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ORIGINAL PAPER

Preparation of organic/inorganic hybrid silica using methyltriethoxysilane and tetraethoxysilane as co-precursors

Yu Ma · Masakoto Kanezashi · Toshinori Tsuru

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Abstract The preparation of a clear, organic/inorganic hybrid silica sol using methyltriethoxysilane (MTES) and tetraethoxysilane (TEOS) as co-precursors under alkaline conditions is reported. Two types of alkaline catalysts—ammonia and tetra-methyl-ammonium hydroxide (TMAH)—were examined for use in the preparation of colloidal sols of <100 nm in diameter, which are suitable for fabrication of nanoporous hydrophobic membranes. Factors that might influence sol preparation were investigated. When ammonia was used as the catalyst, the hydrolysis-polymerization reaction ratio decreased with both an increase in the molar ratio of MTES/TEOS, and a reduction in the water molar ratio. However, when TMAH was used as the catalyst, the water molar ratio had no effect on the hybrid sol preparation reactions. Even systems that employed higher molar ratios of MTES/TEOS or a lower water molar ratio relative to those of the original reactants, allowed for successful preparation of clear sols with a mean sol particle size of <40 nm.

Keywords Organic–inorganic hybrids · Hydrophobic silica · Sol–gel · MTES/TEOS · Contact angle · FTIR

1 Introduction

Recently, much attention has been devoted to porous silica membranes due to their high flux, selectivity and thermal resistance, which make them well-suited for practical applications such as gas separation [1, 2], steam reforming of methane [3], nanofiltration [4], and use in membrane fuel cells [5, 6]. However, pure silica membranes are not stable in an aqueous or humid environment because of the highly hydrophilic silanol groups in the silica structure. The density of amorphous silica structures can be increased by rearrangement of the silanol groups, reducing the performance of the silica membrane (i.e., reduced permeability, selectivity) [2]. Several metal-doped silica membranes and/or organic–inorganic hybrid silica membranes have been developed to improve the hydrothermal stability of silica membranes [7–9]. Hydrophobic silica prepared using MTES and TEOS as co-precursors is one of the most popular organic–inorganic hybrid silica materials. It can be used for preparation of low-reflection glass [10], hydrothermal stable membranes [11], and even for production of bioactive material by composting wollastonite powder with polydimethylsiloxane [12, 13]. Although several research groups have reported on the preparation of hydrophobic silica materials [14–17], additional studies are required to identify and optimize unknown factors that strongly influence the properties of hydrophobic materials. For example, the type of catalyst or the molar ratio of water to Si-alkoxides, etc. might affect the properties of the material. During fabrication of sub-nanoporous silica membranes using a sol–gel method, one of the most important factors is preparation of size-controllable colloidal sols that range in diameter from several hundred nanometers to <100 nm. The ability to control the size of the colloidal particles is so important because the size of pores in porous membranes is

Y. Ma (✉)
Department of Chemistry, College of Sciences, Chongqing Jiaotong University, 400074 Chongqing, China
e-mail: mayu@cquc.edu.cn

M. Kanezashi · T. Tsuru
Department of Chemical Engineering, Hiroshima University, 739-8527 Higashi-Hiroshima, Japan

determined by the void spaces among the packed colloidal particles. In general, an acidic catalyst is used for the preparation of methyl-modified silica sols. Under acidic conditions, MTES can be hydrolyzed ~7 times faster than TEOS [14]. Therefore, to obtain hybrid silica sols that are homogeneous on the molecular level and to avoid formation of bulky polymers, which are not suitable for microporous membranes, TEOS is hydrolyzed before addition of MTES. Improved preparation procedures include acid-catalyzed hydrolysis-polymerization by addition of Si precursors at different reaction stages [15], and two-step, acid–base catalyzed processes [16]. In a previous study, successful preparation of gas-separation membranes was attributed to the microporous structure of acid-catalyzed MTES/TEOS hybrid sols [15].

Only a few published studies have examined the preparation of MTES/TEOS hybrid sols under alkaline conditions. In a previous study, hydrophobic silica sols that were prepared using ammonia as a catalyst were successfully applied in the preparation of hydrophobic nanofiltration membranes with an average pore size in the rage of 2.5–8.2 nm. Average pore sizes of 2.5, 5.1 and 8.2 nm were obtained using methylated silica sols with colloidal diameters of 10, 20, and 50 nm, respectively. Based on these results, it was concluded that colloidal size is a crucial determinant of membrane pore size [18].

