JOURNAL OF CATALYSIS **147**, 15–23 (1994)

# Selective Synthesis of Trialkoxysilanes by the Reaction of Metallic Silicon with Alcohols Using Copper(I) Chloride as the Catalyst

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Received September 10, 1993; revised November 29, 1993

**The reactions of silicon with ethanol, propanols and butanols were studied using copper(I) chloride as the catalyst. Primary alcohols reacted with silicon, while secondary and tertiary alcohols did not. The reactions of silicon with ethanol, 1-propanol, and 1-butanol gave high silicon conversions of 95, 85, and 77%, respectively, at 513 K without heating treatment of the silicon–catalyst mixture. Under these conditions, the selectivities for trialkoxysilanes were very high (>99%). The pretreatment of the silicon–catalyst mixtures at high temperatures (i.e., 723 K) to facilitate the formation of $Cu_3Si$ phase is not favorable for the reactions: Both the silicon conversion and the selectivity for trialkoxysilane are sharply depressed. Metallic copper is easily formed on the silicon surface during the reactions after high temperature pretreatment. The metallic copper catalyzes the dehydrogenation of alcohols to aldehydes, which inhibit the silicon–alcohol reactions. It also catalyzes the reaction of trialkoxysilane with alcohol to give tetraalkoxysilane. This brings about the decrease in the selectivity for the trialkoxysilane. However, the high silicon conversion together with high selectivity was obtained by adding thiophene or propyl chloride, which is a poison for copper catalysts, to the alcohol feed. Though 2-propanol does not react with silicon, dimethoxyisopropoxysilane and methoxydiisopropoxysilane were formed appreciably when 2-propanol was fed to the silicon together with methanol. This phenomenon was discussed in relevance of the mechanism of the silicon–alcohol reactions.** © 1994 Academic Press, Inc.

## INTRODUCTION

The reaction of metallic silicon with methyl chloride has been the subject of the numerous studies, since the reaction is a key step to synthesizing silicon-containing materials such as silicone polymers (1). On the other hand, the reactions of silicon with alcohols have never been explored extensively, though Rochow discovered in 1948 that silicon fused with copper reacted to give tetramethoxysilane (2). Newton and Rochow reported that both trimethoxysilane and tetramethoxysilane were obtained when methanol was fed into silicone oil containing silicon fused with copper (3).

Trialkoxysilanes are important chemicals, since various organosilanes can be derived by their reactions with organic compounds. Therefore, the efforts have been focused to improve the selectivity for trialkoxysilanes (4).

Recently, we have reported the effects of the reaction conditions on the reaction rate and the product selectivity in the reaction of metallic silicon with methanol with a fixed-bed reactor using copper(I) chloride as a catalyst (5–7). We also studied the effect of the conditions of preheating silicon–catalyst mixtures: When the temperature of preheating was lower than 573 K, the selectivity for trimethoxysilane was very high (>98%). On the other hand, the selectivity for trimethoxysilane was rather low (60–70%), when the preheating temperature was above 603 K (5, 7). We further confirmed that trimethoxysilane is a sole primary product and that tetramethoxysilane is formed by the reaction of trimethoxysilane, the primary product, with methanol by the catalytic action of metallic copper formed on the silicon surface under the reaction conditions (8).

The work on the reactions of metallic silicon with higher alcohols has been very limited. Newton and Rochow studied the reactions of silicon with higher alcohols as well as methanol (3). The overall yields of alkoxysilanes were low. The overall yields were 15.5, 4.8, and 8.3% for the reaction of silicon with ethanol, 1-propanol, and isobutyl alcohol, respectively. Several patents describe the reaction of silicon with ethanol (4). However, the overall yields of ethoxysilanes are small in every case and the selectivities for triethoxysilane are low.

This work concerns the direct reactions of metallic silicon with higher alcohols, namely, ethanol, propanols, and butanols. The effects of pretreatment conditions and reaction variables are studied to obtain high yields as well as high selectivities for trialkoxysilanes. The factors determining the selectivity for trialkoxysilane will be discussed.

