

## Surface modification of silica particles with organoalkoxysilanes through two-step (acid-base) process in aqueous solution

Byung Jun Jeon, Hoe Jin Hah and Sang Man Koo\*

Department of Chemical Engineering, Ceramic Processing Research Center, College of Engineering, Hanyang University, Seoul 133-791, Korea

Surface modification of silica particles was achieved by two-step (acid-base) process in an aqueous solution with organoalkoxysilanes, such as methyltrimethoxysilane (MTMS), methyltriethoxysilane (MTES), vinyltrimethoxysilane (VTMS), and vinyltriethoxysilane (VTES). The relative hydrolysis and condensation rates of organoalkoxysilanes could be elucidated from the kinetic data that were obtained by measuring the mixing time (hydrolysis) and the turbid time (condensation) in this system. Surface-modified silica particles were prepared by two-step process separating the hydrolysis and condensation procedures to easily control the condensation rate. The size of the surface-modified silica particles could be controlled by the ratio of monomer/silica seed. Control of the condensation rate and colloidal interaction could prevent the self-aggregation between primary particles. The size and morphology of the resulting particles were examined by FE-SEM and TEM. The particles were characterized by FTIR and TGA.

**Key words:** silica, two-step process, surface modification, organoalkoxysilanes.

### Introduction

Surface-modified silica particles have generated intense interest in a wide range of application fields. The modification of inorganic silica particles with organics leads to the production of organic-inorganic hybrid particles in which the organic components may be chemically bonded to a silica matrix. Somewhat similar to inorganic silicate glasses, the structure of the silica network can be modified by the presence of organic groups. The mechanical, electrical and optical properties of the resulting organic-inorganic hybrid particles are then governed by the type and concentration of the organics used. Furthermore, the utilization of nanosized organic-inorganic hybrid particles for the production of advanced ceramic materials requires high quality with respect to chemical purity, homogeneity, morphology, and a controlled state of agglomeration as well as low production costs. Thus, a large number of methods have been developed to satisfy these requirements.

Among these methods, sol-gel processing enables the preparation of numerous types of new organic-inorganic hybrid materials with controlled size and size distribution that are difficult to synthesize by any other process. Despite many potential advantages in the sol-gel method, the characteristics of the particles prepared by this process are very sensitive to the experimental

conditions, such as the solvent, the  $R$  ( $[H_2O]/[monomer]$ ) value, the concentration of monomer, the amount of catalyst and electrolyte, and the temperature. In addition, organoalkoxysilanes ( $R_xSi(OR)_{4-x}$ ), which are used as the precursors of organic-inorganic hybrid particles, are relatively expensive. This has made it difficult to apply the sol-gel process more widely in industrial production.

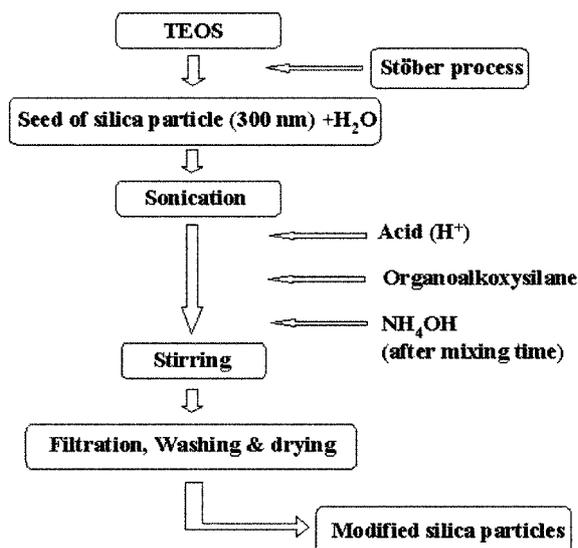
In this study, the preparation of the surface-modified silica particles (core-shell structure) by two-step process in an aqueous system is demonstrated. We show that the hydrolysis and condensation could be controlled by two-step process and the formation of surface-modified silica particles in a two-step (acid-base)/water system is discussed.