The present study focused on the conditions used in the preparation of methyl-modified hybrid sols, with colloids ranging in size from 10 to 100 nm, using MTES and TEOS as silica precursors under alkaline conditions. Two alkali catalysts—ammonia and tetra-methyl-ammonium hydroxide (TMAH)—were examined for use in the preparation of colloidal sols of <100 nm in diameter, which are suitable for fabrication of nanoporous hydrophobic membranes. The effects of colloidal particle size, the MTES/TEOS molar ratio or concentration and the water/Si-alkoxide molar ratio in the initial reactants were investigated. The hydrophobic characteristics of the hybrid silica gels were evaluated by measurement of the water contact angle and by Fourier Transform Infrared spectroscopy (FT-IR).

2 Experimental

2.1 Preparation of MTES/TEOS hybrid silica sols

A silica sol and its gel powder were prepared using hydrolysis-polymerization of TEOS and MTES under alkaline conditions, followed by gelation. Two alkaline catalysts were used in the preparation of the hybrid silica sol—ammonia and TMAH. The concentration of total alkoxides (MTES + TESO) dissolved in ethanol were kept at 5–10 wt% with molar ratios of MTES/TEOS ranging from 0 to 4 (total weight of the investigated sols: 33–34 g). The initial molar ratio of the reactants was as follows: (MTES + TEOS)/water/catalyst = 2/*x*/*y*, where *x* and *y* are the moles of water and catalyst, respectively, per 2 mole of total alkoxides (TEOS + MTES). *x* and *y* ranged from 35 to 70 and 0.001 to 1.5, respectively. The reactants were mixed in an ice-bath for <5 min, and then reacted at 50 °C with stirring for various reaction times, ranging from several to 40 h. The methyl-modified silica gel was prepared by drying the sol at 100 °C in an oven under a N_2 atmosphere. Then, the gel was calcined in a tube furnace at 400 °C (ramping rate: 10 °C min^{-1}) for 15 min under a N_2 stream (50 cc min^{-1}).

To measure the water contact angle of the hybrid silica films, a clean glass slide was coated with the hybrid silica sol, followed by drying at 80 °C for 15 min and calcination at 400 °C for 15 min under a N_2 stream (50 cc min^{-1}).

2.2 Characterization

Thermogravimetric (TG) analysis was used to measure the weight of the non-volatile, residue of the hybrid silica sols. Nitrogen was used as the carrier gas and the flow rate was kept constant at 50 cc min^{-1}. Temperature was increased at a rate of 5 °C min^{-1} and held at 100 °C for 15 min. The weight of the non-volatile residue was then measured. The weight percent of the non-volatile residue (TG residue) was calculated as the weight ratio of the non-volatile residue (g) to the corresponding silica sol (g).

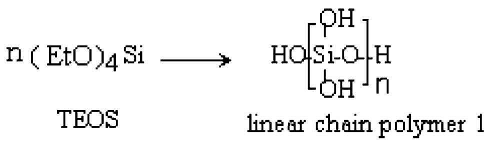
Dynamic light scattering (DLS) was used to measure colloidal particle size (DLS-800, Otsuka Electronics). The hydrophobicity of the methyl-modified silica was evaluated by measurement of the contact angle of the silica film using a microscopic contact angle meter equipped with FAMAS Software (Kyowa DropMaster DM-300, JP), and by examination of the hydroxyl groups in the methyl-modified silica using a Fourier Transform Infrared (FTIR) spectrophotometer (Shimadzu) equipped with software for analysis (Shimadzu Hyper IR for the FTIR 8000 PC series).

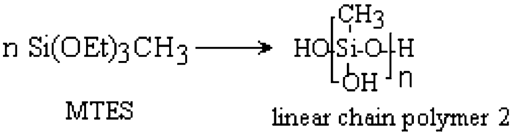
3 Results and discussion

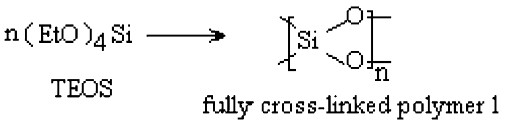
3.1 Calculation of the reaction ratio for hydrolysis-polymerization

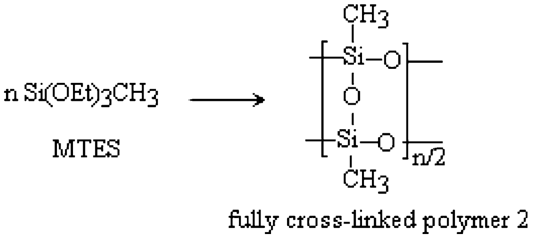
For the hydrolysis and polymerization reactions, silicon precursors were hydrolyzed, and then the silica polymer was gradually formed by polymerization. Hydrolyzed TEOS and MTES are less volatile than unreacted TEOS and MTES, and the silica polymer is a non-volatile substance. Therefore, the TG residual weight (wt%) of the nonvolatile at 100 °C was used to evaluate the reaction rate.