## EXPERIMENTAL

The reactions of silicon with alcohols were carried out in a fixed-bed flow reactor. Silicon grains (45–63 μm; purity 99.9%; Fe as a major impurity) were washed with

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a 46% HF solution for 1 h to remove the $SiO_2$ overlayers. The silicon grains (6 mmol) and copper(I) chloride grains (45–63 $\mu$m; 0.31 mmol; purity 99.9%) were mixed in a small vial with vigorous vibration. The amount of the catalyst is expressed as the percentage weight of Cu in (Si + Cu) in the mixture. The mixture was loaded in the reactor (quartz tube, 10 mm i.d.) and pretreated in a helium stream at 493–723 K for 1 h prior to feeding alcohol. When the heat-treatment was not carried out, alcohol was fed as soon as the temperature of the reactor reached the reaction temperature. For SEM studies, optically polished silicon wafers with (100) crystallographic orientation, containing ca. 0.01 ppm of P as a doped atom, were used. They were obtained from Toshiba Ceramic Co. Ltd. and washed with a 46%-HF solution. A small piece of the wafer (4.5 × 4.5 mm) was embedded in the mixture of silicon and copper(I) chloride grains.

Alcohol (guaranteed reagent grade) was dehydrated over molecular sieve 3A. Alcohol (33–71 mmol $h^{-1}$, 47–101 kPa) and helium (total flow = 71 mmol $h^{-1}$) were fed to the reactor at 473–603 K. The rates of the formation of the products were determined every 5 min by analyzing the effluent gas by a gas chromatograph with a column packed with SE-30.

## RESULTS AND DISCUSSION

### Reaction of Si with Ethanol

(*a*) *Effect of preheating.* As described above, in the case of the Si–methanol reaction, the reaction rate and the selectivity for trimethoxysilane sharply depend on the temperature preheating of Si–CuCl mixture (5, 7). Therefore, the effect of preheating temperature was also studied for the Si–ethanol reaction. The reaction was carried out at 493 K after the pretreatment at a constant temperature for 1 h.

The time courses of the Si–ethanol reactions with different preheating temperatures are shown in Fig. 1. In every case, the rate first increased and then decreased to zero. The overall conversions of silicon were determined by integrating the rate of formation of silanes.

In the case of the reaction without pretreatment, the silicon conversion reached 89%. The products consist of triethoxysilane (99%) and tetraethoxysilane (1%) (Fig. 1a). When the mixture was treated at 493 K for 1 h, the rate slightly increased. The overall conversion of silicon also increased to 92% (Fig. 1b). When the preheating temperature was increased to 513 K, the induction time of 0.5 h was observed and the rate became lower (Fig. 1c). With higher pretreatment temperature of 523 K, the induction time became still longer (0.87 h) and the rate also decreased. At preheating temperature of 603 K, two rate maxima appeared in the rate curve (Fig. 1e). Around the first maximum, the selectivity for triethoxysilane slightly decreased to 97%. At preheating temperature of 723 K, the rate curve had only one maximum. The overall silicon conversion was 73%. The selectivity for triethoxysilane decreased with reaction time. The overall selectivity for triethoxysilane for 5 h was 25%. Most of these features of the pretreatment effect were also found in the Si–methanol reaction.

The results show that the preheating of the Si–catalyst mixture at higher temperatures is not favorable for obtaining high overall conversion of silicon. The selectivity for triethoxysilane was very high (>98%) when the preheating temperature was below 603 K, while it was very low at high pretreatment temperature (723 K).

When no pretreatment was carried out, the reaction at 493 K gave the silicon conversion of 89% together with high triethoxysilane selectivity of 99%. Both of the conversion and the selectivity values are far greater than those found in literature (3, 4).

In conclusion, the pretreatment is not a prerequisite for obtaining high conversion and high selectivity, though high temperature pretreatment facilitates the Si–Cu alloy formation. However, we have shown that high temperature pretreatment was necessary for obtaining high silicon conversion in Si–methanol reactions, when silicon surface is covered by oxide layers, or silicon is not washed with a HF solution (5, 9).

(*b*) *Effect of reaction temperature.* Figure 2 shows the effect of the reaction temperature on the time course of the Si–ethanol reaction in the temperature range of 473–553 K. No pretreatment was given to the Si–catalyst mixture. The rate increase in the first stage of the reaction was faster at higher reaction temperatures. The rate decay after the rate maximum was faster also at higher reaction temperatures. The silicon conversion was high at below 513 K (85–95%), while it was low at higher reaction temperatures. At 553 K, the overall conversion was only 20%. The highest silicon conversion was observed at 513 K. The selectivity for triethoxysilane was always close to 100%.

