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Reaction Pathway of Formation of Methoxysilanes in the Reaction of Silicon with Methanol Catalyzed by Copper(I) Chloride

Masaki Okamoto, Eiichi Suzuki, and Yoshio Ono[1]

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

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The reaction of silicon with methanol using copper(I) chloride as a catalyst gives $HSi(OCH_3)_3$ and $Si(OCH_3)_4$, the selectivity for $HSi(OCH_3)_3$ being dependent on the conditions of the treatment of the silicon–catalyst mixture as well as the reaction conditions. The selectivity for $HSi(OCH_3)_3$ was 64% when a silicon–copper(I) chloride mixture was preheated at 723 K and the reaction was carried out at 513 K. The addition of a small amount of thiophene to the feed increased the selectivity to almost 100%. A separate experiment showed that metallic copper catalyzes the reaction of $HSi(OCH_3)_3$ and methanol to give $Si(OCH_3)_4$, this reaction being completely inhibited by thiophene. It is concluded that $HSi(OCH_3)_3$ is a sole primary product and that $Si(OCH_3)_4$ is formed by the secondary reaction of $HSi(OCH_3)_3$ with methanol on metallic copper, which is formed on the silicon surface during the silicon–methanol reaction. Alkyl chlorides such as methyl and propyl chloride also were found to be effective additives for improving the selectivity. Copper(I) chloride serves as the catalyst for forming intermetallic Cu–Si species. The presence of copper(I) chloride in the reaction system also serves to enhance the selectivity for $HSi(OCH_3)_3$. It is suggested that the chloride ions are transferred to the surface of metallic copper formed in the course of the reaction to poison the catalytic activity for the $HSi(OCH_3)_3$–methanol reaction. The reaction mechanism involving surface silylene species is proposed for the exclusive formation of $HSi(OCH_3)_3$. © 1994 Academic Press, Inc.

INTRODUCTION

Trialkoxysilanes are important chemicals which react with unsaturated organic compounds to give various organosilanes. These organosilanes are used as silane-coupling reagents.

Trimethoxysilane ($HSi(OCH_3)_3$) is directly synthesized by the reaction of silicon and methanol using copper(I) chloride as a catalyst (1–4). In this reaction, the selectivity for $HSi(OCH_3)_3$ depends significantly on the pretreatment conditions of silicon–copper(I) chloride mixtures as well as the reaction conditions, tetramethoxysilane ($Si(OCH_3)_4$) being formed as a by-product (3, 4). In no cases is dimethoxysilane ($H_2Si(OCH_3)_2$) found in the product.

When the pretreatment temperature of a silicon–copper(I) chloride mixture is high (>603 K), the selectivity for $HSi(OCH_3)_3$ is low (60–70%) (4). After this preheating, the formation of Cu_3Si phase has been confirmed by XRD (4). On the other hand, when the pretreatment temperature is low (<553 K), the selectivity for $HSi(OCH_3)_3$ is very high (>98%) (4). With lower pretreatment temperatures, the formation of alloy phase has not been confirmed, indicating that the size of the silicon–copper intermetallic phase is very small (4). This is supported by the small size of the pits, which form on the silicon surface during the course of silicon–methanol reaction (4). These results indicate that the chemical state of the copper species on the silicon surface has a decisive role in determining the selectivity of the reaction.

In fact, metallic copper was observed by XRD at high preheating temperatures. This suggests that Cu_3Si on the surface is at least partly transformed into metallic copper during the silicon–methanol reaction. Metallic copper was not observed entirely or observed only slightly in the reactions at lower pretreatment temperatures, where the selectivity for $HSi(OCH_3)_3$ was high.

It has been reported that metallic copper catalyzes the reaction of $HSi(OCH_3)_3$ with methanol to form $Si(OCH_3)_4$ (5). This suggests the possibility that the formation of $Si(OCH_3)_4$ during silicon–methanol reaction is caused by the secondary reaction of $HSi(OCH_3)_3$ by the action of metallic copper, which is formed on the silicon surface during the reaction.

The aims of this work are to determine the decisive factor in selectively producing $HSi(OCH_3)_3$ and whether $Si(OCH_3)_4$ is a primary product or is formed by the secondary reaction of $HSi(OCH_3)_3$ with methanol. For the latter purpose, selectively poisoning the metallic copper formed was attempted. The effect of the amount of the catalyst on the selectivity for $HSi(OCH_3)_3$ was also examined. Based on the results obtained, the mech-

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[1] To whom correspondence should be addressed.

