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A Kinetic Study on the Copper-catalyzed Reaction of Silicon with Methanol into Trimethoxysilane

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The reaction of methanol with silicon was carried out in a fixed-bed reactor at 463-533 K. In order to determine the kinetics of the reaction per reaction site on the silicon surface, a pressure- (or temperature-) transition method was employed. The reaction order with respect to methanol was 1.0 and 1.4 for the Si-CuCl mixture preheated at 513 and 723 K, respectively, indicating that the rate-determining step is not the diffusion of silicon or copper species to the reaction site, but the chemical process involving methanol. Kinetics also indicate that the nature of the reaction sites changes with the preheating conditions of the mixture.

The vapor-phase synthesis of trimethoxysilane is performd by feeding methanol to a silicon-copper(I) chloride mixture which have been preheated.[1,2] The reactivity of silicon depends on the pretreatment of silicon and the preheating temperature. When the silicon grains with native oxide-layers are used, the almost complete conversion of silicon at 513 K is attained, only when the preheating temperature is above 723 K.[1] On the other hand, when the silicon grains washed with a hydrogen fluoride solution to remove the native oxide-layers are used, the almost complete conversion of silicon is attained by preheating the mixture at such a low temperature as 513 K. The selectivity of the reaction also depends on the temperature of the preheating. When the preheating temperature is below 553 K, the reaction of silicon (HF-washed) with methanol at 513 K gives a very high selectivity for trimethoxysilane (> 98%). When the preheating temperature is higher (> 723 K), the selectivity is low (70-80%). The results described above indicate that the nature of the reaction sites changes with conditions of preheating the silicon - copper(I) chloride mixture. The previous work also showed that the silicon atoms are not uniformly consumed from the surface, but that the reaction proceeds from discrete reaction area to form pits on the surface.

The rate of formation of methoxysilanes ($(CH_3O)_3SiH$ and $(CH_3O)_4Si$) rapidly increases with reaction time (the acceleration-period), and beyond a rate-maximum, it gradually decreases (the decay-period). The overall-rate can be expressed as a product of the number of reaction site on the silicon surface and the rate of silicon consumption per reaction site. In order to determine the kinetics of the rate per reaction site, the number of reaction site should be fixed. This condition cannot be fulfilled under the ordinary reaction conditions, since the number of reaction site changes with reaction time and reaction conditions.

This work concerns the kinetics of silicon consumption per reaction site. To eliminate the effect of the change in the number of reaction site, we used a pressure-transition technique. The change in the reaction rate just before and after the pressure-change must be ascribed solely to the change in the rate per reaction site, since the number of reaction site does not change immediately after the pressure-change. Activation energy for the rate of silicon consumption per reaction site was also evaluated using a temperature-transition technique.

Silicon (99.5% in purity, 45-63 μm) was mildly stirred in a 46% aqueous HF solution at room temperature for 1 h, rinsed with water, and dried. The silicon was mixed with copper(I) chloride (45-63 μm) in a vial with vigorous vibration (copper content, Cu/(Si + Cu)= 5 or 10 wt%). The reactions were carrired out in a fixed-bed flow-reactor. The silicon - copper(I) chloride mixture containing 6 mmol (0.168 g) of silicon was loaded in a reactor of silica tubing (10 mm i.d.) placed in an infrared-image furnace, and then preheated under a helium stream at 493-723 K for 1 h. Methanol, dehydrated over molecular sieve 3A, was fed by a motor-driven syringe into the reactor at 463-533 K. The effluent gas was analyzed automatically every 3.5 min with a gas chromatograph.

Methanol pressure was changed stepwise by varying the speed of pushing the syringe and the flow rate of helium (methanol + helium= 71 mmol h^{-1}). The flow rates and the reaction temperature shifted to a new steady state after 3 min and 45 s of the transitions, respectively, as confirmed by analyzing the effluent gas and by monitoring the temperature.