### Experimental Procedure

Methyltrimethoxysilane (MTMS), methyltriethoxysilane (MTES), vinyltrimethoxysilane (VTMS) and vinyltriethoxysilane (VTES) were purchased from Aldrich Chemicals. Nitric acid (61.0-62.0 wt%) was purchased from Samchun chemicals and ammonium hydroxide (29.2 wt%) from Mallinckrodt, for use as catalysts for hydrolysis and condensation of organoalkoxysilanes, respectively. All chemicals were used as received. Distilled water was used for the preparation of aqueous solutions.

Figure 1 shows the flowchart for the preparation of surface-modified silica particles. The hydrolysis and condensation of organoalkoxysilanes were performed via the successive addition of  $HNO_3$  and  $NH_4OH$  as

\*Corresponding author:  
Tel : +82-2-2290-0527  
Fax : +82-2-2281-4800  
E-mail: sangman@hanyang.ac.kr



**Fig. 1.** Flowchart of two-step process used for surface modification of silica particles.

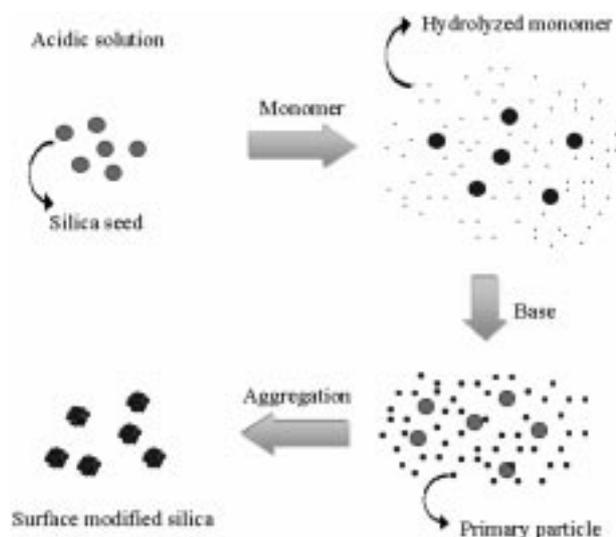
catalysts. Monodisperse silica particles (300 nm) were obtained by the Stöber process [1], and the particles (0.05–0.30 g/L) were dispersed homogeneously in an aqueous solution with agitation and sonication. A  $1.30 \times 10^{-3}$  M solution of  $\text{HNO}_3$  was added to the dispersion. In the acidic condition (first step), an organoalkoxysilane (0.20 M) was added to the silica dispersion and the mixture was stirred at  $60^\circ\text{C}$  for 3 min for the hydrolysis. Then, in the basic condition resulting from addition of  $\text{NH}_4\text{OH}$  (2.22 M) solution (second step), the mixture solution was stirred continuously at  $60^\circ\text{C}$  for 1 h for the condensation. The surface-modified particles thus obtained were collected using a membrane filter and washed with distilled water. The particles were then dried overnight in a drying oven at  $120^\circ\text{C}$ .

The size and morphology of the resulting particles were determined with a field emission scanning electron microscope (FE-SEM) (JEOL JEM-6340F) and a transmission electron microscope (TEM) (JEOL EM-2000EXII). Sample preparation for TEM was performed by placing a few drops of the dispersed solution onto a Formvar-covered copper grid and allowing it to evaporate in air at room temperature. Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) were used to characterize the as-prepared particles.

