November, 1988] *Bull. Chem. Soc. Jpn.*, ***61***, *4087—4092 (1988)* 4087

Transesterification Reaction of Tetraethoxysilane and Butyl Alcohols

Isao Hasegawa and Sumio Sakka*,†
Division of Molecular Engineering, Graduate School of Engineering, Kyoto University,
Sakyo-Ku, Kyoto, Kyoto-Fu 606
†Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611
(Received June 14, 1988)

Tetraethoxysilane was treated with Amberlyst 15 cation-exchange resin in the presence of butyl alcohols. On treating the mixture of tetraethoxysilane and 1-butanol, the transesterification took place in which butoxyl groups were substituted for ethoxyl groups in tetraethoxysilane. The degree of the transesterification depended on the molar ratio of tetraethoxysilane to 1-butanol of the mixture. The distribution of alkoxysilane species present in the tetraethoxysilane–1-butanol solution was compared with the tetrabutoxysilane–ethanol solution, and it was found that the degree of the transesterification depended on the ratio of numbers of alkyl groups in tetraalkoxysilane and alcohol used. The time required for equilibrium in the distribution of alkoxysilane species in the solution was different with the variety of butyl alcohols used, suggesting the presence of steric effect of butyl alcohols on this reaction.

Tetraethoxysilane ($\mathrm{Si(OC_2H_5)_4}$, abbreviated to TEOS) has been widely used for syntheses of silica-based materials as starting material for silica, especially for the synthesis of silica glass by the sol–gel method.[1] For the preparation of silica gels, the mixture of TEOS, alcohol as solvent, water for the hydrolysis and catalyst, such as hydrochloric acid, is usually used. In the course of hydrolysis and polymerization of TEOS, it is reported that transesterification, in which alcohols used displace ethoxyl groups in TEOS to produce ethanols, occurs.[2,3]

The purpose of this study is to investigate the transesterification reaction between TEOS and different isomers of butyl alcohols by using Amberlyst 15 cation-exchange resin. Since no water is used in this study, polymerization reaction caused by the hydrolysis of TEOS can be suppressed to a low percentage.

Amberlyst 15 is a powerful proton donor which acts for the cleavage of siloxane bond in the similar way to trichloroacetic acid and concentrated sulfuric acid.[4] This cation-exchange resin has been used for the post-treatment of trimethylsilylation of silicates, since incompletely trimethylsilylated derivatives with a silanol group or alkoxyl groups are formed in the crude products.[5–7] The trimethylsilylation reaction is completed by treating the crude products in the excess of hexamethyldisiloxane with Amberlyst 15. It is also reported that partially trimethylsilylated derivatives from tetraalkoxysilanes or alkyltriethoxysilanes are produced by treating them with Amberlyst 15 in the presence of hexamethyldisiloxane.[8,9]

Experimental

Materials. Tetraethoxysilane, tetrabutoxysilane ($\mathrm{Si(OC_4H_9)_4}$, TBOS), 1-butanol (Bu^{n}OH), 2-butanol (Bu^{s}OH), 2-methyl-1-propanol (Bu^{i}OH), 2-methyl-2-propanol (Bu^{t}OH), and ethanol (EtOH) were of reagent grade. Amberlyst 15 cation-exchange resin was used after heating in an oven of 80 °C and cooling in a desiccator, as suggested by Garzó et al.[10]

Preparation of Solutions. TEOS was added to 1-butanol so that the mixed solutions might have various mixing molar ratio. The mixing molar ratio of alcohol (ROH) to tetraalkoxysilane (TAOS) is expressed as the ROH/TAOS ratio in this study. After stirring 20 cm^3 of the mixture for 5 min for homogenization of the solution, 0.5 g of Amberlyst 15 was added. After the vessel of the solution was sealed up, the solution was kept standing in an oven of 40 °C. In this way, the solutions with the Bu^{n}OH/TEOS ratios from 1.0 to 10.0 were prepared.

In order to estimate the degree of polymerization of TEOS which occurs as a side reaction, the TEOS–EtOH solutions whose EtOH/TEOS ratios ranged from 1.0 to 10.0 were prepared by mixing TEOS and ethanol. Quantity of the monomeric species after Amberlyst treatment can be estimated as the residual ratio of TEOS, since only the compounds with ethoxyl groups are present in this system even when the transesterification reaction occurs.

