Treatment of Tetraalkoxysilanes with Amberlyst 15 Cation-Exchange Resin in Presence of Hexamethyldisiloxane

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(Received June 11, 1987)

Tetraalkoxysilanes were treated with Amberlyst 15 cation-exchange resin in hexamethyldisiloxane at 40 °C in order to substitute the trimethylsilyl group for the alkyl group in a tetraalkoxysilane partially. Tetramethoxy-, ethoxy-, propoxy-, and butoxysilanes were used for the experiments. After the treatment, $SiO_4R_{4-n}X_n$ ($1 \leqq n \leqq 4$, R=CH_3, C_2H_5, n-C_3H_7, and n-C_4H_9, X=$Si(CH_3)_3$) were detected by gas chromatography and were identified by combined gas chromatography-mass spectrometry. The degree of trimethylsilylation of tetraalkoxysilane changed with the molar ratio of hexamethyldisiloxane to tetraalkoxysilane and quantities of the reaction products in the system depended mainly on the ratio.

Tetraalkoxysilanes (TAOS) are promising materials as a source of silica for the synthesis of inorganic or organosilicon compounds. Hydrolysis and polycondensation of TAOS in the system of TAOS-ethanol-H_2O-HCl produce a variety of silicate species, however, even if the amount of added water for the hydrolysis is little.[1)] This random polymerization would be caused by the tetra-functionality of TAOS. In other words, all four alkoxyl groups on a silicon atom have the same reactivity, making it difficult to control the reaction of a TAOS. In order to synthesize the compounds with controlled structures in their silicate skeletons from TAOS, it will be necessary to substitute functional groups of low reactivity, such as trimethylsilyl groups (-$Si(CH_3)_3$), for some of the functional groups of TAOS. Trimethylsilylation of silicates, originated by Lentz in 1964,[2)] has been developed into several characteristic methods.[3)] When the method of Götz and Masson[4)] is applied to silicate minerals, such as hemimorphite, trimethylsilyl mono-, di-, and trialkoxy derivatives of silicate anions are formed by the side reaction of esterification of the silanol group with an alcohol used in the trimethylsilylating reagent.[5—8)] On the basis of this esterification reaction, Kuroda et al. synthesized silicate-organic copolymer from hemimorphite and ethylene glycol in the reaction mixture for trimethylsilylation.[9)] On the other hand, post-treatment with Amberlyst 15 cation-exchange resin in the presence of an excess of hexamethyldisiloxane ($(CH_3)_3Si$-O-$Si(CH_3)_3$) is necessary for the completion of trimethylsilylation. Such treatment would promote the exchange of the residual silanol groups or alcohol-esterified sites in the silicate skeleton with the trimethylsilyl groups, although there might be some other side reactions.[10—12)]

It is expected that such partially trimethylsilylated alkoxysilanes might be more readily produced from TAOS as a silica source than silicate minerals. In this study, it is aimed to produce partially trimethylsilylated derivatives from 4 TAOS; tetramethoxy-, ethoxy-, propoxy-, and butoxysilanes (abbreviated to TMOS, TEOS, TPOS and TBOS, respectively) by treatment with Amberlyst 15 in hexamethyldisiloxane (HMDS). The effects of the molar ratio of HMDS to TAOS (abbreviated to the HMDS/TAOS ratio) and the time of the treatment on the distribution of the reaction products were studied by gas-liquid chromatography.

Experimental

Materials. Reagent grade tetramethoxy-, ethoxy-, propoxy-, and butoxysilanes were used. Hexamethyldisiloxane was used after a single distillation (bp 100—101 °C). Amberlyst 15 cation-exchange resin was used after heating in an oven at 80 °C for 4 h and cooling in a desiccator for standardization, as was suggested by Garzó et al.[12)]

Preparation of Solutions. The solutions with the HMDS/TAOS ratios from 0.5 to 10.0 were prepared by mixing given amounts of TAOS and HMDS. After stirring for 5 min for homogeneity of the solution, ca. 0.5 g of Amberlyst 15 cation-exchange resin was added to the mixture (20 cm^3) and the vessel was sealed. After keeping standing the vessels in an oven at 40 °C for 85 h, the samples were analyzed by means of gas-liquid chromatography. The effect of the time of treatment was investigated by analyzing the sample with the HMDS/TEOS ratio of 4.0 at various time intervals.