## Results and Discussion

### Surface modification of silica particles

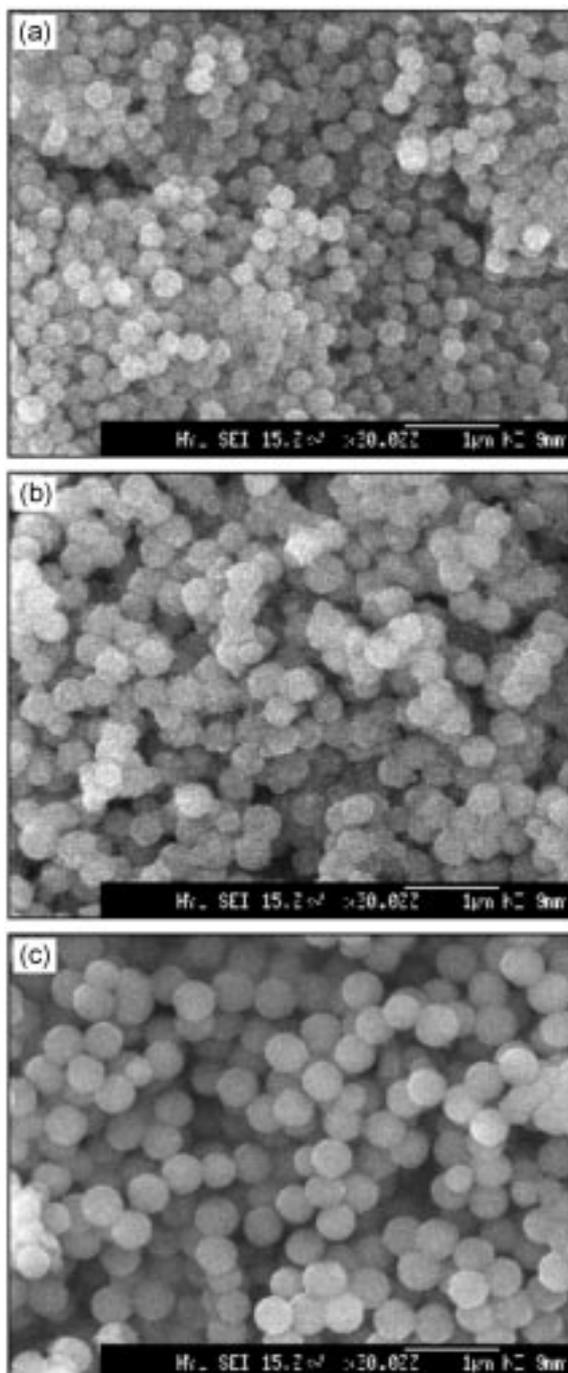
Figure 2 shows the schematic of the preparation of surface-modified silica particles. When an organoalkoxysilane was added to an acidic silica dispersion in the first step, the organoalkoxysilane (silane phase) was not instantaneously miscible with the aqueous solution (water phase) until the silane monomers were hydro-



**Fig. 2.** Schematic of two-step process used for the preparation of surface modified silica particles.

lyzed. With stirring, the macro emulsion was initially formed, and the droplets of silane phase were homogeneously dispersed in solution. As the organoalkoxysilane monomers were gradually hydrolyzed, the silane droplets became smaller and finally disappeared. It was shown that the solution, which was opaque immediately after the addition of an organoalkoxysilane, changed to a transparent one. In the second step,  $\text{NH}_4\text{OH}$  solution was added to the resultant homogeneous solution for the condensation of hydrolyzed silanes. Primary particles were formed during the condensation and then aggregated onto silica particles, which could be called secondary particles (Fig. 2). These nanosized primary particulate systems tended to minimize their surface free energy by growing to larger particles.

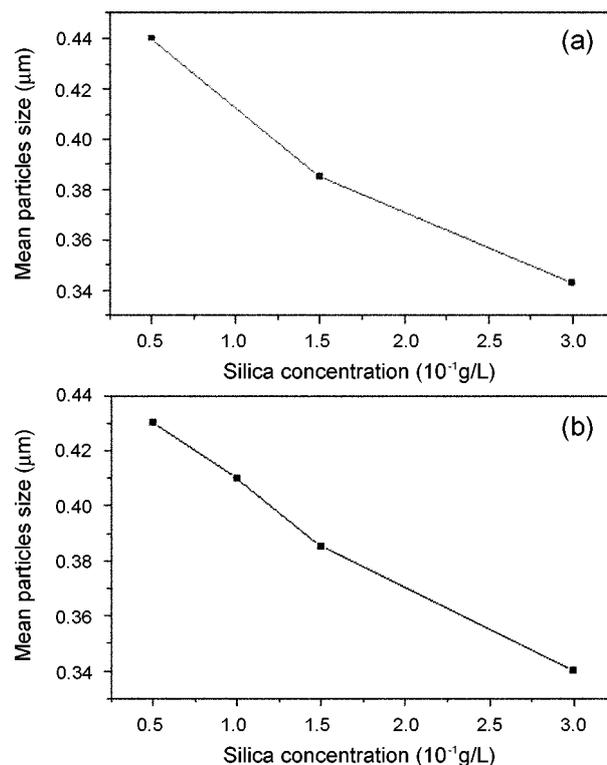
The morphologies and sizes of the pure silica particles and of the modified particles were examined using SEM and TEM. SEM micrographs of pure silica particles and surface-modified silica particles with organoalkoxysilanes are shown in Fig. 3. It is seen that the pure silica particles, 300 nm in size, exhibit a smooth surface. The silica particles modified with organoalkoxysilane monomers show an increase in their average diameter: 440 nm and 430 nm, for VTMS- and MTMS-coated silica particles, respectively. The final particle size depends strongly on the ratio of silica seed particles to organoalkoxysilane monomers. Figure 4 shows the average diameter of silica particles modified with MTMS and VTMS as a function of the silica content at a fixed monomer concentration. The final particle size increased as silica seed content at a fixed monomer concentration decreased. This could be confirmed by the regular growth on the surface of the silica particles. As shown in Fig. 3, there is a difference in morphology between MTMS- and VTMS-coated silica particles. The MTMS-coated silica particles exhibit a smooth surface like pure silica particles, while VTMS-coated silica particles have