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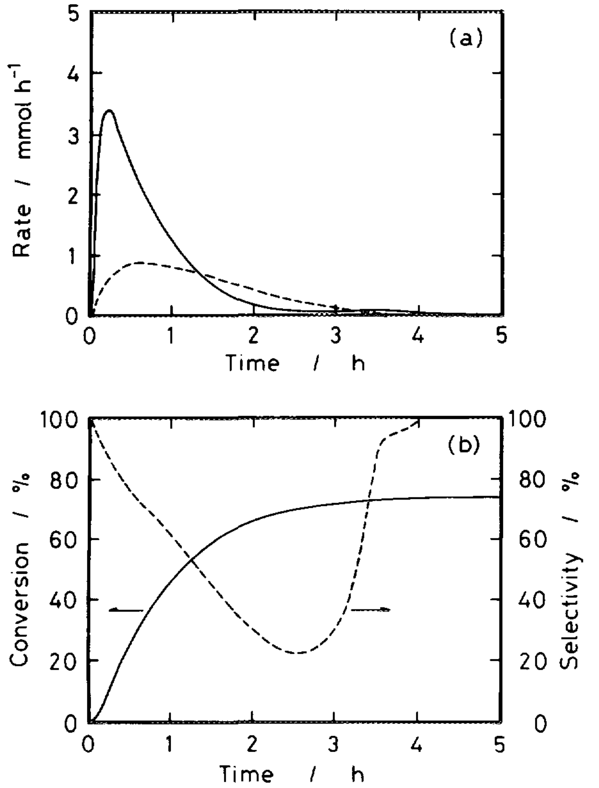


FIG. 1. Reaction of silicon with methanol at 513 K, when a silicon–copper(I) chloride mixture was preheated at 723 K: (a) change in the rate of the formation of $HSi(OCH_3)_3$ (solid line) and $Si(OCH_3)_4$ (dashed line) with time and (b) Silicon conversion (solid line) and selectivity for $HSi(OCH_3)_3$ (dashed line).

anism of formation of alkoxysilanes on a silicon surface is discussed.

EXPERIMENTAL

Pulverized silicon (45–63 μm : purity 99.9%) was washed with a 46% HF solution for 1 h to remove the SiO_2 overlayer. The silicon grains (0.168 g : 6 mmol) and copper(I) chloride grains (45–63 μm : purity 99.9%) were mixed in a small vial with vigorous vibration. The mixture was placed in a quartz tube (i.d. 10 mm) and heated under a helium stream at 533 or 723 K for 1 h. The amount of copper was 0.31 mmol (Cu/(Si + Cu) = 10 wt%, if not otherwise mentioned). Methanol (guaranteed reagent grade) was dehydration over molecular sieve 3 A. Methanol (39 mmol h^{-1}, 56 kPa) and helium (total flow = 71 mmol h^{-1}) were fed to the reactor at 513 K. The rates of the formation of the products were determined by analyzing the effluent by a gas chromatograph (SE-30 packed column) every 3.5 min.

Metallic copper was prepared by the following method (6). An aqueous solution of copper(II) nitrate (1 *M*) was neutralized by adding an aqueous solution of sodium carbonate (1 *M*), and stirring the solution at 363 K for 1.5 h. The precipitate was filtered, calcined in air at 623 K for 3 h and then reduced under a stream of 10% hydrogen and 90% helium at 523 K for 5 h.

X-ray diffraction samples were prepared as follows: After the silicon–copper(I) chloride mixture was preheated or subjected to the reaction with methanol, it was taken out from the reactor and ground with silica quartz (internal standard) in an agate mortar in nitrogen atmosphere. XRD of the mixture was recorded in air on Rigaku Geigerflex 2013 using Cu*Kα* radiation.

RESULTS AND DISCUSSION

1. Time Course of the Reaction

Figure 1a shows the change in the rates of the formation of $HSi(OCH_3)_3$ and $Si(OCH_3)_4$ with reaction time in the silicon–methanol reaction at 513 K when a silicon–copper(I) chloride mixture was preheated at 723 K. Rates of formation of both $HSi(OCH_3)_3$ and $Si(OCH_3)_4$ increase at first to reach a maximum and then decrease. The rate increase in the beginning indicates that reactive sites are created in this stage (4). Figure 1b shows the change in the cumulative conversion of silicon and the change in the selectivity for $HSi(OCH_3)_3$. The conversion of silicon reached 73% in 5 h. The selectivity for $HSi(OCH_3)_3$ was almost 100% at the beginning and sharply decreased with time. At the very final stage it increased again. This indicates that the active sites for the formation of $Si(OCH_3)_4$ are produced as the reaction proceeds. The overall selectivity for $HSi(OCH_3)_3$ for 5 h is 64%.

