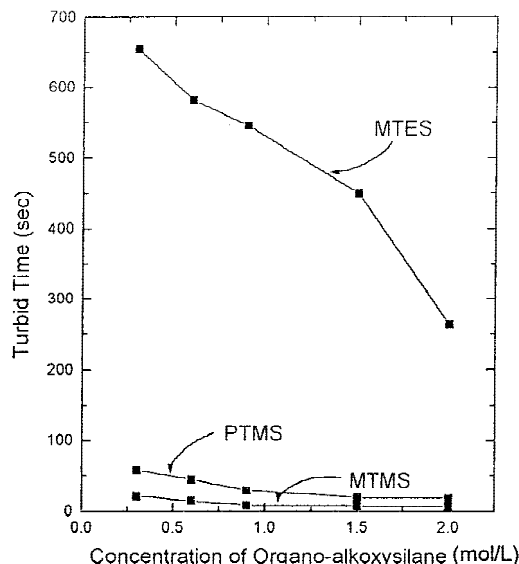


Fig. 2. Variation of turbid time with the concentration of various organo-alkoxysilane. The concentration of ammonia is constant at 1.0 mol/L.

no alcohol was detected in the silane solution. After a few hours, powder formed in the test tube containing the water solution, but there was no change in the silane solution. These results indicate that the silane droplets in the organo-alkoxysilane/water microemulsion dissolve into the water

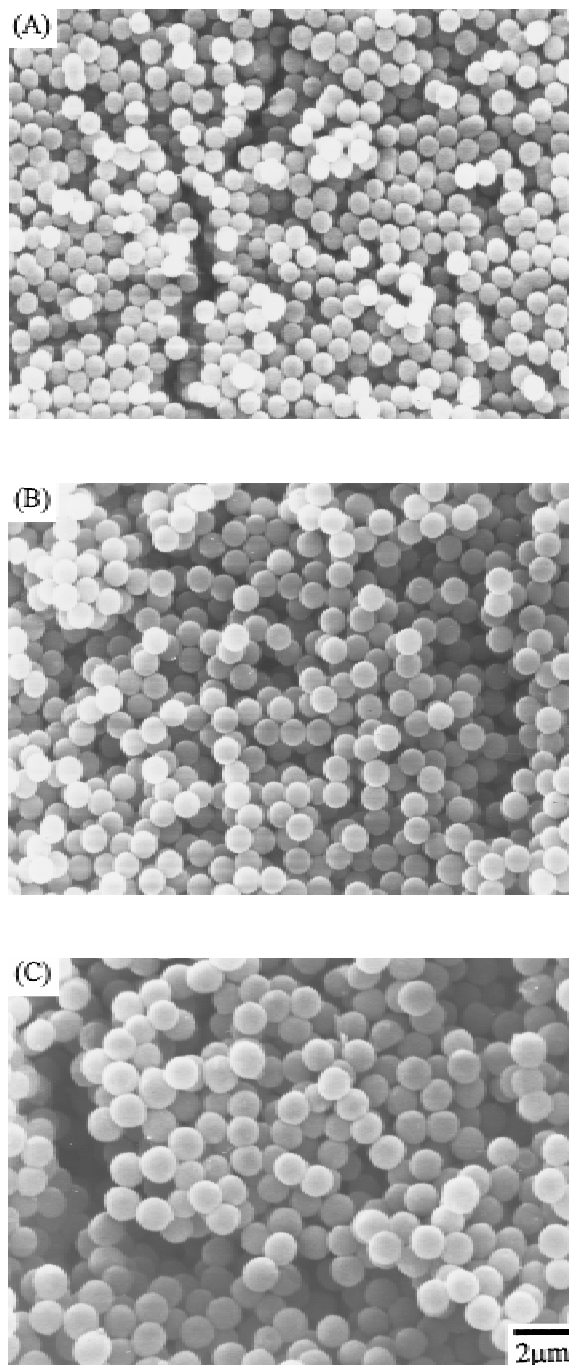


Fig. 3. SEM micrographs of organo-silica powders which are prepared (A) PTMS, (B) MTMS, and (C) MTES. The concentrations of organo-alkoxysilanes and ammonia are 0.6 and 1.0 mol/L, respectively.

phase with hydrolysis and condensation to form organo-silica powder in the water phase (Fig. 1(C)). That is, the silane droplets acted as reservoirs of silane monomer and water phase as a pool for powder formation reactions.