**Fig. 3.** SEM photographs of pure silica (a) and modified silica with VTMS (b) and MTMS (c). The concentrations of organoalkoxysilanes (VTMS and MTMS) and silica particles were 0.2 mol/L and 1.0 g/L, respectively (Bar scale: 1 μm).

a rough surface. This was true regardless of variation of the ratio of silica seed/organoalkoxysilane monomer.

TEM micrographs show direct evidence of the modification of silica particles (Fig. 5). The coating of organoalkoxysilane onto the surface of silica resulted in the increase in surface roughness and in the diameter of the modified silica particles, compared with the pure silica particles. Close observation of the modified silica

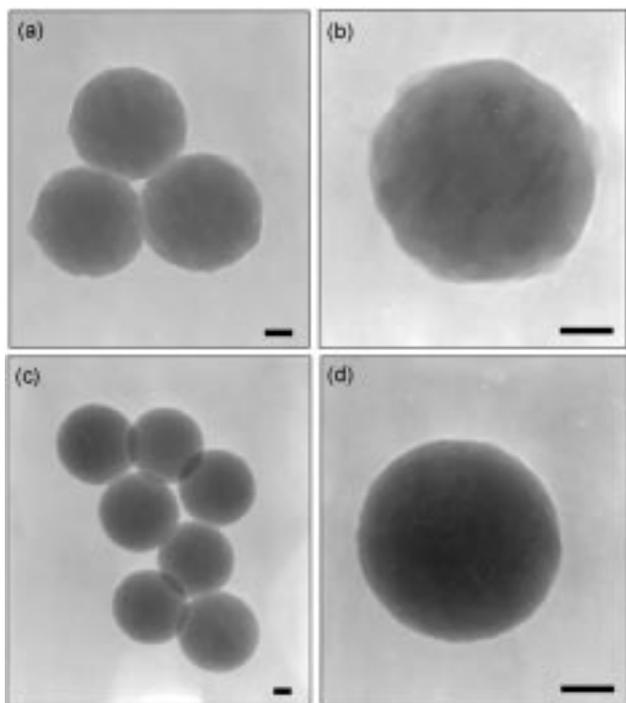


**Fig. 4.** The average size of silica particles coated with VTMS (a) and MTMS (b) as a function of the silica concentration at fixed monomer concentration. The concentration of organoalkoxysilane was constant at 0.2 mol/L.

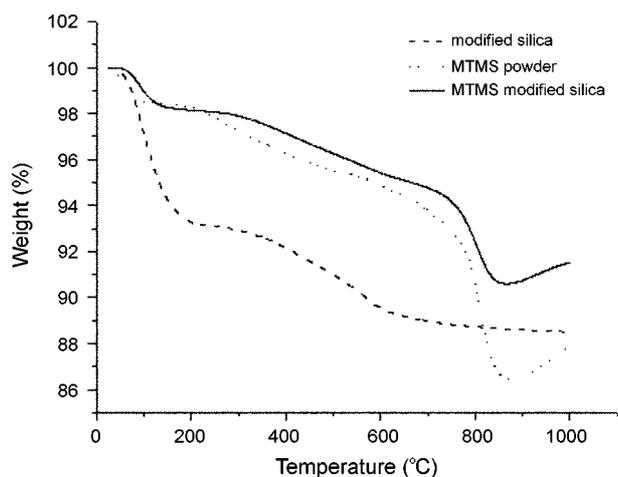
particle surfaces reveals that the coated surface is homogeneously composed of nanoparticles from organoalkoxysilane monomers.