Figure 2 shows the change in the intensity of the diffraction lines due to Cu_3Si and metallic Cu phase in the course of the reaction. The reaction was stopped at different reaction times and the XRD measurements made on the

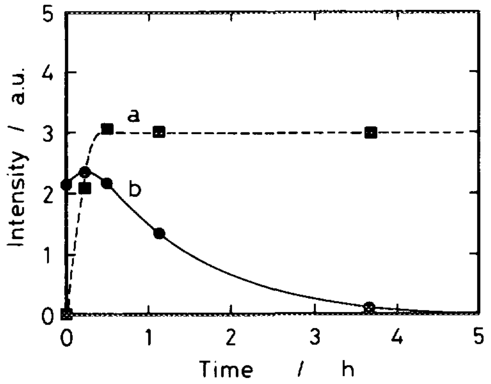


FIG. 2. Change in the intensity of the diffraction lines due to Cu_3Si and metallic copper phase in the course of the reaction: (a) metallic copper and (b) Cu_3Si. Preheating conditions: 723 K; 1 h. Reaction conditions: 513 K; methanol = 39 mmol h^{-1} (56 kPa).

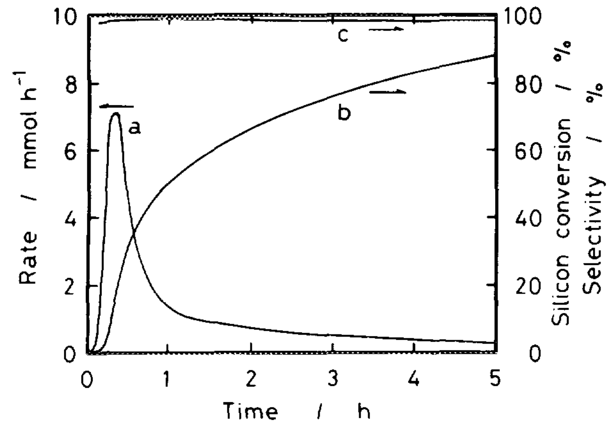


FIG. 3. The rate of formation of methoxysilanes ($HSi(OCH_3)_3$ + $Si(OCH_3)_4$) (a), the cumulative silicon conversion (b), and the selectivity for $HSi(OCH_3)_3$ (c) in the reaction of silicon with methanol, when a silicon–copper(I) chloride mixture was preheated at 553 K. Preheating conditions: 553 K; 1 h. Reaction conditions: 553 K; methanol = 39 mmol h^{-1} (56 kPa).

remaining reaction mixtures. After the pretreatment at 723 K, only the Cu_3Si phase was obtained and the phase of metallic copper was not observed. The formation of Cu_3Si is expressed as

$$12\ CuCl + 7\ Si \rightarrow 4\ Cu_3Si + 3\ SiCl_4.$$

The intensity of the Cu_3Si phase decreases with reaction time, while the metallic copper phase develops in the first 30 min of the reaction. The amount of the Cu_3Si phase monotonically decreases with time. In contrast, the reaction rate increases at the beginning of the reaction (Fig. 1a). This shows that Cu_3Si itself is not a reactive intermediate, but the precursor which is composed of silicon and copper. Silicon is removed from the reactive sites and the remaining copper further reacts with underlying silicon to cycle the reaction. Part of the copper may coagulate to form metallic copper.

When the temperature of the pretreatment was 513 K, the formation of Si–Cu alloy was not observed by XRD since the size of the alloy is very small (4). The silicon conversion after 5 h was 97% (Fig. 3) and the average selectivity for $HSi(OCH_3)_3$ was practically 100% under the same reaction conditions. The metallic copper phase was observed, but the intensity of the diffraction peak was very small.

2. *Effect of Addition to $HSi(OCH_3)_3$ to the Feed*

In order to examine whether $HSi(OCH_3)_3$ is converted into $Si(OCH_3)_4$ by its reaction with methanol, $HSi(OCH_3)_3$ was added to the feed. Figure 4 shows the result. The reaction was started under the same conditions as the experiment shown in Fig. 1. After 0.7 h of the reaction, $HSi(OCH_3)_3$ (4.0 mmol h^{-1}) was added to the methanol feed. The difference between the rates of effluence of $HSi(OCH_3)_3$ just before and just after the addition was smaller than the feeding rate of $HSi(OCH_3)_3$. On the other hand, the rate of effluence of $Si(OCH_3)_4$ increased upon addition of $HSi(OCH_3)_3$ to the feed. The rate of the formation of $Si(OCH_3)_4$ decreased when $HSi(OCH_3)_3$ was eliminated from the feed. These results clearly indicate that a part of $HSi(OCH_3)_3$ added was transformed into $Si(OCH_3)_4$ under the reaction conditions. This suggests that, in the silicon–methanol reaction, at least a part of $Si(OCH_3)_4$ originates from the secondary reaction of $HSi(OCH_3)_3$ with methanol.