In the polycondensation reaction, TEOS or MTES polymerize into either a linear chain polymer or a cross-linked chain polymer, e.g.,









In the linear chain polycondensation, n moles of TEOS (molecular weight: 208.33n (g mol^{-1})) produce 1 mol of HO–(Si(OH)$_2$O)$_n$–H, which has a molecular weight of (78.10n + 18.01) (g mol^{-1}). When n is large enough, the TG residue weight (wt%) of non-volatile residue (TG residue coefficient) is $(18.01 + 78.10n)/208.33n \approx 78.10/208.33 = 0.3749 = 37.49$ wt%.

In the fully cross-linked polycondensation, n moles of TEOS produce one mole of (SiO$_2$)$_n$, which has a molecular weight of 60.08n (g mol^{-1}). The TG residue weight (wt%) of non-volatile residue (TG residue coefficient) is $60.08n/208.33n = 60.08/208.33 = 0.2884 = 28.84$ wt%.

Because the molecular weight of the silica gel based on TEOS is between (78.10n + 18.01) (g mol^{-1}) and 60.08n (g mol^{-1}), the TG residue coefficient of TEOS should be between 37.49 and 28.84 wt%. The theoretical residue weight of silica derived from TEOS can be calculated by multiplying the initial weight (g) of TEOS by the TG residue coefficient.

In the linear chain polycondensation, n moles of MTES (molecular weight 178.30n (g mol^{-1})) produce 1 mol HO–(SiCH$_3$(OH)O)$_n$–H, which has a molecular weight of (18.01 + 76.13n) (g mol^{-1}). In the fully cross-linked polycondensation, n moles of MTES produce one mole of (SiCH$_3$)$_n$O$_{1.5n}$. Prior to the reaction, the molecular weight of the silicon compound was 178.30n (g mol^{-1}), while after the reaction it was 67.12n (g mol^{-1}). Using the calculations described above for TEOS, the TG residue coefficient of MTES is between 42.70 and 37.64 wt%. The theoretical residue weight of methylated-silica derived from MTES was calculated by multiplying the initial weight (g) of MTES by the TG residue coefficient.

Although the theoretical weight of the residue depends on the polycondensation conditions, the reaction ratio, r, for linear chain polymers of TEOS and MTES can be calculated using the following formula:

$$r = \frac{\mathrm{TG\%} \times w}{w_{\mathrm{TEOS}} \times 0.375 + w_{\mathrm{MTES}} \times 0.427}, \qquad (1)$$

where r is the reaction ratio, TG% is the weight of the non-volatile residue, w is the initial total weight (g) of the reaction system (alkoxide and ethanol), and w_{TEOS} and w_{MTES} are the initial weights (g) of TEOS or MTES used in the reaction system, respectively.

3.2 Thermal stability of hybrid silica gel

Figure 1 shows the change in weight of the hybrid silica polymer as a function of temperature. The drastic decrease at temperatures below 100 °C was attributed to evaporation of both ethanol and unreacted alkoxide. After heating at 100 °C for 15 min, the weight of the residue was constant, and this weight was used as the non-volatile residue weight of the silica sols. It should be noted that without the addition of a catalyst the residue weight of the hybrid silica sols was ~0. The significant decrease observed at 150–220 °C might be due to decomposition of unreacted ethoxide groups and/or to dehydration by cross-linking

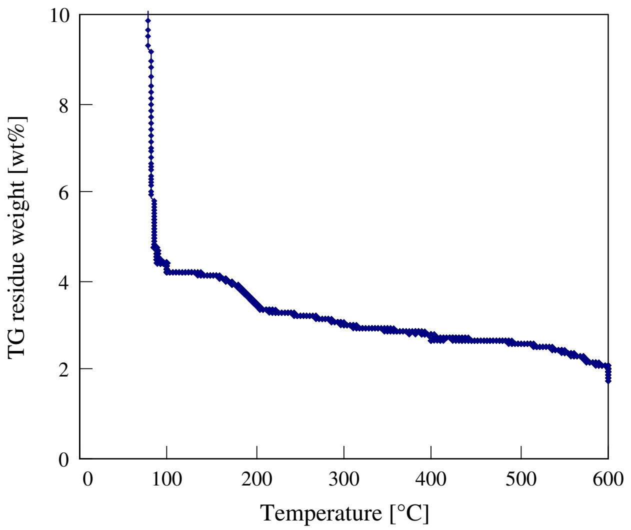


Fig. 1 Weight change of a hybrid silica polymer as a function of temperature (alkoxide: 10 wt%, molar ratio of $M/T = 3$; $(M + T)$/water/NH$_3$ = 2/35/1.5)

