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Reaction of Methanol Vapor with Silicon into Trimethoxysilane with High Selectivity

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Trimethoxysilane was obtained with a 98% selectivity and at an 82% silicon conversion in 5 h of reaction time, when methanol (99 kPa) was fed at 543 K into a fixed-bed reactor containing silicon powder preheated with copper(I) chloride at 623 K for 3 h.

Reaction of silicon with methanol is known to give methoxysilanes. In 1948, Rochow[1)] reported that tetramethoxysilane was obtained when silicon fused with copper was brought into contact with methanol vapor at 553 K in a fixed-bed reactor. Both tri- and tetramethoxysilanes were obtained when methanol was fed at 553 K slowly into a reactor containing the silicon fused with copper in silicone oil, though the reaction stopped at a silicon conversion of 33%.[2)]

Efforts have been focused on obtaining trimethoxysilane with high selectivities, since trimethoxysilane is one of the important chemicals from which various organosilicon compounds can be derived by the reaction with organic compounds. A high selectivity for trimethoxysilane has been obtained by using silicon and copper(I) chloride. A 90% selectivity for trimethoxysilane and a remarkably increased silicon conversion of 92% was obtained, when methanol was fed dropwise into a reactor containing silicon and copper(I) chloride in diundecyl benzene at 513 K for 10 h.[3)] However, when the reaction was conducted in a fluidized-bed reactor containing the silicon - copper(I) chloride - zinc mixture, which had been preheated at 623 K prior to the contact with methanol, trimethoxysilane was obtained with an 84% selectivity and at only a 26% level of silicon conversion in 7 h of reaction time at 618 K.[4)]

We have found that the reactivity of silicon with methanol vapor greatly depends on the temperature of the preheating the silicon - copper(I) chloride mixture. Thus, the reactivity of silicon in the mixtures preheated at below 573 K was low; for the mixtures preheated at elevated temperatures such as 723 and 773 K, silicon was consumed almost completely at 513 K in 3 h of reaction time. In the latter case, however, the selectivity for trimethoxysilane greatly changed with reaction time in a wide range of 52-92%. Here, we wish to report that high selectivities (>92%) for trimethoxysilane can be obtained at any reaction time, when the preheating was carried out at 623 K.

Silicon (99.5% in purity) and copper(I) chloride were sieved into grains of 45-63 μm and were mixed in a glass sample-tube with vigorous vibration. The reactions were carried out in a fixed-bed flow-reactor. A 0.5 g portion of the mixture (Cu/Si= 1/9 wt/wt) was packed in a reactor of silica tubing (10 mm i.d.), and then heated under a helium stream at 623 K for 3 h. Methanol, dehydrated over molecular sieve 3A, (25-99 kPa, methanol + helium= 87 mmol h^{-1}) was fed by a motor-driven syringe into the reactor at 493-543 K. The effluent gas was analyzed automatically every 2.5 min with a gas chromatograph.

After the Si-CuCl mixture was preheated in the reactor at 623 K for 3 h under a helium stream, methanol was fed to the reactor at various temperatures and the formation rate of methoxysilanes ($(CH_3O)_3SiH$ + $(CH_3O)_4Si$) was monitored. As shown in Fig. 1, the change of the rate with reaction time depended greatly on the reaction temperature. Thus, at 493 and 513 K, the rate increased and attained a maximum beyond which it decreased and reached a constant value (Figs. 1 (a) and (b)); at 533 and 543 K, the rate had two maxima and then gradually decreased and reached a constant value (Figs. 1 (c) and (d)).

Figure 2 shows the cumulative silicon conversions as a function of reaction time, which are calculated from the data in Fig. 1. The silicon conversion at 5 h of reaction time was 11, 28, 63, and 82% at 493, 513, 533, and 543 K of reaction temperature, respectively. In Fig. 2, changes of the selectivity for trimethoxysilane with reaction time are also shown. The selectivity slightly decreased to 85-94% shortly after the start of the reaction, but soon approached a constant value of as high as 96-99%. The selectivities averaged for 5 h of reaction time were 94, 96, 98, and 98% at 493, 513, 533, and 543 K, respectively. The highest trimethoxysilane yield of 80% with a 98% selectivity was found at 543 K, the selectivity for trimethoxysilane being in the range of 92-98% at any level of silicon conversion.

The XRD pattern of the silicon sample heated with copper(I) chloride at 623 K for 3 h showed peaks assignable to a Cu_3Si alloy together with those to silicon and copper(I) chloride. This indicates that copper atoms are incorporated into