After the silicon - copper(I) chloride mixture was preheated at 493 K for 1 h, methanol (59 kPa) was fed at 493 K. The rate of methoxysilanes ($(CH_3O)_3SiH$ and $(CH_3O)_4Si$) formation increased with reaction time, and beyond a rate-maximum, it decreased (Fig. 1, curve a). Trimethoxysilane was formed with a 98% selectivity throughout the reaction. In the course of the reaction, methanol pressure was changed to 88 kPa and, after a given time, it was changed back to 59 kPa (Fig. 1, curve b). The first and the second pressure-change processes are denoted as "transition" and "re-transition", respectively. Upon the transition and the re-transition

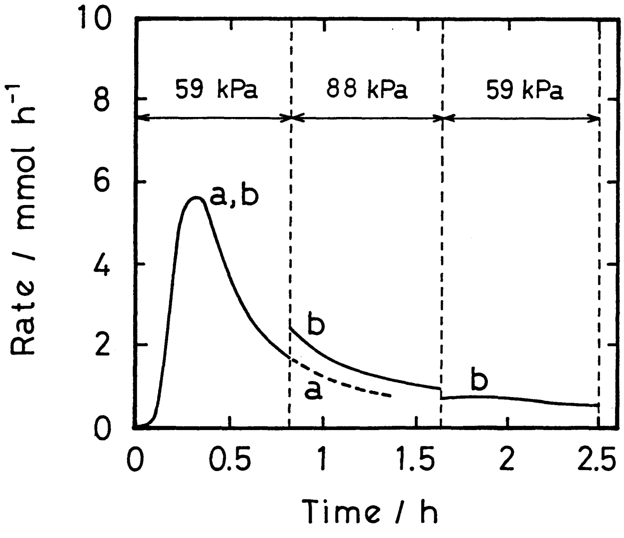

Fig. 1. The change in the rate of methoxysilanes ($(CH_3O)_3SiH$ and $(CH_3O)_4Si$) formation. After the Si-CuCl mixture (copper content= 10 wt%) was preheated at 493 K, methanol (59 kPa) was fed at 493 K (curve a). Curve b shows the rate-change when methanol pressure was changed as indicated in the figure.

Table 1. Relative rates upon stepwise changes of methanol pressure[a)]

Entry	Copper content / wt%	Preheating temperature / K	Reaction temperature / K	Stage[c)]	Methanol pressure[d)] / kPa	Relative rate[e)]	
						Transition	Re-transition
1	10	493	493	D	29	0.39	0.54
2	10	493	493	D	88	1.45	1.39
3	10	493	493	D	99	1.81	1.67
4	5	- b)	463	A	44	0.65	-
5	5	- b)	463	A	88	1.50	-

a) Reactions were started at 59 kPa of methanol pressure.

b) Without preheating of the Si-CuCl mixture.

c) Transition (or re-transition) of methanol pressure was done in the acceleration-period (A) or the decay-period (D) of the rate curve.

d) The starting methanol pressure (59 kPa) was changed to this pressure.

e) Rate relative to the rate at 59 kPa of methanol pressure.

of methanol pressure, the rate immediately increased and decreased, respectively. The relative rates, defined as the ratio of the reaction rate at 88 kPa and that at 59 kPa in the transition and the re-transition stages, were 1.45 and 1.39, respectively.

Experiments were carried out also at 29 and 99 kPa of methanol pressure to which the starting methanol pressure (59 kPa) was changed. The results are summarized in Table 1 (entries 1-3). As shown in Fig. 2 (open circles), the relative rate was proportional to the methanol pressure to which the starting methanol pressure (59 kPa) was changed. In all the above-mentioned experiments, methanol pressure was changed in the decay-period of the rate curve. By the same technique, the methanol pressure - dependence was determined also in the acceleration-period (Table 1, entries 4 and 5). The relative rate was again proportional to the pressure (Fig. 2, closed circles). These results show that the rate of silicon consumption per reaction site is the first order with respect to methanol pressure throughout the reaction. In other words, the same kinetics can be applied to both the acceleration period and the decay period. The rate-change in the course of the reaction is caused solely by the change in the number of reaction site.