polycondensation between silanol groups. By contrast, the gradual decrease in TG from 220 to 400 °C was probably caused by dehydration. At temperatures > 450 °C, the weight of the hybrid silica polymer residue decreased markedly due to decomposition of CH_3 groups [17]. Thus, at temperatures below 450 °C, the CH_3 in the hybrid silica was stable, but at higher temperatures, the Si–CH_3 in the hybrid silica became unstable and decomposed.

3.3 Catalyst

Many different types of catalysts can be used for the preparation of silica sols [19]. Under acidic conditions, the rate of MTES hydrolysis/polymerization is much greater than that of TEOS. Under alkaline conditions, the rate of MTES hydrolysis-polymerization decreases markedly [14]. Therefore, by adjusting the alkalinity of the reaction system or by changing the catalyst species, both the reaction ratio of hydrolysis-polymerization and the silica colloidal particle size distribution can be improved.

Figure 2 shows the weight of the silica polymer residue at 100 °C, that is, the weight of the non-volatile residue of silica sols, as a function of reaction time. After 6 h, the weight of the non-volatile residue approached ~1.8 wt%. There was no difference in the reaction ratio of TEOS to MTES ($M/T = 1$) with use of ammonia compared with TMAH. At reaction times longer than 30 h, the solution became cloudy. The cloudy sols, which had a colloidal particle size greater than several 100 nm by DLS measurement, were too large to be used in the fabrication of the active separation layer of nanoporous membranes. The preferable colloidal size for successful application in nanoporous silica membranes ranges from several nanometers to <100 nm in diameter [18, 20].

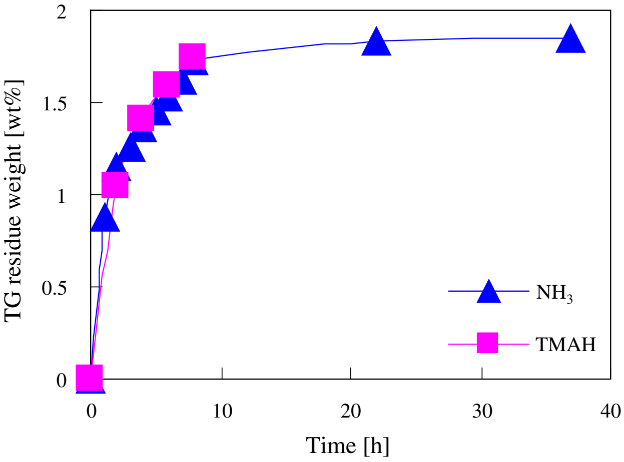


Fig. 2 Weight of a hybrid silica polymer residue at 100 °C as a function of reaction time (alkoxide: 5 wt%, molar ratio of $M/T = 1$; $(M + T)$/water/NH_3 (or TMAH) = 2/70/1.5 (or 0.0065)

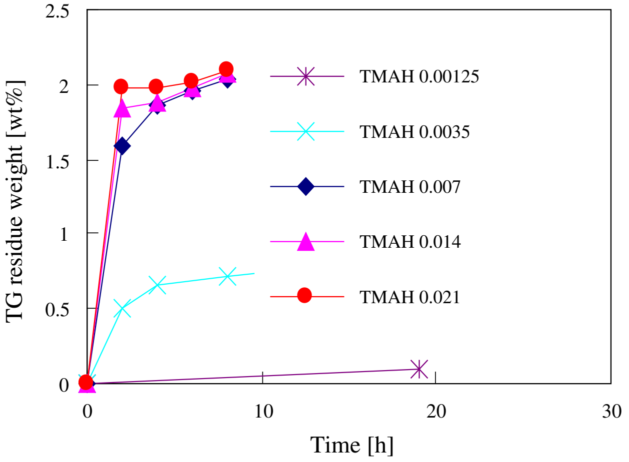


Fig. 3 Time course of the weight of non-volatile residues for different TMAH molar ratios (alkoxide: 5 wt%, molar ratio of $M/T = 3$; $(M + T)$/water/TMAH = 2/35/(0.00125–0.021))