3. *Effect of Addition of Thiophene to the Feed*

It has been reported that metallic copper catalyzes the reaction of methanol and $HSi(OCH_3)_3$ to give $Si(OCH_3)_4$ (5). As described above, metallic copper is formed in the course of the reaction. Thus, it is plausible that metallic copper formed on the silicon surface acts as a catalyst to convert $HSi(OCH_3)_3$ into $Si(OCH_3)_4$. It is known that sulfur compounds poison the catalytic activity of copper catalysts. In this work, thiophene was added to the methanol feed in the silicon–methanol reaction.

Figure 5 shows the change in the rate of formation of methoxysilanes and the selectivity for $HSi(OCH_3)_3$ with the addition of thiophene to the feed. In the absence of thiophene, the silicon conversion at the reaction time of 5 h was 73% and the overall selectivity averaged for 5 h was 64%, as described above. Addition of thiophene affected both the rate and the selectivity. Silicon conversion for 5 h was 84 and 80% when 0.39 and 1.29 mmol h^{-1} of thiophene was added to the methanol feed, respec-

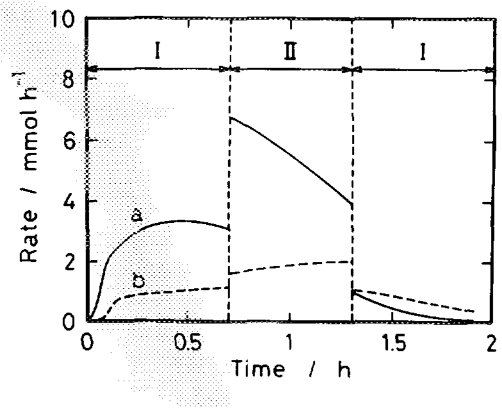


FIG. 4. Change in the effluent rate of methoxysilanes upon the addition of $HSi(OCH_3)_3$ to the feed: (a) $HSi(OCH_3)_3$ and (b) $Si(OCH_3)_4$. Preheating conditions: 723 K; 1 h. Reaction conditions: 513 K; (I) methanol = 39 mmol h^{-1} (56 kPa) and (II) methanol = 39 mmol h^{-1} (56 kPa) and $HSi(OCH_3)_3$ = 4.0 mmol h^{-1} (5.7 kPa).

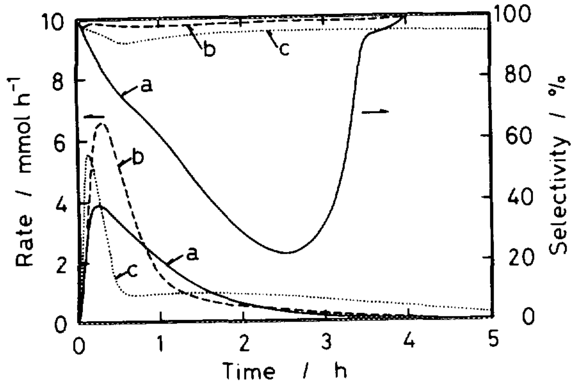


FIG. 5. Effect of thiophene on the change in the rate of methoxysilanes formation and the selectivity for $HSi(OCH_3)_3$ with reaction time. Preheating conditions: 723 K, 1 h. Reaction conditions: 513 K; methanol = 39 mmol h^{-1} (56 kPa) and thiophene = 0 (a), 0.39 (b), and 1.29 mmol h^{-1} (c).

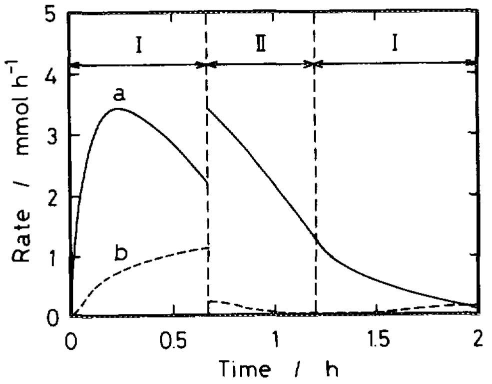


FIG. 6. Change in the rate of methoxysilanes formation upon addition of thiophene: (a) $HSi(OCH_3)_3$ and (b) $Si(OCH_3)_4$. Preheating conditions: 723 K; 1 h. Reaction conditions: 513 K; (I) methanol = 39 mmol h^{-1} (56 kPa) and (II) methanol = 39 mmol h^{-1} (56 kPa) and thiophene = 0.39 mmol h^{-1}.

tively. Thus, the addition of thiophene gave higher silicon conversion.

The selectivity for $HSi(OCH_3)_3$ was significantly improved. The overall selectivity for 5 h upon addition of 0.39 and 1.29 mmol h^{-1} of thiophene was 97 and 94%, respectively. This fact strongly indicates that $HSi(OCH_3)_3$ is exclusively formed in the silicon–methanol reaction and that $Si(OCH_3)_4$ is formed by the secondary reaction of $HSi(OCH_3)_3$ with methanol by catalytic action of metallic copper formed during the silicon–methanol reaction.