IR spectra of the resulting particles show that MTMS- and VTMS-coated silica particles have organic groups such as methyl and vinyl, respectively. In the case of MTMS-coated silica particles, the bands below 3000 cm<sup>-1</sup> are assigned to the methyl group. On the other hand, the absorption bands due to the vinyl group are observed at around 3050 cm<sup>-1</sup> in the VTMS-coated silica particles. All other spectral features are identical to a spectrum of pure silica particles. Pure silica particles have broad and strong absorption bands between 1050 and 1200 cm<sup>-1</sup>, which are assigned to the Si-O-Si stretching mode.

Thermogravimetric analyses (TGA) of pure silica and surface-modified silica obtained in a N<sub>2</sub> flow from 20°C to 1000°C are shown in Fig. 6. All the TGA samples were prepared without solvent evaporation. The first weight loss of 2-6% in the temperature range 20°C to 120°C can be ascribed to the vaporization of the solvent adsorbed on the particles. Further heating to 800°C resulted in an additional weight loss of 4 to 11%. This loss was due in part to the loss of hydrogen and some carbon. Continued heating resulted in black residuals. The TGA data indicate that the residue yield of pure silica is more than that of surface-modified silica. This could be rationalized by the weight loss



**Fig. 5.** TEM micrographs of silica modified with VTMS (a), (b) and MTMS (c), (d). The concentrations of organoalkoxysilanes (VTMS and MTMS) and silica particles were 0.2 mol/L and 1.0 g/L, respectively (Bar scale: 100 nm).



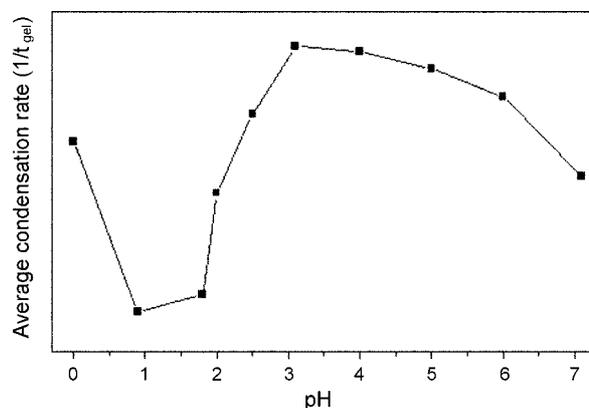
**Fig. 6.** TGA results of pure silica (dash line), MTMS-coated silica (solid line) and MTMS silica particles (dot line) under  $N_2$  flow ( $N_2$  flow: 100 ml/min, heating rate:  $10^\circ\text{C}/\text{min}$ ).

resulting from the presence of organic groups in the particles. However, a weight gain is observed in the MTMS modified silica between 800–1000°C (Fig. 6). We thought that the weight gain may have resulted from the formation of a Si-N bond because the TGA experiment was performed in  $N_2$ . However, no significant difference was observed when the TGA was done in Ar. This behavior may be related to an unexpected thermal effect in the powders.