The effect of reaction temperature on the reaction upon the pretreatment of the Si–catalyst mixture at 723 K, was examined. The rates were much slower than those in the reaction without preheating. The overall conversions at 473, 493, 513, and 533 K were 51, 70, 42, and 30%, respectively. Thus, the higher reaction temperature did not lead to the higher silicon conversion in the reaction after preheating at 723 K as well. The selectivity for triethoxysilane was low upon pretreatment at 723 K, as described above.

(*c*) *Effect of ethanol pressure.* Figure 3 shows the change in the reaction rate with time at three different ethanol pressures. The pretreatment was carried out at 513 K for 1 h and the reaction started at the same tempera-

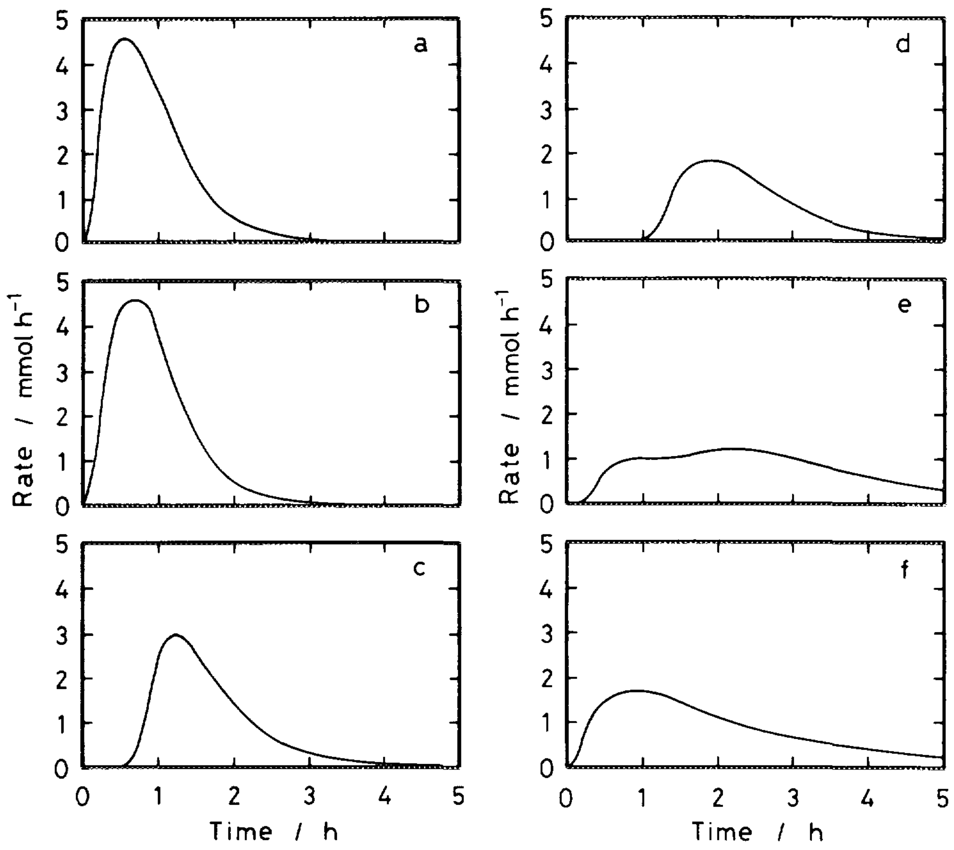


FIG. 1. Effect of the preheating temperature on the rate of formation of ethoxysilanes. Preheating conditions: no preheating (a), preheating at 493 (b), 513 (c), 523 (d), 603 (e), 723 K (f) for 1 h. Reaction condition: reaction temperature = 513 K, ethanol = 94 kPa.

ture. The ethanol pressure gave a great effect on the rate–time curve, especially on the induction time. The induction time was not observed at ethanol pressure of 94 kPa. The induction time over 1 h was observed at 63 kPa. It prolonged to over 3 h at 47 kPa. The rate after the induction time was lower at lower pressure of ethanol. The overall conversion of silicon was 95, 92, and 45% at 94, 63, and 47 kPa of ethanol pressure, respectively.