Analytical Procedure. The solutions were analyzed by a Shimadzu GC-12A gas-liquid chromatograph equipped with a hydrogen flame-ionization detector and a CLH-702 split sample injection for capillary gas chromatography. The capillary column (length 25 m, i.d. 0.25 mm) of fused silica cross-linked immovable layer (ULBON HR-101, similar polarity to OV-101) as a stationary phase was used. The injection temperature was 330 °C. The column temperature was programmed to rise at 4 $°C\,min^{-1}$ from 100 to 330 °C. The carrier gas was nitrogen and its flow rate was 0.34 $cm^3\,min^{-1}$ at the split rate of 1 : 104. Standard solutions of the mixed derivatives were not prepared, and so the results of gas-liquid chromatography are expressed in terms of percentages of total peak area. Although it is impossible to elucidate the distribution of the products quantitatively, the main product in the system can be determined from the peak area ratio.

Identification of the peaks on the gas chromatograms was made by conducting combined gas chromatograph-mass spectrometric analyses with a JEOL JMS-DX 300 gas chromatograph-mass spectrometer using an ionizing energy of 70 eV. The ion source block was maintained at 200 °C and the molecular separator at 230 °C. The column consisted of 1 m coiled glass packed with SE-30. The column was operated isothermally. The carrier gas was He (15 cm^3 min^{-1}).

Results and Discussion

Gas chromatograms of the products obtained by treating the TAOS-HMDS solutions at the HMDS/TAOS ratio of 4.0 with Amberlyst 15 for 85 h in an oven at 40 °C are shown in Fig. 1(a)—(d). Five peaks are seen in each gas chromatogram.

These peaks were identified by a combined gas chromatography-mass spectrometry. It is known from the mass spectra of trimethylsilylated derivatives of silicates[13] that the molecular ion is either of very low abundance or below detection limit and the most structurally informative ion is the one produced by the loss of a methyl radical from the molecular ion, $[M-15]^+$. Moreover, substitution of a trimethylsilyl group for an alkyl group is indicated by the difference in the mass numbers of $[M-15]^+$, in regard to neighboring peaks on the gas chromatogram. This difference corresponds to the difference between $-Si(CH_3)_3$ and $-C_nH_{2n+1}$ (n=1—4), an alkyl group in a TAOS.[5,6] These characteristics of the mass spectra were confirmed on four of the five peaks on the gas chromatogram. The mass number for the molecular ion corresponding to the other peak is that of TAOS used for preparation of the sample. Actually, the retention time of the peak corresponded to that of pure TAOS. Table 1 shows the assignments of peaks in each gas