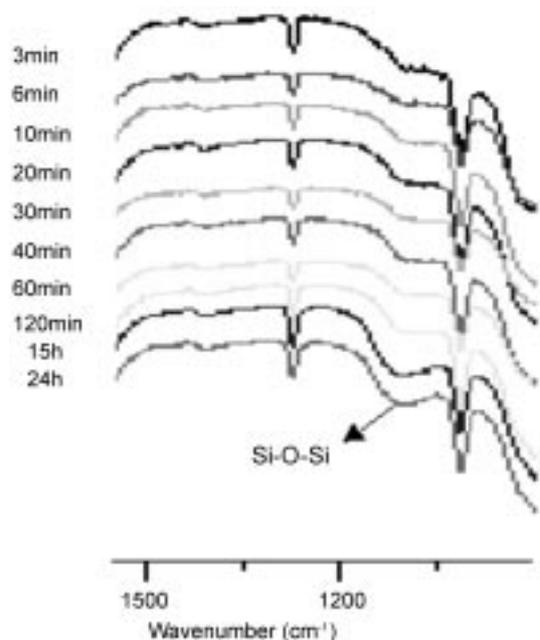
### Two-step process

In general, alcohol has been used as a mutual solvent in the sol-gel process, and the water content has been limited to prevent the phase separation between the silane and water phases [2–4]. However, Bridger *et al.* [4] synthesized monodisperse silica powders in an immiscible system (TEOS-methanol-water) where the added methanol was not enough to prevent phase separation. Choi *et al.* [5] also prepared ORMOSIL (organically modified silicate) powders in an immiscible system (organoalkoxysilane-water). When the reaction mixture was stirred in those systems, silane droplets were dispersed in the reaction medium. Choi *et al.* [5] suggested that silane droplets acted as reservoirs of the monomer and dissolved into the continuous phase. As the hydrolyzed silane monomers on the surface of droplets dissolved into the continuous phase, silica particles were formed through the condensation of the monomers in the continuous phase, and finally, silane droplets disappeared. In our study, we found that silane droplets were also formed and dissolved into the aqueous  $\text{HNO}_3$  solution (water phase) because alkoxide groups (OR) were replaced by hydroxyl groups (OH) as the hydrolysis proceeded. According to Coltrain *et al.* [6], the overall condensation rate was minimized at pH 1.5, which corresponded to the isoelectric point (IEP) of silica (Fig. 7). In comparison with tetraethyl orthosilicate (TEOS), the electron-providing organic groups in organoalkoxysilanes reduced the acidity of silanols, which could shift the isoelectric point toward higher pH values. In Fig. 8 the FTIR spectra of MTMS are shown as a function of time after the addition of MTMS monomers to an aqueous  $\text{HNO}_3$  solution. The increase of the peak assigned to the siloxane bond (Si-O-Si) slowly appeared after 15 h. This indicates that under the acidic condition (pH 1.8), the first step retarded the condensation. The condensation occurred only after the addition of  $\text{NH}_4\text{OH}$  solution in the second step. It is therefore possible to control separately the hydrolysis and condensation through a two-step process.

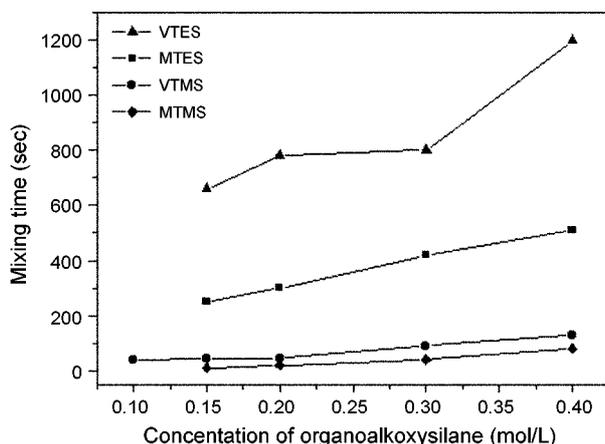
Figure 9 shows the variation of the mixing time with



**Fig. 7.** Average condensation rates ( $1/t_{\text{gel}}$ ) for TEOS hydrolyzed with  $\text{HNO}_3$  solution [7].

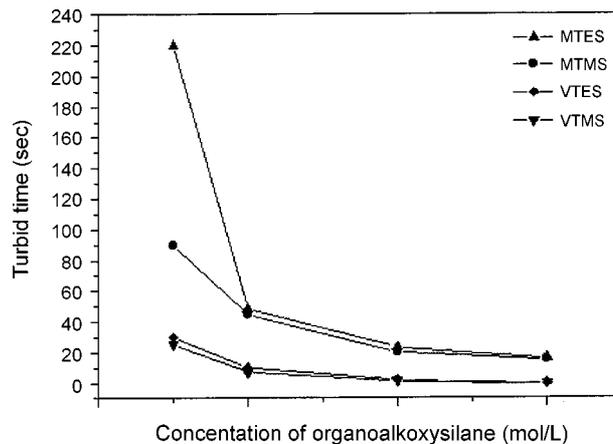


**Fig. 8.** FT-IR spectra of MTMS as a function of time under an acidic condition. The appearance of siloxane bond (Si-O-Si) after 15 h resulted from the condensation of MTMS monomers hydrolyzed.