For comparison of the distribution of ester-exchanged derivatives in the TEOS–Bu^{n}OH solutions, the TBOS–EtOH solutions with the EtOH/TBOS ratios from 1.0 to 8.0 were prepared in the same way as described above by using TBOS and ethanol.

Moreover, for investigating the effect of the structure of butyl alcohols on the transesterification reaction, TEOS–Bu^{i}OH, TEOS–Bu^{s}OH, TEOS–Bu^{t}OH solutions at the BuOH/TEOS ratio of 4.0 were also prepared in the same way.

Analytical Procedure. All the solutions were analyzed with a Shimadzu GC-12A gas chromatograph equipped with a hydrogen flame ionization detector and a CLH-702 split sample injector for capillary gas chromatography. The analytical conditions were the same as those described in the previous paper.[8] Each peak on the gas chromatograms was identified with a JEOL JMS-DX 300 gas chromatograph-mass spectrometer in the same analytical conditions described previously.[9]

Quantitative analysis was performed on TEOS and TBOS by using tetradecane as an internal standard. Since standard samples of other compounds formed could not be obtained, however, the distribution of each alkoxysilane species in the solutions was expressed in terms of the peak area ratio.

Results and Discussion

Gas Chromatography. Figure 1 shows the gas chromatograms of (a) the TEOS–$\mathrm{Bu^nOH}$ solution without Amberlyst treatment, (b) the TEOS–EtOH solution with Amberlyst treatment and (c) the TEOS–$\mathrm{Bu^nOH}$ solution with Amberlyst treatment. These solutions were kept standing in an oven of 40 °C for 120 h and the ROH/TEOS ratios of the solutions are all 4.0. When Amberlyst 15 is not added, only the peak of TEOS, which is the starting material, is detected, indicating that no transesterification reaction occurs. When Amberlyst 15 is added, however, other peaks than TEOS appear, as seen in Fig. 1 (b) and (c). These peaks were identified by conducting combined gas chromatograph-mass spectrometry and the assignments of the peaks on Fig. 1 (a)—(c) are summarized in Table 1.

In this table, it is seen that polymerization of TEOS occurs by treating the TEOS–EtOH solution with Amberlyst 15, as hexaethoxydisiloxane ($Si_2O_7(C_2H_5)_6$) and octaethoxytrisiloxane ($Si_3O_{10}(C_2H_5)_8$) were detected. The peaks corresponding to other compounds than TEOS on the gas chromatogram shown in Fig. 1 (c) are assigned to partially or fully ester-exchanged products formed from TEOS and those from hexaethoxydisiloxane. This fact indicates that the transesterification reaction occurs by treating the mixture of TEOS and $\mathrm{Bu^nOH}$ with Amberlyst 15, although the polymerization occurs slightly at the same time.

Polymerization of TEOS by Amberlyst Treatment. Figure 2 shows the variation in the distribution of alkoxysilane species and the residual ratio of TEOS in the TEOS–EtOH solutions with the EtOH/TEOS ratio after treating with Amberlyst 15 at 40 °C for 120 h. With the increase of the EtOH/TEOS ratio, TEOS decreases, and the dimer ($Si_2O_7(C_2H_5)_6$) and trimer ($Si_3O_{10}(C_2H_5)_8$) increase, and the residual ratio of TEOS is only 66% at the EtOH/TEOS ratio of 10.0, suggesting that the polymerization as a side reaction

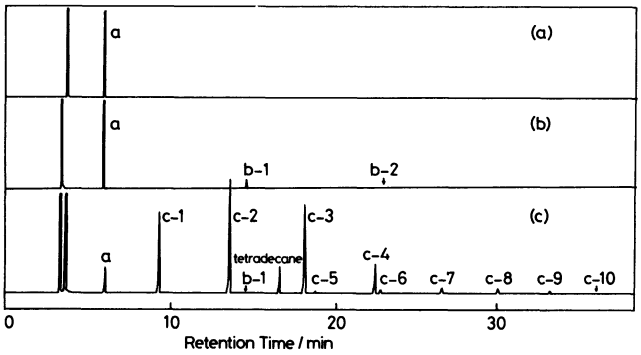

Fig. 1. Gas chromatograms of alkoxysilane species present in (a) the TEOS–$\mathrm{Bu^nOH}$ solution without Amberlyst treatment, (b) the TEOS–EtOH solution, and (c) the TEOS–$\mathrm{Bu^nOH}$ solution with Amberlyst treatment after keeping the solutions standing in an oven of 40 °C. The ROH/TEOS ratios of the solutions are all 4.0.