The effect of ethanol pressure was also studied for the reaction after preheating the Si–catalyst mixture at 723 K. In contrast to the reaction with pretreatment at lower temperature (513 K), no induction time was observed even at 47 kPa. However, the rate was low and the overall

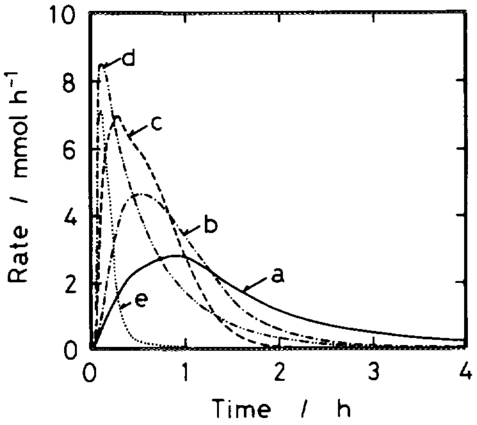


FIG. 2. Change in the rate of ethoxysilanes formation with time at various reaction temperatures. No preheating. Reaction conditions: ethanol = 94 kPa, reaction temperature = 473 (a), 493 (b), 513 (c), 533 (d), 553 K (e).

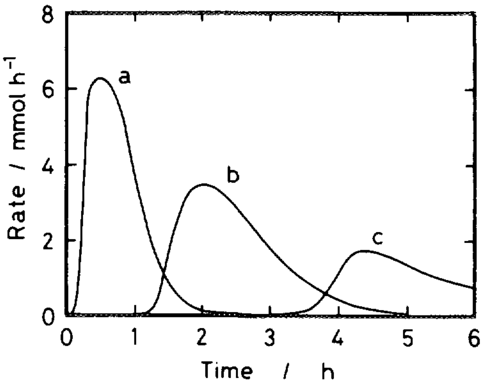


FIG. 3. Change in the rate of ethoxysilanes formation with time at various ethanol pressures when the preheating was carried out at 513 K. Preheating condition: 513 K, 1 h. Reaction conditions: reaction temperature = 513 K, ethanol = 94 (a), 63 (b), 47 kPa (c).

conversion of silicon after 5 h was 40% at 94 kPa and about 20% at 63 and 47 kPa.

(*d*) *Effect of the catalyst amount.* Figure 4 shows the effect of the amount of CuCl on the rate and the selectivity for triethoxysilane at 513 K. The amount of silicon was fixed and the amount of the catalyst was varied. No pretreatment was carried out for the Si–catalyst mixtures. The rate increased with increasing the amount of the CuCl catalyst. The overall conversion of silicon was high in every case. Thus, it was 83, 90, 95, and 93% for the reactions with catalyst amount of 2.5, 5, 10, and 20 wt%, respectively.

The amount of copper(I) chloride is far greater than that expected from the stoichiometry for the reactions

$$4\mathrm{CuCl} + \mathrm{Si} \rightarrow \mathrm{SiCl_4} + 4\mathrm{Cu}$$

$$x\mathrm{Cu} + \mathrm{Si} \rightarrow \mathrm{Cu}_x\mathrm{Si}\ \text{(reactive site)}.$$

This indicates that the CuCl grains which directly contact silicon surface are effective for reaction sites formation and that the transfer of CuCl to the silicon surface through vapor phase is not important at the reaction temperature of 513 K, where the vapor pressure of CuCl is very low. In fact, when the CuCl layer was placed on the top of the silicon grains, the reaction did not proceed.

The selectivity for triethoxysilane also depended on the catalyst amount. It was almost 100% in the reactions when the catalyst amount was 5 wt% or more, while it was 94% in the case of the catalyst amount of 2.5 wt%. The fact, that the selectivity for trialkoxysilane was low when the catalyst amount was small, was also observed in the Si–methanol reaction (7). This was attributed to the transfer of the halide ions on the surface of metallic copper, where the ions prevent the reaction of trimethoxysilane with methanol by poisoning the catalytic action of metallic copper (8). This point will be discussed later.

(*e*) *SEM observation of the surface of reacting silicon.* In the case of the Si–methanol reaction, the formation of pits was observed on the silicon surface (5, 7). The size and number of the pits greatly depended on the pretreatment conditions of the Si–CuCl mixtures (7). Here, we examined the surface of Si wafers, embedded in the mixtures of silicon and CuCl grains by scanning electron microscopy (SEM).

One mixture containing a silicon wafer was pretreated at 723 K. The reaction with ethanol was started at 493 K and stopped when the silicon conversion reached 6.5%. Figures 5a and b show the scanning micrographs of this silicon wafer. The pits were scattered on the surface and their surface was 112 $\mathrm{mm}^{-2}$. This concentration is close to that of the pits found after the Si–methanol reaction at the 10% conversion (110 $\mathrm{mm}^{-2}$) (7).