Generally, in the sol-gel process using silanes, alcohol is used as mutual solvent because silanes and water are immiscible.^{3,18,20} For monodisperse powder, the water content has been limited so as not to cause phase separation. However, Bridger *et al.*²⁰ synthesized monodisperse silica powder using a reaction mixture of TEOS, methanol, and water at water concentrations of 25–30 mol/L where TEOS was no longer totally miscible. Stirring the reaction mixtures dispersed TEOS as droplets. They pointed out that TEOS droplets acted as reservoirs of monomer. Similarly, we obtained monodisperse

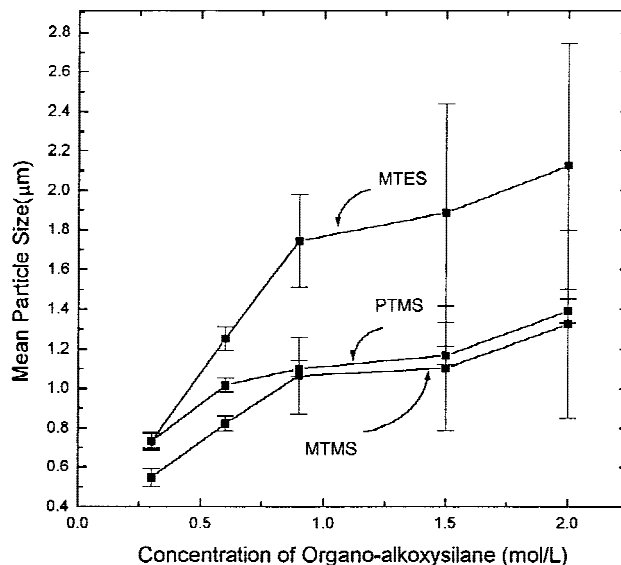


Fig. 4. Variation of mean particle size and standard deviation with the concentration of various organo-alkoxysilanes. The concentration of ammonia is constant at 1.0 mol/L. Error bar indicates the standard deviation.

organo-silica powder from an immiscible mixture of organo-alkoxysilane and water (no alcohol). Both of the two results are similar to the emulsion polymerization process²¹ consisting of water, oil, and surfactant. The surfactant is used for emulsion formation. In the emulsion polymerization, stability of emulsion is important for the control of powder size and size distribution. In this study, silane droplets, which form initially due to the phase immiscibility, act as reservoirs of silane monomer and finally dissolve because alcohol formed during the reaction acts as a mutual solvent. But it seems that silane droplets can be retained in a rather stable fashion in the water phase to provide silane monomer to water and disappear slowly. It was observed that transparent silane droplets were retained in a white turbid water phase where organo-silica powder has formed. This is attributed to the slow reaction kinetics of silanes with water. Reaction kinetics of silanes are much slower than other metal alkoxides. Furthermore, reaction kinetics of organo-alkoxysilanes are slower than those of tetraalkoxysilanes in a base-catalyzed reaction, because of the inductive effect of organic groups in organo-alkoxysilanes. Those formation behaviors, where silane droplets acts as reservoirs of silane monomer, have a similarity to the case of the silane addition process. In the process, silane was added to a mixture of silica powder, water, and alcohol to increase the particle size of the silica.^{3,14}

From the above discussion, it can be said that dissolving of silane droplets can supply monomer sources to water phase, and the dissolving rates affect the nucleation and growth of organo-silica powder in water phase. As shown in Fig. 2, the turbid times of MTMS are the fastest and MTES the slowest, which is attributed to the steric effect of bulky phenyl and ethoxy groups in the organo-alkoxysilanes. It indicates that the dissolving rate of MTMS to water phase is the fastest and MTES the slowest, with hydrolysis and condensation rates having the same trends. A high dissolving rate causes high initial supersaturation level in water phase for nucleation, which induces more nuclei resulting in the formation of smaller powder, as shown in Fig. 4, where the size of organo-silica powder from MTMS is the smallest and MTES the largest. Figure 4 also shows that increasing silane concentrations causes the increase of particle size. It can be said that increasing silane concentration has two kinds of effects; one is the increase of monomer supply for the growth of powder which causes the increase of particle size, and the other is the increase of initial supersatu-