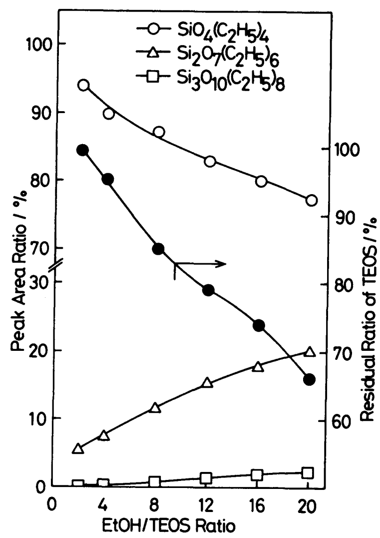

Fig. 2. Variation in the distribution of alkoxysilane species and the residual ratio of TEOS with the EtOH/TEOS ratio in the TEOS–EtOH solutions after treating with Amberlyst 15 at 40 °C for 120 h.

Table 1. Identification of Peaks on the Gas Chromatograms Shown in Fig. 1(a)—(c)

Peak	Retention time/min	Formula	Molecular weight
a	5.6	$SiO_4(C_2H_5)_4$	208
b-1	14.4	$Si_2O_7(C_2H_5)_6$	342
b-2	23.3	$Si_3O_{10}(C_2H_5)_8$	428
c-1	9.0	$SiO_4(C_2H_5)_3(C_4H_9)$	236
c-2	13.4	$SiO_4(C_2H_5)_2(C_4H_9)_2$	264
c-3	18.1	$SiO_4(C_2H_5)(C_4H_9)_3$	292
c-4	22.5	$SiO_4(C_4H_9)_4$	320
c-5	18.7	$Si_2O_7(C_2H_5)_5(C_4H_9)$	370
c-6	22.8	$Si_2O_7(C_2H_5)_4(C_4H_9)_2$	398
c-7	26.6	$Si_2O_7(C_2H_5)_3(C_4H_9)_3$	426
c-8	30.1	$Si_2O_7(C_2H_5)_2(C_4H_9)_4$	454
c-9	33.3	$Si_2O_7(C_2H_5)(C_4H_9)_5$	482
c-10	36.2	$Si_2O_7(C_4H_9)_6$	510

proceeds by this treatment.

It was reported that the recovery of the monomeric silicate species was only 0.3% after soaking the TEOS–EtOH–water–hydrochloric acid solution at the TEOS : EtOH : water : hydrochloric acid molar ratio of 1 : 7 : 2 : 0.01 in a water bath of 40 °C.11) Although the residual ratio of TEOS is fairly low in the solutions at higher EtOH/TEOS ratios as is shown in Fig. 2, the value is much higher than the recovery of monomeric silicate species in the TEOS–EtOH–water–hydrochloric acid system, that is, water containing system after only 10 h of soaking at 40 °C. This fact suggests that polymerization of TEOS in the present study is fairly suppressed because of the absence of water. Therefore, it is thought that the ester-exchange reaction in TAOS–ROH solutions can be investigated with the Amberlyst treatment.

Transesterification of TEOS with 1-Butanol. Figure 3 shows the variation in the distribution of each alkoxysilane species present in the TEOS–Bu^{n}OH solutions with the Bu^{n}OH/TEOS ratio after Amberlyst treatment at 40 °C for 120 h and the recoveries of TEOS and TBOS at each Bu^{n}OH/TEOS ratio are shown in Fig. 4. The degree of transesterification varies with the Bu^{n}OH/TEOS ratio, increasing with increasing Bu^{n}OH/TEOS ratio. At the Bu^{n}OH/TEOS ratio of 20.0, 35.5% of TEOS added to the solution changes to TBOS after the treatment. It seems that there are optimum conditions for the formations of species with different ester-exchanged ratios. The optimum conditions for the formation of Si(OEt)$_3$(OBu^n), Si(OEt)$_2$(OBu^n)$_2$, and Si(OEt)(OBu^n)$_3$ can be determined as the ratios of 2.0, 4.0, and 8.0, respectively, from Fig. 3.