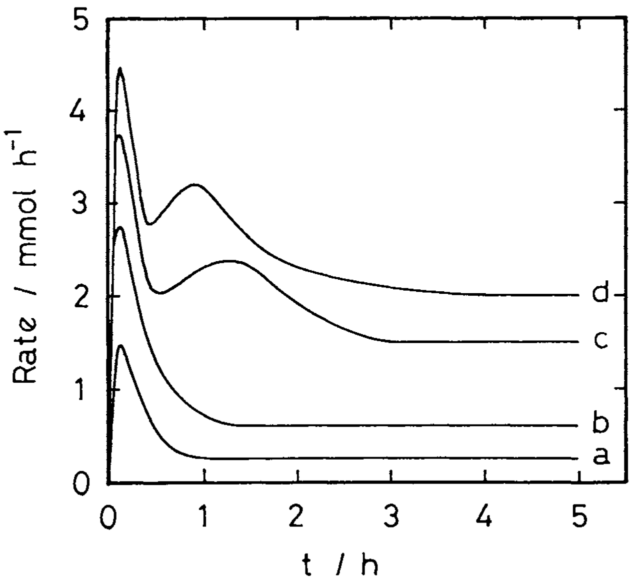

Fig. 1. Change in the rate of methoxysilanes ($(CH_3O)_3SiH$ + $(CH_3O)_4Si$) formation with reaction time at various reaction temperatures.
Reaction conditions: reaction temperature= 493 K(a), 513 K(b), 533 K(c), and 543 K(d), CH_3OH= 99 kPa.

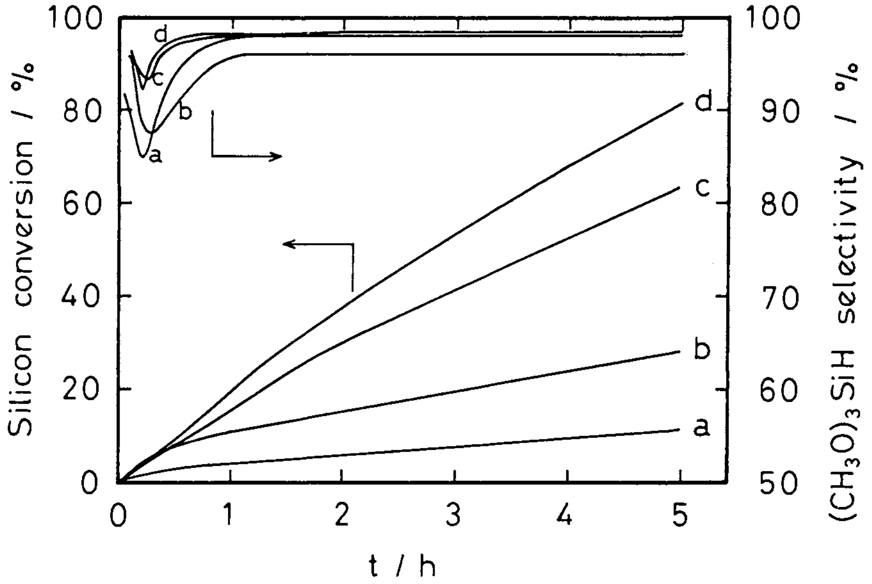

Fig. 2. Change in the silicon conversion and the selectivity for trimethoxysilane with reaction time at various reaction temperatures.
Reaction conditions: reaction temperature= 493 K(a), 513 K(b), 533 K(c), and 543 K(d), CH_3OH= 99 kPa.

the matrix of silicon atoms with a cleavage of Si-Si bond upon the preheating, which may lead to the activation of Si-Si bond. The rapid increase in the rate just after the start of the reaction may be due to the formation of active sites by the reaction of methanol with the Cu_3Si alloy formed. The importance of the Cu_3Si alloy has been proposed also for the reaction of silicon with methyl chloride.5-8)

The XRD examination showed that the metallic copper phase developed as the reaction of silicon with methanol proceeded, the Cu_3Si phase being not detected. Thus, we suppose that, as the reaction proceeds, copper species constituting active sites are transformed into the metallic copper which is inactive as a catalyst or a catalyst precursor for the reaction of silicon with methanol. This accounts for the rate decrease after the maximum of the rate. The formation of the Cu_3Si alloy may occur also during the reaction by the migration of a coppper compound (CuCl or a product from CuCl and methanol) onto the silicon surface and by the subsequent reaction of the copper compound with silicon. At 533 and 543 K of reaction temperature, a broad maximum of the rate follows the initial maximum. This would be because the deactivation of active sites initially present is overcome by the formation of new active sites during the course of reaction. The constant rate at the final stage is explained by assuming that there is a balance between the formation and deactivation of the active sites.

Table 1. Effect of partial pressure of methanol on the synthesis of trimethoxysilane[a]

CH_3OH / kPa	$(CH_3O)_3SiH$ Selectivity[b] / %	Silicon Conversion[c] / %	CH_3OH Conversion[b] / %
25	99	53	22
38	97	60	16
75	98	47	7
99	98	63	7

a) Reaction conditions: reaction temperature= 533K and CH_3OH= 99 kPa (87 mmol h^{-1}).

b) Averaged for 5 h of reaction time.

c) At 5 h of reaction time.

Table 1 shows the effects of methanol partial pressure on the selectivity for trimethoxysilane and the silicon and methanol conversions at 533 K. A high selectivity (97-99%) was obtained irrespective of the partial pressure. The partial pressure of methanol had little influence on the silicon conversion (47-63%); the methanol conversion was at a low level of 6% at 99 kPa, but increased with the decrease in the partial pressure of methanol, and was 22% at 25 kPa.

In conclusion, from methanol and silicon preheated with copper(I) chloride at 623 K, trimethoxysilane was formed in a fixed-bed reactor at 543 K with a 98% selectivity and at an 82% silicon conversion in 5 h of reaction time.

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