We have already shown by XRD and SEM that the patches of $\mathrm{Cu_3Si}$ phase develop on the silicon surface upon heating Si–CuCl mixture at 723 K and that the concentration of the patches was 129 $\mathrm{mm}^{-2}$ (7). This concentration is close to those of the pits found in the Si–ethanol reaction with the preheating at 723 K. This clearly indicates that the Si–ethanol reaction starts in the vicinity of the $\mathrm{Cu_3Si}$ patches as in the case of the Si–methanol reaction.

A second mixture of Si and CuCl containing a silicon wafer was pretreated at 513 K. Then the reaction with ethanol was run at 513 K and stopped at a silicon conversion of 1%. The number of pits found on the surface of this wafer (Figs. 5c, d) is far greater than that found on the wafer after the pretreatment at 723 K (Figs. 5a, b).

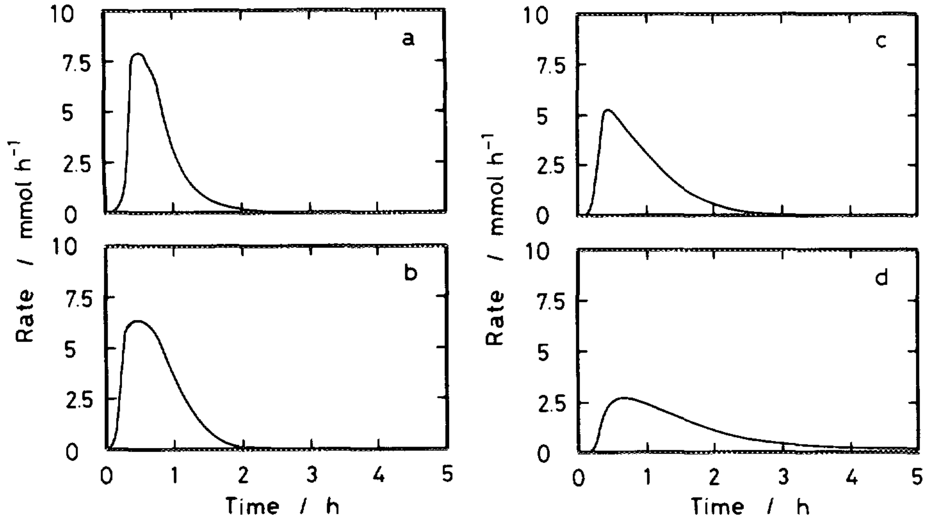


FIG. 4. Effect of the catalyst amount on the rate of formation of ethoxysilanes. Preheating condition: 513 K, 1 h. Reaction conditions: reaction temperature = 513 K, ethanol = 94 kPa, catalyst amount = 20 (a), 10 (b), 5 (c), 2.5 wt% (d).