XRD analysis showed that thiophene addition inhibited the formation of metallic copper during the silicon–methanol reaction. This suggests that thiophene suppresses the deactivation of the catalytic system by inhibiting the growth of metallic copper. Thiophene (or sulfur) probably covers the surface of the small copper particles to prevent their coagulation.

In order to further confirm the effect of thiophene on the selectivity, the reaction was started by feeding methanol to the reactor and then thiophene was added to the feed at a later stage. Figure 6 shows the change in the rate of the formation of methoxysilanes upon addition of thiophene. At reaction time of 0.7 h, thiophene (0.39 mmol h^{-1}, 1% of methanol) was added to the methanol feed. Upon addition of thiophene, the rate of $Si(OCH_3)_4$ formation decreased and that of $HSi(OCH_3)_3$ increased, while the sum of the rates of the formation of the two methoxysilanes remained constant. This indicates that $Si(OCH_3)_4$ is formed at the expense of $HSi(OCH_3)_3$. It is concluded that $Si(OCH_3)_4$ is formed exclusively by the secondary reaction of $HSi(OCH_3)_3$ with methanol over metallic copper, which is formed during the silicon–methanol reaction. It should be noted that thiophene does not inhibit the silicon–methanol reaction at all.

As described above, when thiophene was added to the feed from the beginning, the reaction rate depends on thiophene pressure. This shows that thiophene also affects the stage of reaction site formation.

Selective poisoning by thiophene was also observed in the reaction of silicon and ethanol. Thus, $HSi(OC_2H_5)_3$ was almost exclusively formed when thiophene was added to the system.

4. The Reaction of $HSi(OCH_3)_3$ with Methanol over Metallic Copper

In order to confirm that metallic copper catalyzes the reaction of $HSi(OCH_3)_3$ and methanol to form $Si(OCH_3)_4$, the reaction was carried out using metallic copper as a catalyst at 513 K. Figure 7 shows the change in the yield

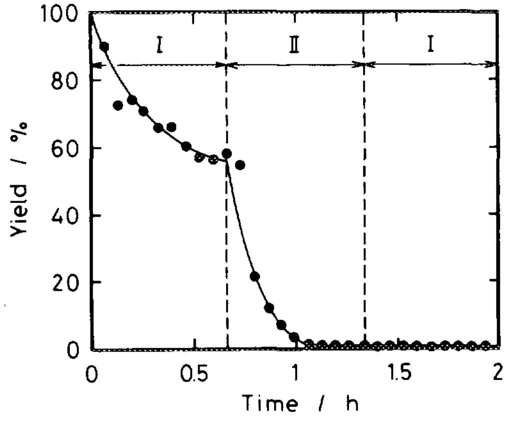


FIG. 7. Poisoning of the metallic copper catalyst by thiophene in the reaction of $HSi(OCH_3)_3$ with methanol. Reaction temperature = 513 K; metallic copper = 0.33 g; (I) methanol = 39 mmol h^{-1} (56 kPa), $HSi(OCH_3)_3$ = 4.0 mmol h^{-1} (5.7 kPa) and (II) methanol = 39 mmol h^{-1} (56 kPa), HSi $(OCH_3)_3$ = 4.0 mmol h^{-1} (5.7 kPa), and thiophene = 0.39 mmol h^{-1} (0.56 kPa).

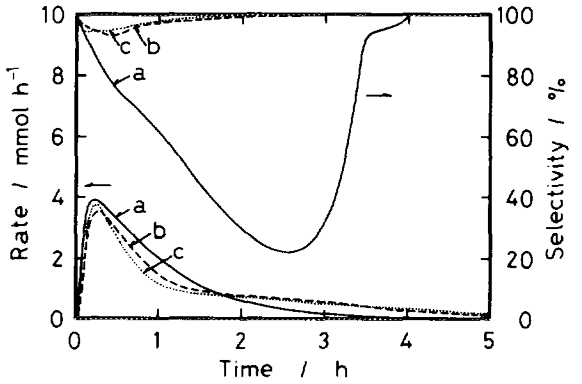


FIG. 8. Effect of methyl of propyl chloride on the change in the rate of methoxysilanes formation and the selectivity for $HSi(OCH_3)_3$ with reaction time. Preheating temperature = 723 K. Reaction temperature = 513 K; (a) methanol = 39 mmol h^{-1} (56 kPa), (b) methanol = 39 mmol h^{-1} (56 kPa) + methyl chloride = 1.29 mmol h^{-1}, and (c) methanol = 39 mmol h^{-1} (56 kPa) + propyl chloride = 0.39 mmol h^{-1}.

of $Si(OCH_3)_4$ with time. The yield of $Si(OCH_3)_4$ was 100% in the beginning, though it decreased with reaction time. Figure 7 also shows the effect of addition of thiophene. Upon addition of thiophene at 0.67 h reaction time, the yield of $Si(OCH_3)_4$ decreased quickly to zero. Even after the feed of thiophene was stopped at 1.33 h, the formation of $Si(OCH_3)_4$ was not observed. These results clearly indicate that the reaction of $HSi(OCH_3)_3$ and methanol is catalyzed by metallic copper and that thiophene irreversibly inhibits the reaction.