Figure 3 shows the time course of the weight of the non-volatile residue for different TMAH molar ratios. When the TMAH molar ratio reached or exceeded 0.007, the catalyst was very effective as evidenced by a 8 h-TG residue weight of >2 wt%. Table 1 summarizes the effect of TMAH on the characteristics of hybrid silica sols. At all TMAH concentrations studied, the solutions were clear and the DLS values of all the sol particle sizes were <30 nm after 5 h. All the reaction ratios were >90% after 8 h. At higher TMAH concentrations, slightly viscous compounds formed and seemed to attach to the surface of the reaction vessel. A possible explanation for this observation is that, at higher TMAH concentrations, the reaction rate was too fast during the initial stages, resulting in gelation. Therefore, the suitable molar ratio of TMAH for the preparation of the hybrid sol using MTES and TEOS as Si-precursors appears to be ~0.007, which corresponds to a TMAH concentration of 0.001 mol L^{-1} at an alkoxide concentration of 5 wt%.

3.4 Control of colloidal particle size

Separation performance of silica membranes depends on both pore size and pore distribution in the membranes. To prevent formation of mesopores and/or pinholes, it is necessary to avoid bulky polymers by controlling the polymer particle size in the sols. During sol preparation, sol particle size is affected by various factors, such as the pH of the sol solution, the nature of the reactants, and the molar ratio of reactants, etc. Figure 4 shows the effect of the concentration of the Si-precursors on sol particle size. Use of 10 wt% Si-precursor produced larger sol particles compared with a precursor concentration of 5 wt%. This result is consistent with that previously reported for silica

Table 1 Effect of TMAH on the characteristics of hybrid silica sol after reaction for several hours (alkoxide: 5 wt% ($M + T$)/H_2O/TMAH = 2/35/y, $M/T = 3$)

TMAH ratio, y	0.007	0.014	0.021
Reaction ratio (%)	92.6 (8 h)	93.7 (8 h)	94.9 (8 h)
Colloidal size (nm)	21.5 (5 h)	22.4 (5 h)	19.7 (5 h)
Sol appearance	Clear sol	Clear sol, but a viscous compound was adhered to the wall of the reaction vessel	

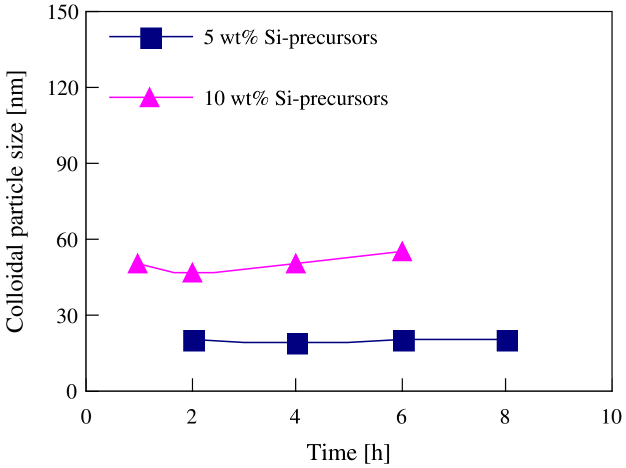


Fig. 4 Effect of Si-alkoxide concentration on sol particle size (molar ratio of $M/T = 1$; the molar ratio in the initial reactants: ($M + T$)/water/NH_3 = 2/70/1.5)

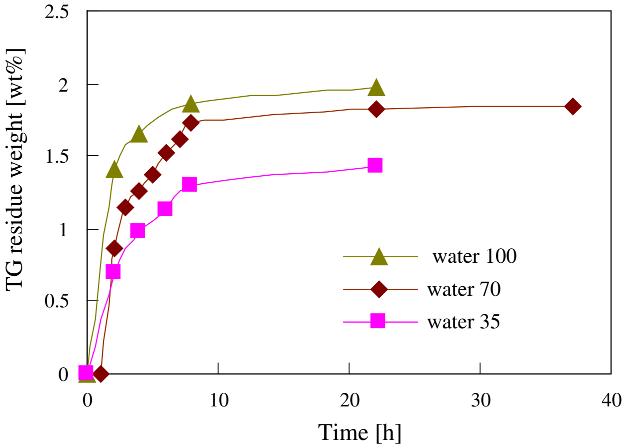


Fig. 5 Time course of TG residue weight for hybrid sols (MTES/TEOS = 1/1) with water molar ratios of 35, 70, and 100 (alkoxide: 5 wt%, molar ratio of $M/T = 1$; ($M + T$)/water/NH_3 = 2/(35–100)/1.5)

sols prepared using TEOS [20]. It should be noted that sol particle sizes for both the 10 and 5 wt% Si-precursors were approximately independent of reaction time over the range of 2–8 h. However, TG residue weight increased gradually and reached a constant value after 10 h (ammonia-catalyzed 5 wt%-Si-precursor in Fig. 2). Considering the faster reaction rate using TEOS compared with MTES under alkaline conditions, a plausible model of MTES/TEOS colloidal growth under alkaline conditions, is as follows. TEOS hydrolyzes and condenses on colloidal silica sols during the initial reaction stage (probably <1 h), and then MTES, which reacts at a slower rate, hydrolyzes and condenses on the surface of the silica, resulting in a core-shell structure [18].