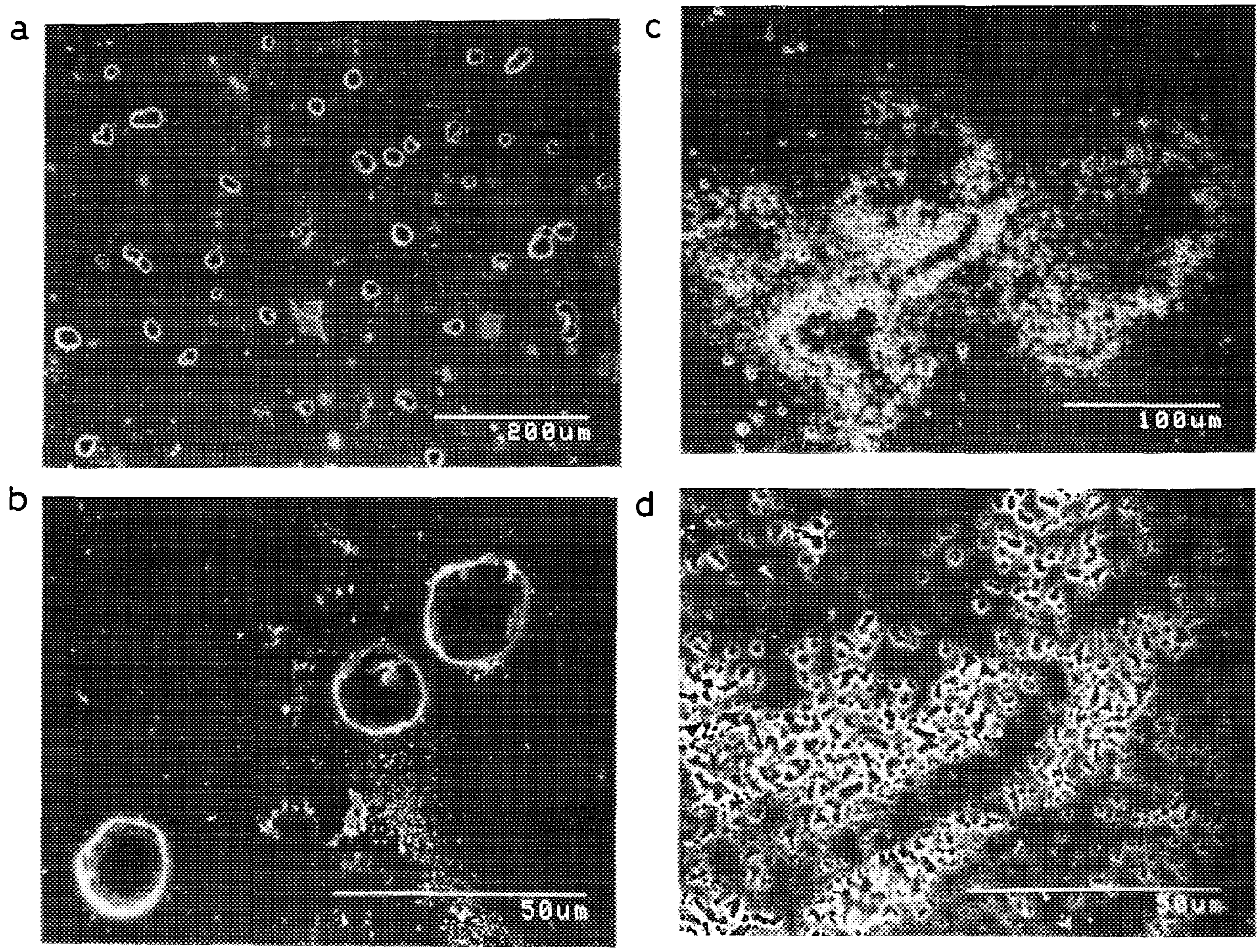


FIG. 5. Scanning electron micrographs of silicon wafers reacted with ethanol. (a), (b) preheating temperature = 723 K, reaction temperature = 493 K, ethanol = 93 kPa, silicon conversion = 6.5%. (c), (d) preheating temperature = 513 K, reaction temperature = 513 K, ethanol = 93 kPa, silicon conversion = 1%. Magnification: (a) × 110, (b) ×720, (c) ×220, (d) ×720.

This shows that very small patches of silicon–copper intermetallics are formed on the silicon surface during the period of raising the temperature to the reaction temperature and/or the preheating period even when no pretreatment was made or when the pretreatment temperature was low.

These features of the pit concentration in the Si–ethanol reaction are similar to those found in the Si–methanol reaction (7).

*Reaction with 1-Propanol*

Figure 6 shows the change in the rate of the reaction of silicon with 1-propanol with time at various reaction temperatures. No pretreatment was done to the Si–catalyst mixtures. As in the case of the reaction with ethanol, the rate acceleration in the beginning of the reaction was

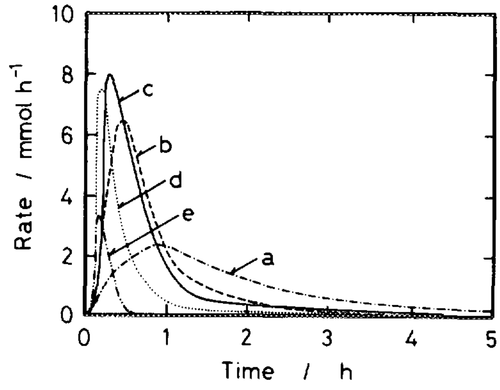


FIG. 6. Change in the rate of propoxysilanes formation with time at various reaction temperatures. No preheating. Reaction conditions: 1-propanol = 96 kPa, reaction temperature = 473 (a), 493 (b), 513 (c), 533 (d), 573 K (e).

faster at higher reaction temperatures. At the same time, the decay of the rate was also faster at higher temperatures. The overall conversions of silicon for 5 h were 82, 85, and 82% at 473, 493, and 513 K, respectively. The overall conversion significantly decreased at higher temperatures. Thus, the silicon conversions were 43 and 13% at 533 and 573 K, respectively. The conversion values of 82–85% at 473–513 K in this work are far higher than that (4.8%) reported by Newton and Rochow (3). The selectivity for tripropoxysilane was practically 100% at all reaction temperatures studied.