5. *Effect of Addition of Alkyl Chlorides*

It has been reported in a patent that addition of alkyl halides enhances the selectivity for $HSi(OCH_3)_3$ (7). Here, the effect of addition of methyl or *n*-propyl chloride as an alkyl halide on the selectivity was examined. Figure 8 shows the effect of methyl chloride and *n*-propyl chloride. Under the reaction conditions, no alkylchlorosilanes were formed. The overall selectivity for $HSi(OCH_3)_3$ for 5 h increases in the addition of alkyl chlorides. Upon addition of methyl chloride (1.3 mmol h^{-1}) and propyl chloride (0.39 mmol h^{-1}) to the methanol feed, the selectivity for $HSi(OCH_3)_3$ increased to 95 and 98% from 64%, respectively. Propyl chloride is more effective than methyl chloride in enhancing the selectivity.

In order to find if the effect of alkyl chlorides results from poisoning of metallic copper as in the case of thiophene addition, propyl chloride was added to the feed in the course of the reaction of $HSi(OCH_3)_3$ and methanol over metallic copper, as shown in Fig. 9. The catalytic activity of copper disappeared upon addition of propyl chloride, indicating that propyl chloride poisons metallic copper. When the feed of propyl chloride was stopped, the catalytic activity was completely recovered in 20 min, indicating that the adsorption of propyl chloride on metallic copper is reversible.

These results strongly suggest that the enhancement of the selectivity upon adding alkyl chlorides is caused by poisoning of metallic copper formed during the silicon–methanol reaction.

6. *Poisoning of Metallic Copper by Copper(I) Chloride in the Silicon–Methanol Reaction*

We found that the selectivity for $HSi(OCH_3)_3$ depends on the amount of copper(I) chloride even when the temperature of the pretreatment is low. Figure 10 shows the effect of the amount of copper(I) chloride on the reactivity of silicon and the selectivity for $HSi(OCH_3)_3$ at 553 K. When the amount of Cu is less than 2 wt% of silicon, the selectivity for $HSi(OCH_3)_3$ starts to decrease sometime after starting the reaction. On the other hand, the selectivity is very high throughout the reaction, when the amount of Cu exceeds 2.5%. When 10 wt% CuCl was used, the SEM image showed that the copper(I) chloride grains still remained even after the pretreatment of the silicon–copper(I) chloride mixture at 553 K. This indicates that the formation of metallic copper is inhibited or that the metallic copper is poisoned even when it is formed, as long as excess copper(I) chloride exists in the system. In a previous section, we showed that alkyl halides inhibit the formation of $Si(OCH_3)_4$. The fact that the selectivity for $HSi(OCH_3)_3$ depends on the catalyst amount indicates that chloride ions from copper(I) chloride are somehow transferred onto the copper surface to inhibit the activity of the metal formed during the silicon–methanol reaction.

The overall conversion of silicon was also a function

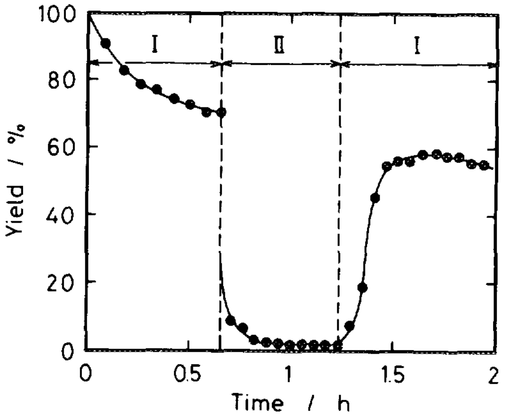


FIG. 9. Poisoning of the metallic copper catalyst by propyl chloride in the reaction of $HSi(OCH_3)_3$ with methanol. Reaction temperature = 513 K; metallic copper = 0.33 g: (I) methanol = 39 mmol h^{-1} (56 kPa) and $HSi(OCH_3)_3$ = 4.0 mmol h^{-1} (5.7 kPa) and (II) methanol = 39 mmol h^{-1} (56 kPa), $HSi(OCH_3)_3$ = 4.0 mmol h^{-1} (5.7 kPa), and propyl chloride = 0.39 mmol h^{-1} (0.56 kPa).