3.5 Effect of the H_2O molar ratio

Figure 5 shows the time course of TG residue weight for hybrid sols (MTES/TEOS = 1, catalyst: ammonia) with water molar ratios of 35, 70, and 100. The non-volatile residue weight of the hybrid silica sol drastically increased with reaction time and approached a constant value, regardless of the water molar ratio. For equivalent reaction times, TG residue weight increased with the water molar ratio. Because TG residue weight can be assumed to be an estimate of reaction rate, greater water molar ratios accelerated the hydrolysis of Si-precursors and the entire hydrolysis-polymerization-gelation reaction when ammonia was used as the catalyst. This phenomenon was more apparent in the system with the high MTES/TEOS molar ratio. Reaction ratios, defined as the weight ratio of a non-volatile-substance to the initial alkoxide (Eq. 1), are summarized in Tables 2 and 3 (catalyst: ammonia). Only 55.9% of the alkoxide (MTES/TEOS = 3) reacted at a water ratio of 70, compared with 77.7% for the alkoxide (MTES/TEOS = 1). When the water molar ratio in the initial reactants was reduced, both the reaction rate and the sol particle size decreased sharply. Because the TMAH catalysts showed reaction ratios >90% at a water ratio of 35 (Table 1), we determined that ammonia is unsuitable for use as a catalyst in preparation of the more hydrophobic colloidal sols.

Table 2 Effect of water molar ratio on the characteristics of hybrid silica sol after reaction for several hours (alkoxide: 5 wt% ($M + T$)/H_2O/NH_3 = 2/x/1.5, $M/T = 3$)

Water ratio, x	70	35	20
Reaction ratio (%)	55.9 (6 h)	33.4 (6 h)	29.5 (6 h)
Colloidal size (nm)	129.8 (6 h)	32.3 (6 h)	25.2 (6 h)
Sol appearance	5 h: cloudy	24 h: cloudy	25 h: blue

Table 3 Effect of the MTES/TEOS molar ratio on the characteristics of hybrid silica sol (alkoxies: 5 wt% $(M + T)/H_2O/NH_3 = 2/70/1.5$)

M/T molar ratio	0	0.5	1	1.3	2.4
Reaction ratio (%)	89.8 (8 h)	82.9 (8 h)	77.7 (8 h)	69.0 (8 h)	59.4 (6 h)
Colloidal size (nm)	55 (6 h)	28 (6 h)	20 (6 h)	21 (6 h)	Cloudy (6 h)

Table 4 Effect of the MTES/TEOS molar ratio on the characteristics of hybrid silica sol (alkoxide: 5 wt% $(M + T)/H_2O/NH_3 = 2/35/1.5$)

M/T molar ratio	2.37	3.06
Reaction ratio (%)	41.5 (8 h)	40.8 (8 h)
Colloidal size (nm)	23 (6 h)	32 (6 h)

3.6 Effects of the MTES/TEOS molar ratio

3.6.1 Effects on the reaction ratio and the sol particle size

Tables 3 and 4 show the effects of the MTES/TEOS molar ratio on sol preparation using ammonia and water ratios of 70 and 35, respectively. Both the reaction ratio and sol particle size decreased with an increase in the MTES/TEOS molar ratio. A likely explanation for this observation is that as the polarity of the methylated silica sols decreased with an increase in M/T ratio, the methylated polymer dispersed more readily in the system, resulting in the smaller colloid size.

Table 5 shows the characteristics of the hybrid silica sol prepared using TMAH as a catalyst. The characteristics of these hybrid sols were quite different from those prepared using ammonia. Because TMAH is an organic alkali, it may retain its catalytic activity in hydrophobic systems. Despite the high MTES/TEOS molar ratio of 4, the reaction ratio was 88% after 6 h with an average colloidal particle size of <40 nm. Because ammonia is an inorganic chemical with alkalescence, it loses catalytic activity in hydrophobic systems. The hydrophobic properties of the reaction system increased with an increase in the MTES/TEOS molar ratio, resulting in a decrease in the reaction ratio when ammonia was used as the catalyst.