Figure 3 also indicates that there may be no linear relationship on the optimum Bu^{n}OH/TEOS ratio for obtaining a species with a specific degree of transesterification as a main product. It appears, however, that larger amounts of Bu^{n}OH against TEOS are required to change Si(OEt)$_2$(OBu^n)$_2$ to Si(OEt)(OBu^n)$_3$ than to change Si(OEt)$_3$(OBu^n) to Si(OEt)$_2$(OBu^n)$_2$. Actually, even when the solution with the Bu^{n}OH/TEOS ratio of 80.0 is treated in the same manner, the change of TEOS to TBOS is not complete. The peak area ratio of Si(OBu^n)$_4$ is 66.9 %, that of Si(OEt)(OBu^n)$_3$ is 9.5% and that of Si(OEt)$_2$(OBu^n)$_2$ is 2.2%, while Si(OEt)$_4$ and Si(OEt)$_3$(OBu^n) are hardly confirmed on the chromatogram. This fact suggests that the transesterification reaction does not occur at a constant rate on relative steps and larger amounts of Bu^{n}OH to TEOS are required to form the species with higher degrees of transesterification.

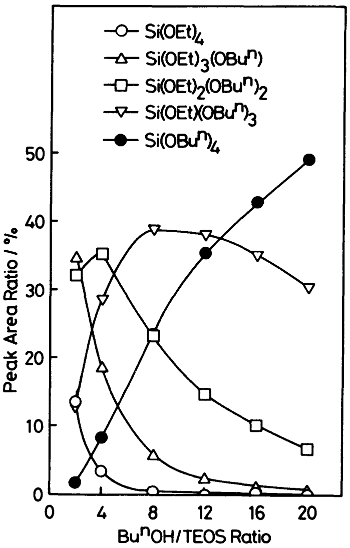

Fig. 3. Variation in the distribution of alkoxysilane species in the TEOS–Bu^{n}OH solutions with the Bu^{n}OH/TEOS ratio after Amberlyst treatment at 40 °C for 120 h.

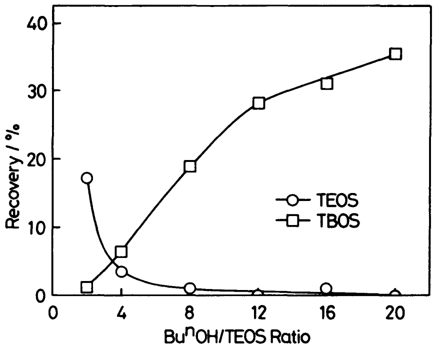

Fig. 4. Variation in the recoveries of TEOS and TBOS in the TEOS–Bu^{n}OH solutions with the Bu^{n}OH/TEOS ratio after Amberlyst treatment at 40 °C for 120 h.

Transesterification of TBOS with Ethanol. Figure 5 shows the variation in the distribution of each species present in the TBOS–EtOH solutions with the EtOH/TBOS ratio after Amberlyst treatment at 40 °C for 120 h. With the increase of this ratio, the degree of substitution of ethoxyl group for butoxyl increases. Compared with the distribution in TEOS–Bu^{n}OH solutions shown in Fig. 3, peak area ratios of each alkoxysilane species at the EtOH/TBOS ratios of 1.0, 2.0, 4.0, and 8.0 show almost the same values as those at the Bu^{n}OH/TEOS ratios of 16.0, 8.0, 4.0, and 2.0, respectively. This fact means that the distribution of alkoxysilane species after Amberlyst treatment depends on the ratio of number of alkyl group in TAOS and that in ROH used, since the ratio of -C$_2$H$_5$/-C$_4$H$_9$ (the ratio of number of ethyl group to that of butyl group) both at the EtOH/TBOS ratio of 1.0 and the Bu^{n}OH/TEOS ratio of 16.0 is 0.25 and the ratio of -C$_2$H$_5$/-C$_4$H$_9$ both at the EtOH/TBOS ratio of 8.0 and the Bu^{n}OH/TEOS ratio of 2.0 is 2.0.