The first-order dependence with respect to methanol pressure indicates that the rate-determining step is a chemical process involving methanol at the reaction sites and that the diffusion of silicon atoms to the reaction sites or the formation of a silicon-copper intermetallic species (plausible reaction site) cannot be the rate-determining step. For the copper-catalyzed reaction of silicon with methyl chloride, Voohoeve et al. concluded from the kinetics that the rate-determining step is a reaction step involving chemisorbed methyl chloride.[3)]

The effect of changing reaction temperature stepwise in the course of silicon-methanol reaction was examined using the mixture preheated at 493-553 K. Figure 3 shows a typical change in the rate upon the temperature-change. Experiments were also carried out where the starting reaction temperaure (493-533 K) was changed to 483-533 K. The Arrhenius plot for

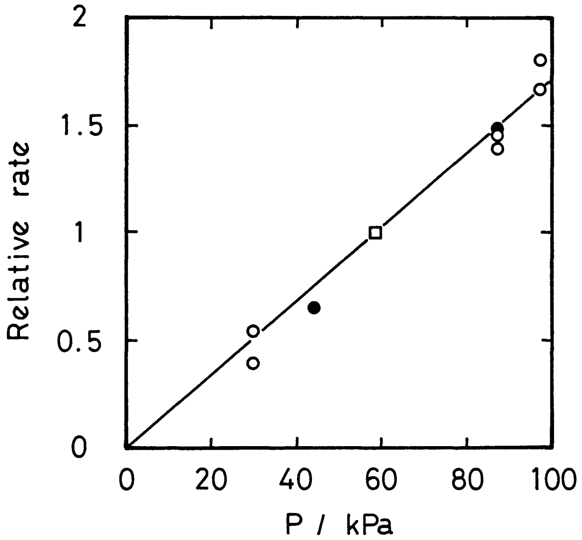

Fig. 2. Dependence of the relative rate on methanol pressure.
Experimental conditions are listed in Table 1. Open and closed circles show data for the transition in the decay- and the acceleration-periods, respectively. Rates at 59 kPa are taken as unity (open square).

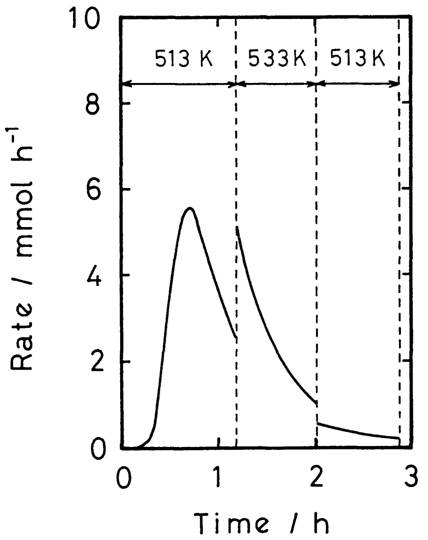

Fig. 3. The change in the rate of methoxysilanes formation upon the stepwise change of reaction temperature. After the Si-CuCl mixture (copper content= 10wt%) was preheated at 553 K, methanol (59 kPa) was fed at 513 K. Reaction temperature was changed as indicated in the figure.

the rates relative to the rate at 513 K gave an 88 kJ mol^{-1} of the activation energy.

The preheating of the silicon - coper(I) chloride mixture was carried out at more elevated temperatures (673-723 K) than those in the above-mentioned experiments. In this case, the reaction at 513 K gave trimethoxysilane with only 70-80% levels of the selectivity. The activation energy and the reaction order with respect to methanol pressure were similarly evaluated to be 44 kJ mol^{-1} and 1.4, respectively. The difference in the kinetic parameters with the preheating temperature indicates that the nature of reaction sites on the silicon surface changes with the preheating temperature.

The powder X-ray diffraction (XRD) measurement of the preheated Si-CuCl sample and the microscopic observation of silicon also revealed that the nature of reaction site depends on the preheating temperature. The formation of Cu_3Si patches was observed for samples preheated at 723 K and the number of the patches was close to that of the pits formed on the reacting silicon, indicating that Cu_3Si is a precursor of the reaction sites. On the other hand, the Cu_3Si phase was not detected for samples preheated at 513 K, but the number of the pits was much larger compared with the sample preheated at 723 K. These results also suggest that the nature of the reaction sites (or their precursor) for sample preheated at 513 K is different from that preheated at the higher temperature.

References

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