3.6.2 Characterization of the hydrophobic properties of silica

The hydrophobic properties of the silica materials were evaluated by measurement of the water contact angle (θ) between the silica film on a slide glass and a water droplet, which was placed on the surface of the hydrophobic silica film. Figure 6 shows a photograph of water droplets on the hybrid silica films. Larger water droplets were applied to the more hydrophobic surfaces due to the difficulty in placing small droplets on the hydrophobic surfaces. It was previously reported that the contact angle decreased as the drop diameter increased [21]. At MTES/TEOS molar ratios ranging from 1 to 4, the corresponding contact angles (θ) were 124°, 135°, 141° and 145°, respectively, i.e., the contact angle (θ) increased with the MTES/TEOS molar ratio. At higher MTES/TEOS molar ratios, more hydrophilic OH groups in the silica were replaced with the hydrophobic methyl groups, increasing the hydrophobicity compared to silica.

Table 5 Characteristics of the hybrid silica sol using TMAH as a catalyst (alkoxide: 5 wt% $(M + T)/H_2O/TMAH = 2/35/0.007$)

M/T molar ratio	2	3	4
Reaction ratio (%)	91.9 (6 h)	90.7 (6 h)	88.7 (6 h)
Colloidal size (nm)	37.5 (6 h)	29.3 (6 h)	31.6 (6 h)

Figure 7 shows FT-IR spectra of hybrid silica gel powders with MTES/TEOS molar ratios of 0 to 4. For the hybrid silica gel, there were several absorption peaks corresponding to $Si–CH_3$ bonds. The absorption peaks at ~2,950 and 1,400 cm^{-1} were attributed to methyl groups, corresponding to asymmetric and symmetric C–H stretching modes [22]. The peaks at 1,260 and 850 cm^{-1} were attributed to Si–C bonding [23]. The wide bands at 3,450 and 1,638 cm^{-1} were attributed to the stretching vibrations of OH groups due to adsorbed water molecules [24]. The peaks at 470 and 810 cm^{-1} were due to Si–O–Si bending vibrations [13], and the peaks at 3,640–3,740 cm^{-1} were due to hydrogen-bonded internal silanols and free surface silanols [17, 25]. The absorbance of OH groups decreased markedly as the MTES molar ratio increased from 0 to 2; however, no significant differences were observed when the MTES/TEOS molar ratio ranged between 2 and 4. When the MTES/TEOS molar ratio was >1, the differences in the

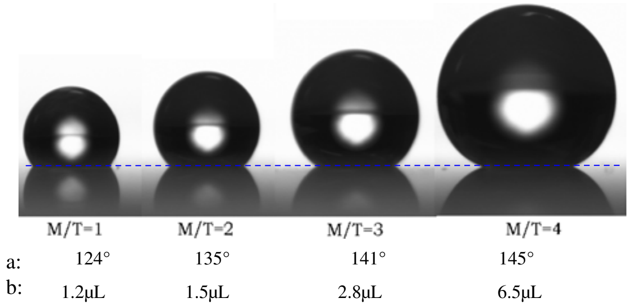


Fig. 6 Photograph of water droplets on the hybrid silica films (alkoxide: 5 wt%, $(M + T)$/water/TMAH = 2/(35–100)/0.007). a: contact angle (6 h), b: water droplet volume

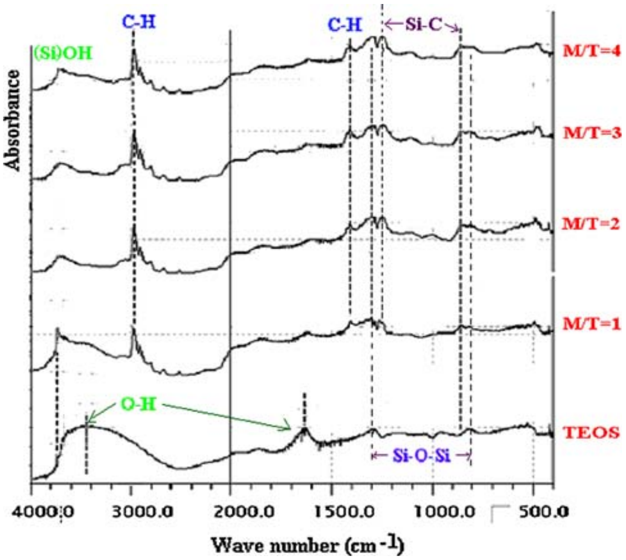


Fig. 7 FT-IR spectra of the hybrid silica gel powder with MTES/TEOS molar ratios ranging from 0 to 4

absorbance of the methyl groups were small. These results suggest that a MTES/TEOS molar ratio ranging from 1 to 3 is appropriate for the preparation of hydrophobic silica sols with colloidal particles smaller than 100 nm.