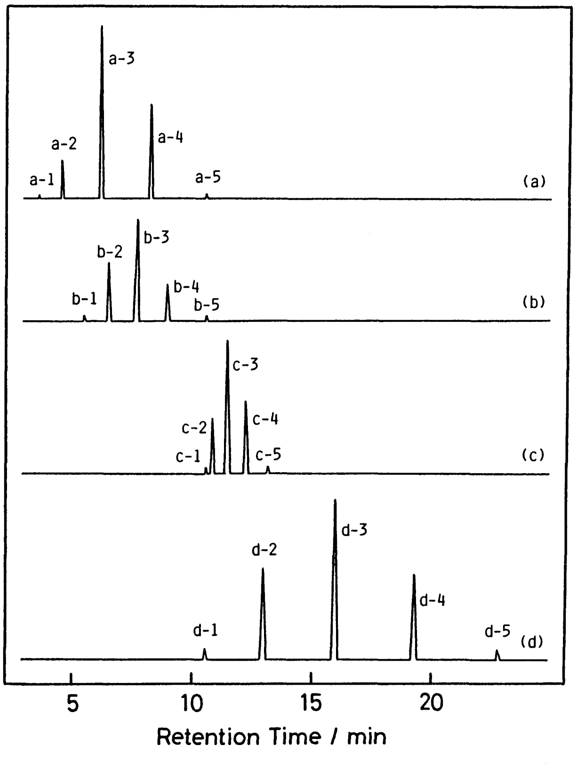

Fig. 1. Gas chromatograms of the products obtained by treating the TAOS-HMDS solutions at the HMDS/TAOS ratio of 4.0 with Amberlyst 15 at 40°C for 85 h. TAOS: (a) TMOS, (b) TEOS, (c) TPOS, and (d) TBOS.

Table 1. Identification of the Peaks on the Gas Chromatograms in Fig. 1

TAOS	Peak	Formula
TMOS	a-1	$SiO_4(CH_3)_4$
	a-2	$SiO_4(CH_3)_3[Si(CH_3)_3]$
	a-3	$SiO_4(CH_3)_2[Si(CH_3)_3]_2$
	a-4	$SiO_4(CH_3)[Si(CH_3)_3]_3$
	a-5	$SiO_4[Si(CH_3)_3]_4$
TEOS	b-1	$SiO_4(C_2H_5)_4$
	b-2	$SiO_4(C_2H_5)_3[Si(CH_3)_3]$
	b-3	$SiO_4(C_2H_5)_2[Si(CH_3)_3]_2$
	b-4	$SiO_4(C_2H_5)[Si(CH_3)_3]_3$
	b-5	$SiO_4[Si(CH_3)_3]_4$
TPOS	c-1	$SiO_4[Si(CH_3)_3]_4$
	c-2	$SiO_4(C_3H_7)[Si(CH_3)_3]_3$
	c-3	$SiO_4(C_3H_7)_2[Si(CH_3)_3]_2$
	c-4	$SiO_4(C_3H_7)_3[Si(CH_3)_3]$
	c-5	$SiO_4(C_3H_7)_4$
TBOS	d-1	$SiO_4[Si(CH_3)_3]_4$
	d-2	$SiO_4(C_4H_9)[Si(CH_3)_3]_3$
	d-3	$SiO_4(C_4H_9)_2[Si(CH_3)_3]_2$
	d-4	$SiO_4(C_4H_9)_3[Si(CH_3)_3]$
	d-5	$SiO_4(C_4H_9)_4$

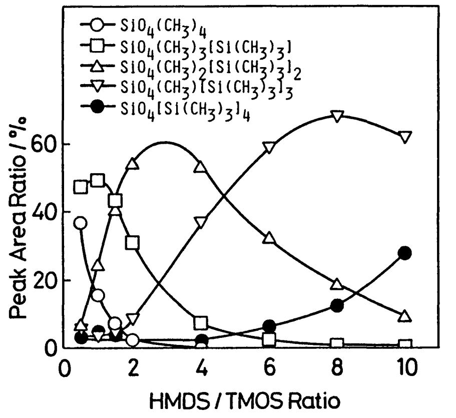

Fig. 2. Effect of the HMDS/TMOS ratio on the peak area ratios of the derivatives from TMOS ($SiO_4(CH_3)_4$) by Amberlyst treatment at 40°C for 85 h.

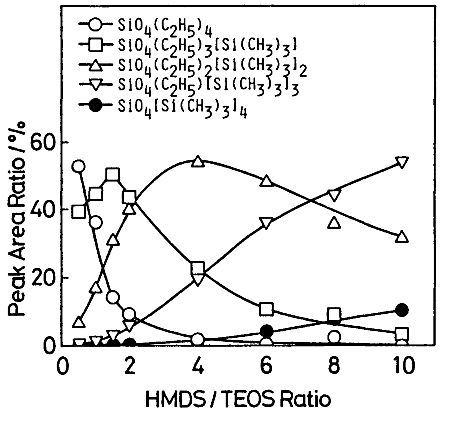

Fig. 3. Effect of the HMDS/TEOS ratio on the peak area ratios of the derivatives from TEOS ($SiO_4(C_2H_5)_4$) by Amberlyst treatment at 40°C for 85 h.

chromatogram. It is seen that TAOS is partially or fully trimethylsilylated by Amberlyst treatment in HMDS.