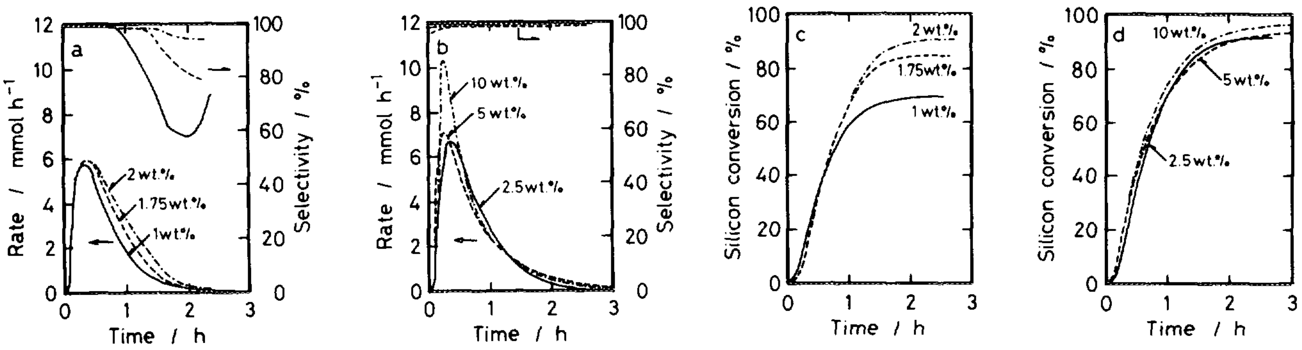


FIG. 10. Effect of the amount of copper(I) chloride on the rate of methoxysilanes formation and the selectivity for $HSi(OCH_3)_3$. Amount of copper(I) chloride was indicated in wt% as Cu. (a, b) Change in the rate of methoxysilanes formation and the selectivity for $HSi(OCH_3)_3$. (c, d) Change in the cumulative conversion of silicon. Preheating conditions: 553 K, 1 h. Reaction conditions: 553 K, methanol = 39 mmol h^{-1} (56 kPa).

of the amount of copper(I) chloride. As shown in Figs. 10c and 10d, the conversion of silicon exceeds 90%, when the amount of copper was 2 wt% or more. In contrast, it was only 70 or 80% when the catalyst amount was 1 and 1.75 wt%, respectively. The increase in silicon conversion with increasing the catalyst amount again suggests that excess copper(I) chloride serves to suppress the deactivation of the silicon–methanol reaction probably by inhibiting the formation of metallic copper. If this were the case, a high selectivity as well as high conversion would be attained by adding proper additives to the system even when the amount of the catalyst were small.

Figure 11 shows the result of such an experiment. The silicon–methanol reaction was carried out with only 0.1 wt% Cu, after the silicon–copper(I) chloride mixture was preheated at 553 K for 1 h. Without any additives, the selectivity for $HSi(OCH_3)_3$ was sharply dropped just after starting the reaction. When 0.56 kPa of propyl chloride was added to the methanol feed, the selectivity for $HSi(OCH_3)_3$ was 100% throughout the reaction. The overall conversion of silicon also increased from 71 to 89% by adding propyl chloride to the feed.

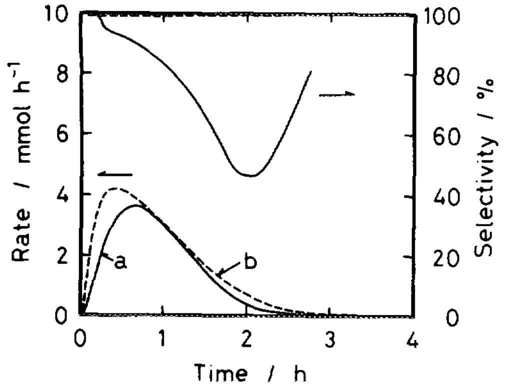


FIG. 11. Effect of propyl chloride on the selectivity for $HSi(OCH_3)_3$. Catalyst: copper(I) chloride (0.1 wt% of Si as Cu); (a) methanol = 39 mmol h^{-1} (56 kPa) and (b) methanol = 39 mmol h^{-1} (56 kPa) + propyl chloride = 0.39 mmol h^{-1} (0.56 kPa). Preheating conditions: 553 K; 1 h. Reaction temperature: 553 K.

These results strongly indicate that the chloride ions are somehow transferred to the surface of metallic copper formed during the reaction to poison the catalytic activity for the $HSi(OCH_3)_3$–methanol reaction.