The effect of the 1-propanol pressure was studied. The great effect was observed on the induction time. At 96 kPa, the induction time was about 5 min. The induction time was prolonged to 70 and 300 min by lowering the pressure to 88 and 72 kPa, respectively. The great dependence of the induction time on the 1-propanol pressure indicates that the alcohol is directly involved in the reaction-site formation.

When the Si–CuCl mixtures were treated at 723 K, the reaction of silicon with 1-propanol (96 kPa) was slow and the overall conversion was also low. Thus, the conversion values were 20 and 33% at 453 and 513 K, respectively.

The silicon surface after the reaction with 1-propanol was examined with SEM. The results were very similar to those in the Si–ethanol reaction: When the reaction was carried out at 513 K after pretreating the Si–CuCl mixture at 723 K for 1 h and stopped when the silicon conversion reached 4.5%. The pits were observed and the surface concentration of the pits was 113 $mm^{-2}$, practically equal to those observed in Si–methanol (112 $mn^{-2}$) as well as in Si–ethanol reaction (110 $cm^{-2}$).

### *Reaction of 2-Propanol*

2-Propanol did not react with silicon. This is in conformity with the result reported by Newton and Rochow (3).

As described above, the reaction of methanol, ethanol, or 1-propanol with silicon, the induction time depends significantly on the alcohol pressure, indicating that alcohol molecules are involved in the formation of the reactive sites on the silicon surface. This suggests that 2-propanol might be incapable of forming the reactive sites. If this is the case, the reaction of 2-propanol with silicon should proceed when the induction time was eliminated. However, this idea was refuted by the following experiment (Fig. 7).

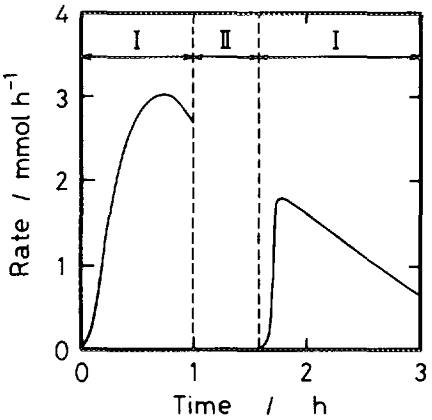


FIG. 7. Reaction of silicon with 2-propanol after the activation of silicon by 1-propanol. No preheating. Reaction conditions: reaction temperature = 483 K, (I) 1-propanol = 96 kPa, (II) 2-propanol = 101 kPa.

The reaction of 1-propanol with silicon was started at 483 K without any pretreatment. The reaction occurred as expected, indicative of the formation of the reactive sites on the silicon surface. After 1 h of the reaction, the reactant alcohol was switched to 1-propanol to 2-propanol. No reaction of 2-propanol with silicon was observed. At 2 h, the reactant alcohol was switched back to 1-propanol. The reaction of 1-propanol resumed.

To further elucidate the reactivity of 2-propanol towards silicon, 2-propanol (30 kPa) was fed together with methanol (63 kPa) to silicon grains at 513 K. No pretreatment of the Si–CuCl mixture were done. Figure 8 shows the change in the rates of the formation of the products with time. The products mainly consist of trimethoxysilane (27%), dimethoxyisopropoxysilane (63%), methoxydiisopropoxysilane (9%). No tetraalkoxysilanes were formed. Triisopropoxysilane was only slightly formed (0.8%).

In a previous paper, we proposed the reaction mechanism for explaining the selective formation of trimethoxysilane in the Si–methanol reaction.

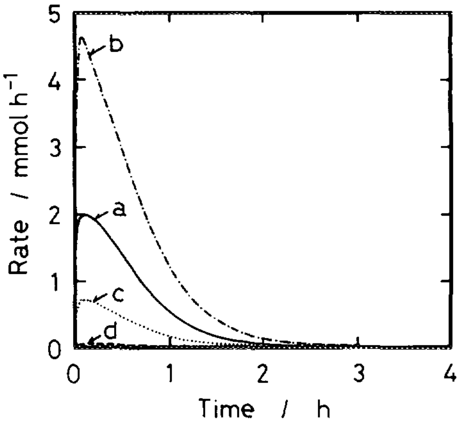
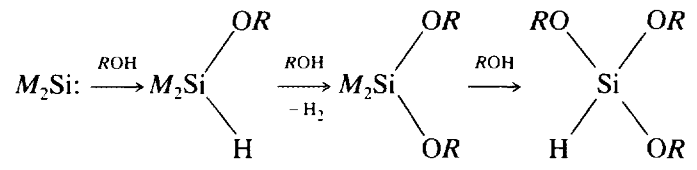