Figures 2 and 3 show the effect of the HMDS/TAOS ratio on the distribution of the products in the TMOS- and TEOS- HMDS systems, respectively. The main product of the derivatives from TAOS varies with the HMDS/TAOS ratio, indicating that the degree of trimethylsilylation of TAOS is governed mainly by the HMDS/TAOS ratio. The tendencies of the variations in the distribution of products with the ratio in the TPOS- and TBOS-HMDS systems are almost the same as that in the TEOS-HMDS system. In the TEOS-, TPOS-, and TBOS-HMDS systems, the optimum conditions for partial trimethylsilylation are determined, regardless of the type of alkyl group, as follows; the HMDS/TAOS ratio of 1.5 for monosubstitution, the ratio of 4.0 for disubstitution and the ratio of 10.0 for trisubstitution. In the TMOS-HMDS system, however, the optimum ratios for the substitutions are slightly lower than those noted above.

On the other hand, a few peaks are slightly traced at longer retention time on the gas chromatograms. These peaks appear more clearly at lower HMDS/TAOS ratios or longer treating times. A typical gas chromatogram is shown in Fig. 4. This is the chromatogram for the sample at the HMDS/TEOS ratio of 1.0 treated with Amberlyst 15 for ca. 7 months at room temperature. Around the retention time from 14 to 17 min, three peaks (labeled a, b, and c in Fig. 4) appear, which can not be detected in such large peak areas when treated for 85 h at 40 °C.

In the combined gas chromatograph-mass spectrometric analyses, the peak a is assigned to $Si_2O_5(C_2H_5)_6$, which has the dimeric structure in the silicate skeleton. Also, from the rule on mass spectra of trimethylsilylated derivatives of silicates described above, it is considered that the peaks b and c are identified as $Si_2O_5(C_2H_5)_5[Si(CH_3)_3]$, whose molecular weight is 386 and $[M-15]^+$ is 371 (The mass spectrum of this compound is shown in Fig. 5.), and $Si_2O_5(C_2H_5)_4[Si(CH_3)_3]_2$, whose molecular weight is 430 and $[M-15]^+$ is 415. These compounds are also in the dimeric state of silicate structure. This dimerization might be caused by high TAOS concentrations in low HMDS/TAOS ratios. Moreover, these facts suggest that a long treatment time with Amberlyst 15 is not required for substitution of the trimethylsilyl group for the alkyl group in a TAOS, and makes the reactions between TAOS or partially trimethylsilylated alkoxysilanes proceed.

In order to clarify the effect of treatment time, the variation in the distribution of derivatives from TEOS at the HMDS/TEOS ratio of 4.0 with treatment time at 40 °C was investigated and the result is shown in Fig. 6. The main product at this ratio is $SiO_4(C_2H_5)_2[Si(CH_3)_3]_2$, as shown in Fig. 3. In initial ten hours, the less the degree of trimethylsilylation of the species is, the larger the peak area ratio is. However, $SiO_4(C_2H_5)_2[Si(CH_3)_3]_2$ becomes the main product after 14 h treatment. Although the peak area ratios of $SiO_4(C_2H_5)_3[Si(CH_3)_3]$ and $SiO_4(C_2H_5)[Si(CH_3)_3]_3$ vary further with the time of treatment, that of $SiO_4(C_2H_5)_2[Si(CH_3)_3]_2$ hardly varies on and after 48 h