Effect of Treatment Time. Figure 6 shows the

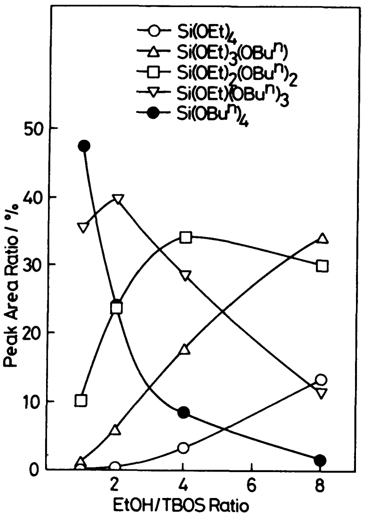

Fig. 5. Variation in the distribution of alkoxysilane species in the TBOS-EtOH solutions with the EtOH/TBOS ratio after Amberlyst treatment at 40 °C for 120 h.

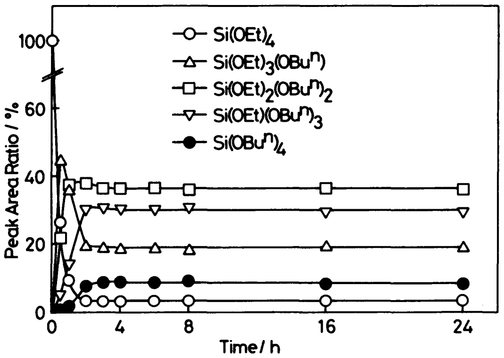

Fig. 6. Variation in the distribution of alkoxysilane species in the TEOS-Bu^{n}OH solution at the Bu^{n}OH/TEOS ratio of 4.0 with time of Amberlyst treatment at 40 °C.

variation in the distribution of alkoxysilane species in the TEOS-Bu^{n}OH solution at the Bu^{n}OH/TEOS ratio of 4.0 with time of Amberlyst treatment at 40 °C. In this figure, it is seen that the distribution of each alkoxysilane species does not vary and the equilibrium on the distribution is established on and after 2 h, indicating that the transesterification reaction between TEOS and Bu^{n}OH proceeds very rapidly.

Effect of the Structure of Butyl Alcohols. Variations in the distribution of alkoxysilane species with time of Amberlyst treatment at 40 °C in the TEOS-Bu^{i}OH and the TEOS-Bu^{s}OH solutions both at the BuOH/TEOS ratio of 4.0 are shown in Figs. 7 and 8, respectively. It is seen that the equilibrium on the transesterification is achieved in 6 h in the TEOS-Bu^{i}OH solution and in 50 h in the TEOS-Bu^{s}OH solution. The times for attaining the equilibrium in the TEOS-Bu^{i}OH and TEOS-Bu^{s}OH solutions are longer than that in the TEOS-Bu^{n}OH solution and the time is shorter in the TEOS-Bu^{i}OH system than in the TEOS-Bu^{s}OH system. It is considered that these differences are attributed to the steric effect of butyl alcohols on this transesterification reaction, and the time for the equilibrium seems to be shorter when the number of branching of alkyl group in a butyl alcohol is less and the number of C–C bond at the carbon atom to which a hydroxyl group attaches in a butyl alcohol is less.

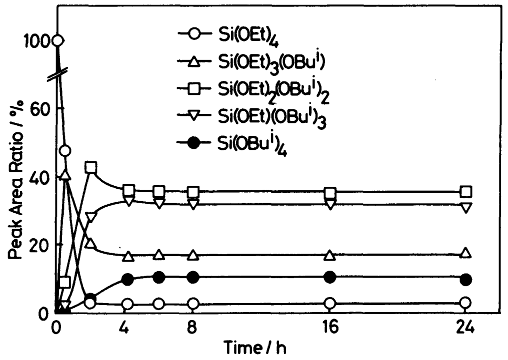

Fig. 7. Variation in the distribution of alkoxysilane species in the TEOS-Bu^{i}OH solution at the Bu^{i}OH/TEOS ratio of 4.0 with time of Amberlyst treatment at 40 °C.