**Fig. 9.** Variation of mixing time with concentration of various organoalkoxysilanes at 60°C. The concentrations of HNO<sub>3</sub> and NH<sub>4</sub>OH were 0.013 and 2.22 M, respectively.

the concentration of organoalkoxysilanes. The mixing time was defined as the time required for the organoalkoxysilane/water solution to become transparent due to the partially hydrolyzed monomer changing from alkoxy (-OR) group to hydroxyl (-OH) group. The mixing time of methyl group-contained organoalkoxysilanes, MTMS and MTES, is shorter than that of vinyl group-contained organoalkoxysilanes, VTMS and VTES (MTMS < VTMS, and MTES < VTES). In addition, the mixing time of methoxy group-contained organoalkoxysilanes, MTMS and VTMS, is shorter than that of ethoxy group-contained organoalkoxysilanes, MTES and VTES (MTMS < MTES, and VTMS < VTES). This could



**Fig. 10.** Variation of turbid time with concentration of various organoalkoxysilanes at 60°C. The concentrations of HNO<sub>3</sub> and NH<sub>4</sub>OH were 0.013 and 2.22 M, respectively.

be explained by the hydrolysis rate of organoalkoxysilanes, which is attributed to the inductive effect of methyl and vinyl groups and the steric effect of methoxy and ethoxy groups in organoalkoxysilanes [3]. Figure 10 shows the variation of the turbid time with the concentration of organoalkoxysilanes measured after NH<sub>4</sub>OH addition in the second step, where turbid time was defined as the time required until the transparent mixture solution from the first step changed to an opalescent one. The turbid time is related to the condensation rate of organoalkoxysilane already hydrolyzed in the first step (acid-step). The turbid time depends on organic groups in organoalkoxysilanes and it is shorter for the higher electron-donating group of organoalkoxysilanes: (MTES < MTMS << VTES < VTMS). It could also be understood by the inductive effect. Thus, MTES exhibited the shortest turbid time and has the fastest condensation rate.

According to the above results, it can be said that the precipitation takes place in the second step and the condensation rate affects the nucleation and growth mechanism. For the surface modification of silica particles, the primary particles obtained from the condensation procedure in the second step could be aggregated onto the surface of silica seed particles without the nucleation of primary particles by controlling the condensation rate and colloidal stability. As shown in Fig. 4, the average size of organoalkoxysilane-coated silica particles varied directly with the monomer/silica seed ratio. This indicates that when the surface-modified silica particles were formed by the aggregation of primary particles onto silica seed particles (Fig. 2), the control of the condensation rate and the colloidal interaction could prevent the self-aggregation between primary particles.

## Conclusions

This work has demonstrated that the surface modifi-

cation of silica particles (core-shell structure) could be achieved by two-step process in an aqueous solution with organoalkoxysilanes such as MTMS, MTES, VTMS, and VTES. The hydrolysis and condensation rates have also been elucidated in this system: the hydrolysis rate in the acid catalyzed condition follows an order of  $MTMS > VTMS > MTES > VTES$  and the condensation rate in the base catalyzed condition follows an order of  $VTMS > VTES \gg MTMS > MTES$ . Although the formation and growth mechanisms have usually been demonstrated by the hydrolysis, this system enables the investigation of the formation and growth mechanisms related to the condensation.

Surface modification of silica particles was performed by two-step process separating hydrolysis and condensation procedures to easily control the condensation rate. We found that the size of the surface-modified silica particles could be controlled by the ratio of monomer/silica seed and that the control of condensation rate and colloidal interaction could prevent the self-aggregation between primary particles. Thus, the coating thickness of the surface-modified silica particles

could be controlled by the ratio of monomer/silica seed, the condensation rate and the colloidal stability of primary small colloids.

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