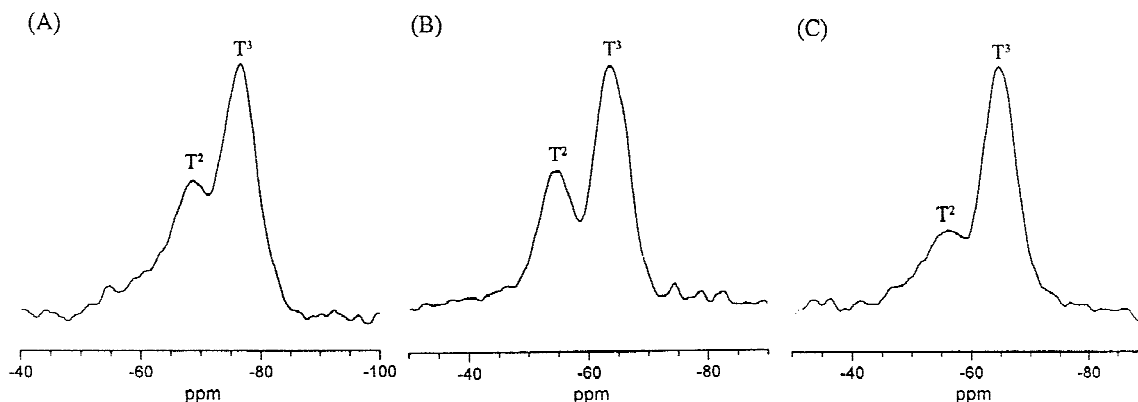


Fig. 5. Solid-state MAS ^{29}Si NMR spectra of the organo-silica powders prepared from (A) PTMS, (B) MTMS, and (C) MTES. Initial solution contained 0.6 mol/L organo-alkoxysilane and 1.0 mol/L ammonia.

ration level which causes the decrease of particle size. From the above results, it seems that the former effect is more dominant than the latter in this system.

(2) Characterization of Organo-Silica Powders

Solid-state ^{13}C and ^{29}Si NMR spectroscopy is a powerful method to characterize the chemical structure of the powders prepared from (organo-) alkoxysilanes.¹⁴ Solid-state MAS ^{29}Si NMR spectroscopy provides quantitative information about the condensation reaction, and solid-state ^{13}C NMR spectroscopy is particularly useful in determining the extent of the hydrolysis reaction.

Solid-state MAS ^{29}Si NMR spectra of the organo-silica powders are shown in Fig. 5. In the case of the powder derived from PTMS, peaks at -77.2 and -69.3 ppm can be assigned to T^2 and T^3 , respectively. T^1 peaks were too small to be analyzed in all the spectra.

Figure 6 shows solid-state CP/MAS ^{13}C NMR spectra of organo-silica powders. In Fig. 6(A), which is a spectrum of the organo-silica powder derived from PTMS, peaks at 134.6, 131.1, and 128.4 ppm are due to the carbons in the phenyl group. Because R groups are nonhydrolyzable,^{14,18} they can remain in the molecular structure of the organo-silica powders after reaction. In this case, R groups are the phenyl for PTMS and the methyl for MTMS and MTES. Any peaks for residual methoxy groups were not observed in this spectrum. In the case of organo-silica powder from MTMS (Fig. 6(B)) and MTES (Fig. 6(C)), there are peaks only for the methyl group, not for the residual methoxy (Fig. 6(B)) and ethoxy (Fig. 6(C)). These results indicate that all the alkoxy groups in organo-alkoxysilanes were hydrolyzed during the reaction, and the functional groups that remained without condensation in the T^1 or T^2 silicons (Fig. 5) are OH groups. This is contrasted with the case of the silica powder prepared from tetraethoxysilane in the aqueous alcohol solution containing ammonia (SFB process). Figure 7 shows the solid-state CP/MAS ^{13}C NMR spectra of the silica powder synthesized from the SFB process.¹ In the spectrum, the ethoxy signal was observed at close to 60.8 and 17.5 ppm. These peaks can be assigned to the residual ethoxy groups which remained in the silica powder without hydrolysis. In this work, extremely high concentrations of water (aqueous NH_4OH solution) in the reaction solution leads the alkoxy groups of the organo-alkoxysilanes to be fully hydrolyzed to hydroxy groups. Therefore, the only carbon source in the organo-silica powders was the nonhydrolyzable R groups, which is an important carbon source for the formation of SiC during further heat treatment.

IV. Conclusions

Monodisperse, spherical organo-silica powders were synthesized from the organo-alkoxysilane (PTMS, MTMS, and

MTES)/water macroemulsion. In the emulsion, organo-alkoxy silane droplets dissolved into the water phase through the droplet-water interface, and the organo silica powder was formed by the hydrolysis and condensation of the organo-alkoxysilane. Because silanes react slowly with water, silane droplets could be dispersed stably in water to produce silane monomer to water phase.