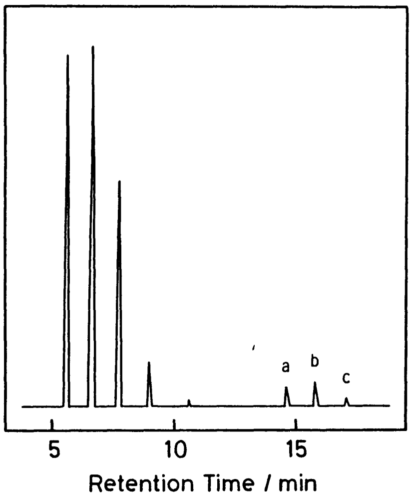

Fig. 4. Gas chromatogram of the TEOS-HMDS solution at the HMDS/TEOS ratio of 1.0 treated with Amberlyst 15 for ca. 7 months at room temperature.

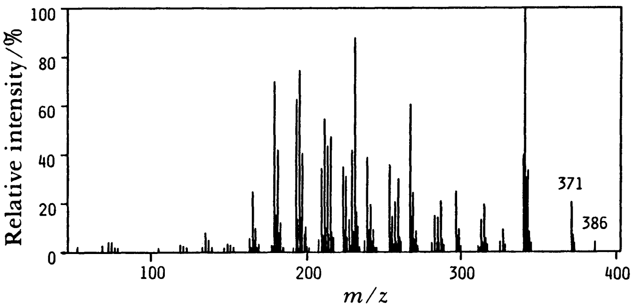

Fig. 5. Mass spectrum of $Si_2O_5(C_2H_5)_5[Si(CH_3)_3]$.

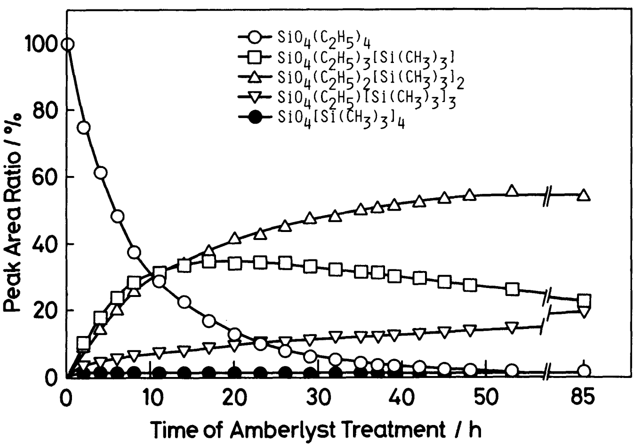

Fig. 6. Effect of the time of Amberlyst treatment on the peak area ratios of the derivatives formed in the TEOS-HMDS solution at the HMDS/TEOS ratio of 4.0 at 40°C.

treatment at 40 °C. This indicates that the distribution of the derivatives varies with the time of treatment and the equilibrium relating to the formation of $SiO_4(C_2H_5)_2[Si(CH_3)_3]_2$ appears to be established on and after 48 h treatment at 40 °C.

In addition, the peaks at longer retention times on the gas chromatograms are traced in very small peak areas, indicating that the reactions between TEOS or partially trimethylsilylated ethoxysilanes hardly occur and only the substitution occurs in 85 h treatment.

From these results, it is concluded that TAOS is partially or fully trimethylsilylated by treating in HMDS with Amberlyst 15 cation-exchange resin. The degree of trimethylsilylation is governed by the HMDS/TAOS ratio. Within the treatment time of 85 h, reactions between TAOS or between partially trimethylsilylated alkoxysilanes scarcely occur and only substitution by the trimethylsilyl group proceeds. At lower HMDS/TAOS ratios, however, not only the substitution but also the dimerization occurs because of high concentrations of TAOS in the systems.

The present 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. The authors wish to express their sincere thanks to Dr. Kazuyuki Kuroda at Department of Applied Chemistry, Waseda University for useful discussions. Thanks are also due to Mr. Nakashi Nakamura at Science and Engineering Research Laboratory, Waseda University for measuring mass spectra.

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