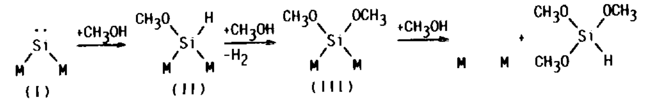
7. *Addition of Thiophene or Propyl Chloride in the Reaction of Methanol and Silicon with Overlayered Oxide*

The results described above are all obtained with silicon grain, which had been washed with a HF solution, since silicon grain is usually covered with native oxide overlayer. We have reported that the reactivity of silicon with SiO_2 overlayer is too low to get a high silicon conversion when the pretreatment temperature was low (8). Therefore, it is essential to pretreat a silicon–copper(I) chloride mixture at a high temperature to obtain a high silicon conversion (3, 8). However, under this preheating condition, the selectivity for $HSi(OCH_3)_3$ is low, as described above. It may not be industrially practical to remove the oxide overlayer from silicon grains before using them for the reaction. The method of poisoning might be useful to improve the selectivity also for the oxide-covered silicon.

The effect of addition of propyl chloride or thiophene on the reaction of silicon with the silica overlayer was examined. When the silicon with oxide layer was used for the reaction, the silicon conversion and the overall selectivity for 5 h were 62 and 57%, respectively. When thiophene was added to the feed, the conversion and the overall selectivity for 5 h increased to 69 and 97%, respectively. Addition to propyl chloride also enhanced the conversion and the overall selectivity. They were 76 and 98%, respectively. It is clear that a very high selectivity can be attained without decreasing the silicon conversion when a proper additive is added to methanol feed.

8. *Mechanism of $HSi(OCH_3)_3$ Formation*

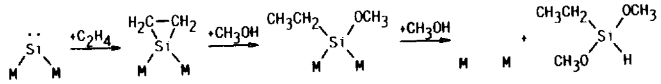
The results shown above clearly show that the $HSi(OCH_3)_3$ is an exclusive primary product in the silicon–methanol reaction. We speculate the mechanism of $HSi(OCH_3)_3$ on silicon surface as follows:



(M denotes Cu)

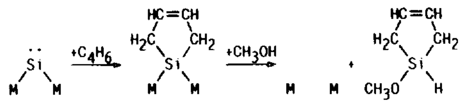
On the surface of silicon, there may be a copper-rich region as indicated by the formation of a Cu–Si alloy phase. The migration of silicon to this region may give silicon species having a silylene character (I). This species reacts with methanol to form surface species (II). The reaction of methanol with silylene is well established (9, 10). The surface Si–H bond undergoes an attack from another methanol molecule to form dimethoxysilicon species (III), which undergoes further attack from methanol to form $HSi(OCH_3)_3$. Silicon atoms migrate from the bulk of the metal to the surface to regenerate copper–silicon intermetallic species. A certain fraction of the copper species on the surface combines to form metallic copper, which catalyzes the reaction of $HSi(OCH_3)_3$ with methanol.

Further evidence for the presence of silylene species was obtained by the reaction of methanol with silicon in the presence of alkenes. When ethylene was fed with methanol, ethyldimethoxysilane $HSi(C_2H_5)(OCH_3)_2$ was observed in the product in addition to $HSi(OCH_3)_3$. The formation of ethyldimethoxysilane may be explained as follows:



The reaction of silylene with ethylene is known to form vinylsilanes through silacyclopropane intermediates (11, 12). In the reaction of silylene with alkenes in the presence of methanol, the methanolysis products of silacyclopropane intermediates, alkylmethoxysilanes, were obtained (12–14). The mechanism described above is in conformity with the known chemistry of silylenes.

The methanol–silicon reaction in the presence of butadiene gave a small amount of 1-methoxysilacyclopent-3-ene. This type of the products is typical of silylene reactions with butadiene (11, 15, 16). On the surface of silicon, this product may be formed as follows:



The formation of the organosilanes in these reaction systems strongly indicates the presence of silylene species on the surface, and methanol seems to be essential to cleave metal silicon bonds.

CONCLUSIONS

The selectivity for $HSi(OCH_3)_3$ in the reaction of silicon with methanol with using copper(I) chloride sharply increases when thiophene or an alkyl halide was added to the feed. Separate experiments showed that metallic copper is an active catalyst for the reaction of $HSi(OCH_3)_3$ and methanol to form $Si(OCH_3)_4$. These facts show that $HSi(OCH_3)_3$ is exclusively formed in the silicon–methanol reaction and a part of $HSi(OCH_3)_3$ is converted into $Si(OCH_3)_4$ by metallic copper, which is formed in the silicon–methanol reaction.

The presence of an excess amount of a copper(I) chloride catalyst also has an enhancing effect on the selectivity. This indicates that the chloride ions are transferred onto the surface of metallic copper formed in the course of the reaction to poison the catalytic activity for the $HSi(OCH_3)_3$–methanol reaction.

The reaction mechanism involving surface silylene species is proposed to explain the exclusive formation of $HSi(OCH_3)_3$.

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