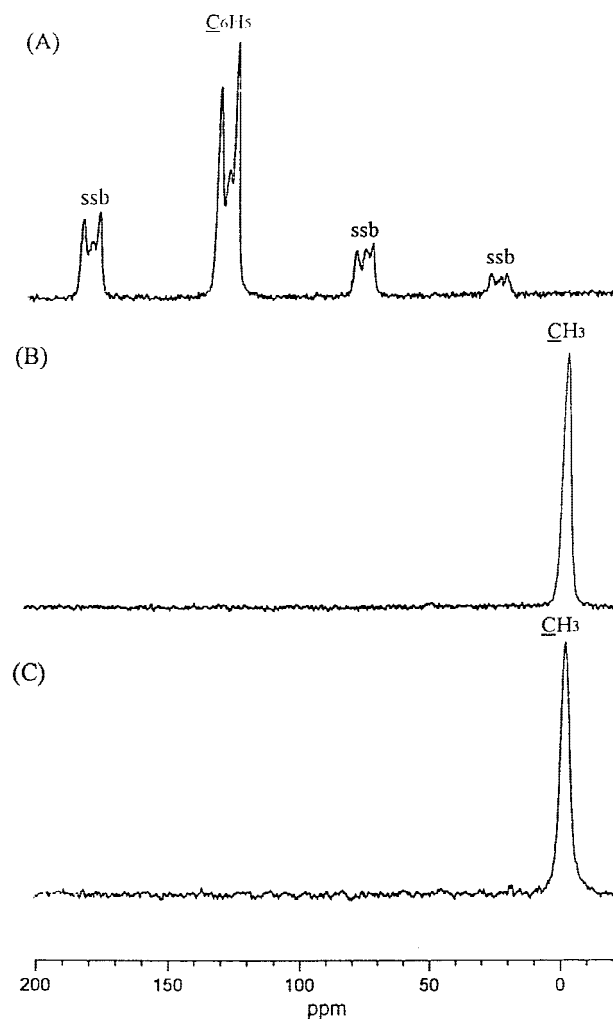


Fig. 6. Solid-state CP/MAS ^{13}C NMR spectra of organo-silica powders prepared from (A) PTMS, (B) MTMS, and (C) MTES. The concentrations of organo-alkoxysilanes and ammonia are 0.6 and 1.0 mol/L, respectively. (ssb) represents a spinning side band.

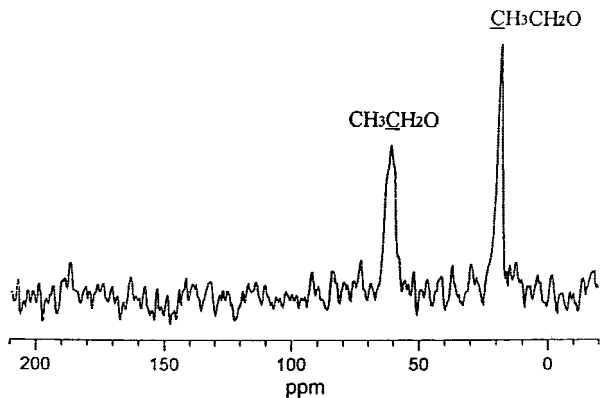


Fig. 7. Solid-state CP/MAS ^{13}C NMR spectrum of silica powder prepared by the hydrolysis of TEOS in aqueous ethanol solution containing ammonia. The concentrations of TEOS, ammonia, and water were 0.25, 1.0, and 20 mol/L, respectively.

Monodisperse powder was obtained reproducibly under broad concentrations of the organo-alkoxysilanes: 0.3–1.5 mol/L for PTMS, 0.3–0.6 mol/L for MTMS, and MTES, with the concentration of ammonia ranging from 0.0625 to 2.0 mol/L.

In contrast with the SFB process-derived silica powder, which contains residual alkoxy groups in the powder, the organo-silica powders produced in this study did not contain any residual alkoxy groups. This indicated that the alkoxy groups of organo-alkoxysilanes were fully hydrolyzed in the aqueous NH_4OH solution to be hydroxy groups. Therefore, the only carbon source in organo-silica powders was the nonhydrolyzable alkyl or phenyl group, which are important carbon sources for the formation of SiC ceramics during further heat treatment.

References

¹W. Stöber, A. Fink, and E. Bohn, "Controlled Growth of Monodispersed Silica Spheres in the Micro Size Range," *J. Colloid Interface Sci.*, **26**, 62–69 (1968).
²A. Van Blaaderen and A. P. M. Kentgens, "Particle Morphology and Chemical Microstructure of Colloidal Silica Sphere Made from Alkoxysilanes," *J. Non-Cryst. Solids*, **149**, 161–78 (1992).