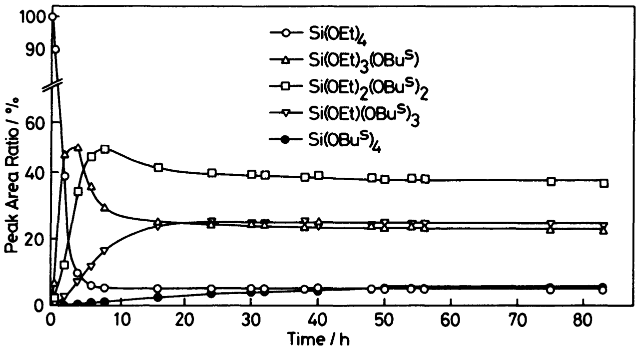

Fig. 8. Variation in the distribution of alkoxysilane species in the TEOS-Bu^{s}OH solution at the Bu^{s}OH/TEOS ratio of 4.0 with time of Amberlyst treatment at 40 °C.

When the TEOS-Bu^{t}OH solution at the Bu^{t}OH/TEOS ratio of 4.0 is treated with Amberlyst 15, however, the peak of TEOS become smaller with the treatment time and is hardly seen on the gas chromatogram after keeping the solution standing in an oven of 40 °C for 84 h. Then the solution gels after ca. 20 days. This suggests that the main reaction in this system is polymerization of TEOS. Typical gas chromatogram of the TEOS-Bu^{t}OH solution is shown in Fig. 9. By identifying the peaks on Fig. 9 with combined gas chromatograph-mass spectrometry, the peak a is assigned to $Si(OC_2H_5)_3(OH)$ (M, 180), which hardly appears in the other systems, and

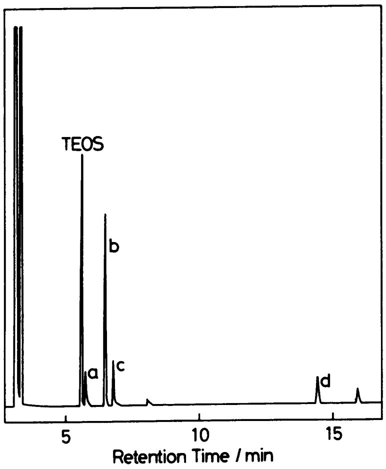

Fig. 9. Gas chromatogram of the TEOS-Bu^tOH solution at the Bu^tOH/TEOS ratio of 4.0 after Amberlyst treatment at 40 °C for 16 h.

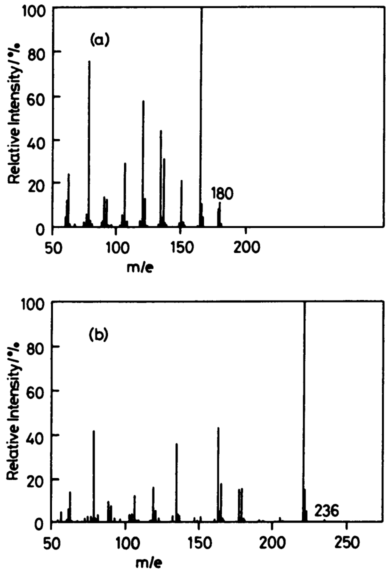

Fig. 10. 70-eV mass spectra of (a) $Si(OEt)_3(OH)$ and (b) $Si(OEt)_3(OBu^t)$ corresponding to peaks a and b in Fig. 9.

the peak b is assigned to $Si(OC_2H_5)_3(OBu^t)$ (M, 236). The mass spectra of these compounds are shown in Fig. 10 (a) and (b), respectively. The peak c is assigned to $Si(OC_2H_5)_2(OBu^t)(OH)$ and the peak d is assigned to $Si_2O_7(C_2H_5)_6$. It is considered that the polymerization rather than the transesterification occurs in this system because of the presence of the species with a reactive silanol group.

General Reaction Mechanism. The results described above suggest that the fundamental reaction of the transesterification in the present study may proceed as follows;

$$A\text{-}H + Si(OR^1)_4 \longrightarrow A\text{-}Si(OR^1)_3 + R^1OH \qquad (1)$$

(A-H : Amberlyst-H)

$$A\text{-}Si(OR^1)_3 + R^2OH \longrightarrow A\text{-}H + Si(OR^1)_3(OR^2) \qquad (2)$$

The ester-exchange reaction would proceed to the degree which is determined by the ROH/TAOS ratio.