4 Conclusions

Hydrophobic silica sols were prepared in a one-step, sol–gel process with MTES and TEOS as silica co-precursors for possible use in hydrophobic, nanoporous silica membranes.

1. The hydrophobicity of the methyl-modified silica increased at higher molar ratios of MTES/TEOS, and the sol particle size increased with Si-precursor concentration.
2. A simple calculation of the reaction ratio was used to evaluate the degree to which the Si-precursors underwent hydrolysis-polymerization. When ammonia was used as the catalyst, the reaction ratio decreased as the MTES/TEOS molar ratio increased and the water molar ratio was reduced. However, when TMAH was used as the catalyst, the water molar ratio and the MTES/TEOS molar ratio did not affect the reaction ratio of the methyl-modified silica sol. Therefore, TMAH was found to be a suitable catalyst for the preparation of hydrophobic silica sols, probably because TMAH is an organic alkali.
3. Hydrophobic silica sols with a particle of size <40 nm, which are suitable for the preparation of the microporous separation layer during the later stages of membrane preparation, were successfully produced.

References

1. Kim Y-S, Kusakabe K, Morooka S, Yang S-M (2001) Korean J Chem Eng 18(1):106–112
2. Asaeda M, Yamasaki S (2001) Sep Pur Tec 25:151–159
3. Tsuru T, Morita T, Shintani H, Yoshioka T, Asaeda M (2008) J Membr Sci 316:53–62
4. Tsuru T, Wada S, Izumi S, Asaeda M (1998) J Membr Sci 149:127–135
5. Wang K, McDermid S, Li J, Kremliakova N, Kozak P, Song C, Song C, Tang Y, Zhang JL, Zhang JJ (2008) J Power Sources 184:99–103
6. Zhong Z, Chen J, Peng R (2009) Chin J Chem Eng 17(2):298–303
7. Kanezashi M, Yada K, Yoshioka T, Tsuru T (2009) J Am Chem Soc 131:414–415
8. Igi R, Yoshioka T, Ikuhara YH, Iwamoto Y, Tsuru T (2008) J Am Cer Soc 91:2975–2981
9. Zhang H, He X, He F (2009) J Alloys Comp 469:366–369
10. Makita K, Akamatsu Y, Takamatru A (1999) J Sol-Gel Sci Tech 14:175–186
11. Castricum HL, Sah A, Geenevasen JAJ, Kreiter R, Blank DHA, Vente JF, ten Elshof JE (2008) J Sol-Gel Sci Tech 48:11–17
12. Toledo-Fernandez JA, Mendoza-Serna R, Morales V, de la Rosa-Fox N, Pinero M, Santos A, Esquivias L (2008) J Mater Sci: Mater Med 19:2207–2213
13. Vijayalakshmi U, Balamurugan A, Rajeswari S (2005) Trends Biomater Artif Organs 18(2):101–105
14. van Bommel MJ, Bernards TNM, Boonstra AH (1991) J Non-Cryst Solids 128(5):231–242
15. de Vos RM, Maier WF, Verweij H (1999) J Membr Sci 158:277–288
16. Cao G, Tian H (1998) J Sol-Gel Sci Tech 13:305–309
17. Innocenzi P, Abdirashid MO, Guglielmi M (1994) J Sol-Gel Sci Tech 3:47–55
18. Nakasuji T, Yoshioka T, Tsuru T (2008) Proceedings of 10th ICIM, Tokyo, p 49
19. Venkateswara Rao A, Pajonk GM, Parvathy NN (1994) J Mater Sci 29:1807–1817
20. Tsuru T (2008) J Sol-Gel Sci Technol 46:349–361
21. Tadmor R, Yadav PS (2008) J Colloid Interf Sci 317:241–246
22. Rao AV, Kalesh RR, Amalnerkar DP, Seth T (2003) J Porous Mater 10:23–29
23. Lee S, Cha YC, Hwang HJ et al (2007) Mater Lett 61:3130–3133
24. Yang J, Chen J (2008) J Porous Mater. doi: 10.1007/s10934-008-9256-1
25. Singh AK, Pantano CG (1997) J Sol-Gel Sci Tech 8:371–376