³G. H. Bogush, M. A. Tracy, and C. F. Zukoski IV, "Preparation of Monodisperse Silica Particles: Control of Size and Mass Fraction," *J. Non-Cryst. Solids*, **104**, 95–106 (1988).
⁴G. H. Bogush and C. F. Zukoski IV, "Uniform Silica Particle Precipitation: An Aggregative Growth Model," *J. Colloid Interface Sci.*, **142**, 19–34 (1991).
⁵M. Yamane, S. Inoue, and A. Yasumori, "Sol–Gel Transition in the Hydrolysis of Silicon Methoxide," *J. Non-Cryst. Solids*, **63**, 13–21 (1984).
⁶D. A. White, S. M. Oleff, R. D. Boyer, P. A. Budinger, and J. R. Fox, "Preparation of Silicon Carbide from Organosilicon Gels: I, Synthesis and Characterization of Precursor Gels," *Adv. Ceram. Mater.*, **2**, 45–52 (1987).
⁷F. Hatakeyama and S. Kanzaki, "Synthesis of Monodispersed Spherical β -Silicon Carbide Powder by a Sol–Gel Process," *J. Am. Ceram. Soc.*, **73** [7] 2107–10 (1990).
⁸I. S. Seog and C. H. Kim, "Preparation of Monodispersed Spherical Silicon Carbide by the Sol–Gel Method," *J. Mater. Sci.*, **28**, 3277–83 (1993).
⁹K. Kamiya, M. Ohya, and T. Yoko, "Nitrogen-Containing SiO_2 Glass Fibers Prepared by Ammonolysis of Gel Made from Alkoxides," *J. Non-Cryst. Solids*, **83**, 208–22 (1986).
¹⁰Y. F. Yu and T. I. Mah, "Si–O–N Ceramics from Organosilicon Polymers"; pp. 559–64 in *Better Ceramics Through Chemistry II*. Edited by C. J. Brinker, D. E. Clark, and D. R. Ulrich. Materials Research Society, Pittsburgh, PA, 1986.
¹¹H. Zhang and C. G. Pantano, "Synthesis and Characterization of Silicon Oxycarbide Glasses," *J. Am. Ceram. Soc.*, **73** [4] 958–63 (1990).
¹²F. Babonneau, L. Bois, and J. Livage, "Silicon Oxycarbides via Sol–Gel Route: Characterization of the Pyrolysis Process," *J. Non-Cryst. Solids*, **147&148**, 280–84 (1992).
¹³K. Kamiya, T. Yoko, T. Sano, and K. Tanaka, "Distribution of Carbon Particles in Carbon/ SiO_2 Glass Composites Made from $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$ by the Sol–Gel Method," *J. Non-Cryst. Solids*, **119**, 14–20 (1990).
¹⁴A. Van Blaaderen and A. Vrij, "Synthesis and Characterization of Monodisperse Colloidal Organo-Silica Spheres," *J. Colloid Interface Sci.*, **156**, 1–18 (1993).
¹⁵T. Iwamoto, K. Morita, and J. D. Mackenzie, "Liquid State ^{29}Si NMR Study on the Sol–Gel Reaction Mechanisms of Ormosils," *J. Non-Cryst. Solids*, **159**, 65–72 (1993).
¹⁶Y. Sugahara, S. Okada, K. Kuroda, and C. Kato, " ^{29}Si -NMR Study of Hydrolysis and Initial Polycondensation Process of Organoalkoxysilanes, I. Dimethyldiethoxysilane," *J. Non-Cryst. Solids*, **139**, 25–34 (1992).
¹⁷J. Y. Choi, Y. T. Moon, C. H. Kim, and D. K. Kim, "Pyrolytic Conversion of Spherical Organo-Silica Powder to Silicon Nitride under Nitrogen," *J. Am. Ceram. Soc.*, in press.
¹⁸C. J. Brinker and G. W. Scherer, *Sol–Gel Science*; pp. 108. Academic Press, New York, 1990.
¹⁹T. Ogihara, H. Nakajima, T. Yanagawa, N. Ogata, K. Yoshida, and N. Matsushita, "Preparation of Monodisperse, Spherical Alumina Powders from Alkoxides," *J. Am. Ceram. Soc.*, **74** [9] 2263–69 (1991).
²⁰K. Bridger, D. Fairhurst, and B. Vincent, "Nonaqueous Silica Dispersions Stabilized by Terminally-Grafted Polystyrene Chains," *J. Colloid Interface Sci.*, **68**, 190–95 (1979).
²¹K. Osseo-Asare and F. J. Arrigada, "Synthesis of Nanosize Particles in Reverse Microemulsions"; pp. 6–16 in *Ceramic Transactions*, Vol. 12, *Ceramic Powder Science III*. Edited by G. L. Messing, S. Hirano, H. Hausner. American Ceramic Society, Westerville, Ohio, 1990. □