The differences in the time for establishing the equilibrium in the TEOS-Bu^nOH, TEOS-Bu^iOH, and TEOS-Bu^sOH systems may be attributed to the steric effect of butyl alcohols. It is supposed that the differences arise in Reaction (2). In Reaction (2), butyl alcohol molecules present in the solution and EtOH formed by Reaction (1) would react with $A\text{-}Si(OR)_3$ competitively. In the final stage, however, the quantity of a butyl alcohol in the solution is expected to determine the degree of transesterification, since the main products in these three systems are $Si(OEt)_2(OBu)_2$ in spite of the variety of butyl alcohols.

The presence of alkoxydisiloxane and alkoxytrisiloxane species, as is seen in Fig. 1 (b) and (c), and the occurrence of gelation in the TEOS-Bu^tOH solution indicate that polymerization of TEOS occurs together with the transesterification. The following polymerization reactions are assumed.

$$A\text{-}H + Si(OR)_4 \longrightarrow A\text{-}R + Si(OR)_3(OH) \qquad (3)$$

$$Si(OR)_3(OH) + Si(OR)_4 \longrightarrow (RO)_3Si\text{-}O\text{-}Si(OR)_3 + ROH \qquad (4)$$

$$Si(OR)_3(OH) + A\text{-}Si(OR)_3 \longrightarrow (RO)_3Si\text{-}O\text{-}Si(OR)_3 + A\text{-}H \qquad (5)$$

$$Si(OR)_3(OH) + Si(OR)_3(OH) \longrightarrow (RO)_3Si\text{-}O\text{-}Si(OR)_3 + H_2O \qquad (6)$$

The occurrence of gelation in the TEOS-Bu^tOH solution may be explained by the presence of the species with a reactive silanol group formed by Reaction (3), which may lead to the polymerization.

Conclusion

Transesterification reaction took place when the mixture of TEOS and a butyl alcohol was treated with Amberlyst 15 cation-exchange resin except for Bu^tOH. A slight degree of polymerization of TEOS also took place as a side reaction. The degree of transesterification of TEOS depended mainly on the ratio of mixing of TEOS and a butyl alcohol, indicating that alkoxysilane species with a specific ester-exchanged ratio can be obtained as the main product in a solution by choosing the optimum ratio of mixing of TAOS and ROH. Additionally, the distribution of alkoxysilane species with different degrees of transesterification in a solution was governed by the ratio of numbers of alkyl groups in TAOS and ROH used, regardless of the kinds of TAOS and ROH used as starting materials. The kind of butyl alcohols also affected the time for attaining the equilibrium of transesterification reaction. When Bu^tOH was used as a butyl alcohol, polymerization of TEOS was more dominant than the transesterification, which led to the gelation of the solution.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas, New Functionality Materials—Design, Preparation and Control, The Ministry of Education, Science and Culture, No. 62604011.

References

1) S. Sakka, "Treatise on Material Science and Technology, Vol. 22," Academic Press, New York (1982), p. 129.

2) C. J. Brinker, K. D. Keefer, D. W. Schaefer, R. A. Assink, B. D. Kay, and C. S. Ashley, *J. Non-Cryst. Solids*, **63**, 45 (1984).

3) J. C. Pouxviel, J. P. Boilot, J. C. Beloeil, and J. Y. Lallemand, *J. Non-Cryst. Solids*, **89**, 345 (1987).

4) W. Noll, "Chemistry and Technology of Silicones," Academic Press, New York (1968), p. 230.

5) C. W. Lentz, *Inorg. Chem.*, **3**, 574 (1964).

6) G. Eglinton, J. N. M. Firth, and B. L. Welters, *Chem. Geol.*, **13**, 25 (1974).

7) J. Götz and C. R. Masson, *J. Chem. Soc. A*, **1970**, 2683.

8) I. Hasegawa and S. Sakka, *Bull. Chem. Soc. Jpn.*, **60**, 4313 (1987).

9) I. Hasegawa and S. Sakka, *J. Organomet. Chem.*, **340**, 31 (1988).

10) G. Garzó, A. Vargha, T. Székely, and D. Hoebbel, *J. Chem. Soc., Dalton Trans.*, **1980**, 2068.

11) I. Hasegawa and S. Sakka, *J. Non-Cryst. Solids*, **100**, 201 (1988).