FIG. 8. Change in the rates of formation of the products with time in the reaction of silicon, 2-propanol and methanol. (a) trimethoxysilane, (b) dimethoxyisopropoxysilane, (c) methoxydiisopropoxysilane, (d) triisopropoxysilane. No preheating. Reaction condition: reaction temperature = 513 K, methanol = 63 kPa and 2-propanol = 30 kPa.



(I) (II) (III)
Step 1 Step 2 Step 3
($M$ = Cu, $R$ = $CH_3$)

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 gives silicon species having a silylene character (I). This species reacts with methanol to form surface species (II). The surface Si–H bond undergoes an attack of another methanol molecule to dimethoxysilicon species (III), which undergoes further attack of methanol to form trimethoxysilane. The presence of the silylene species are supported by the formation of alkyldimethoxysilanes in the reaction of silicon with methanol in the presence of alkenes (8, 10).

There are three steps that alkoxy groups are bonded to a silicon atom; Step 1: The reaction of alcohol with surface silylene species (I), Step 2: The reaction of the hydride (II) with alcohol, Step 3: The simultaneous cleavage of the two Si–Cu bonds with alcohol. The last step may be the most difficult step to occur. The negligible formation of triisopropoxysilane indicates that 2-propanol is only involved in only two steps out of the three. We presume that 2-propanol is involved only in steps 1 and 2. This mechanism explains why 2-propanol does not react with silicon and why isopropoxy groups are incorporated in the product silane when 2-propanol was added to methanol in the Si–methanol reaction.

### *Reaction of Butanols*

When 1-butanol (94 kPa) was reacted with silicon at 493 K without heat-pretreatment of Si–CuCl mixture, the silicon conversion of 77% was obtained, the selectivity for tributoxysilane being above 99%. This result is shown in Fig. 9.

The reactions of silicon with *sec*- and *t*-butyl alcohol did not occur. Silicon reacted slowly with isobutyl alcohol (101 kPa) after long induction time (2 h) at 513 K.

### *Deactivation by Aldehydes*

One of the features of the reactions of silicon with alcohols (except methanol) is the sharp decline of the rate at higher reaction temperatures as shown in Figs. 2 and 6. This does not mean that the silicon surface entirely changes during the reactions at higher reaction temperature.

As shown in Fig. 10, the reaction of silicon with ethanol completely stopped at 45 min, where the silicon conversion was 18%. At this time, the feed was switched from ethanol to methanol. The reaction of the silicon with methanol proceeded to silicon conversion of 70%. This suggests that the deactivation is originated from the Si–ethanol reaction itself.

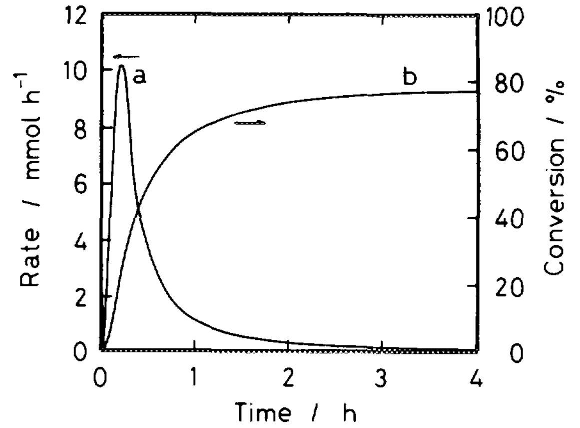


FIG. 9. Change in the rate of butoxysilanes formation (a) and the silicon conversion (b) with time. No preheating. Reaction temperature = 493 K, 1-butanol = 94 kPa.

The reaction products of the Si–ethanol reaction were analyzed. Besides alkoxysilanes, acetaldehyde, ethylene, diethyl ether, and water were found in the products. The amount of acetaldehyde and water reached at most 3.4 and 0.1%, respectively. The effects of the two by-products on the reaction were examined. Addition of water to the ethanol feed gave no apparent change in the rate of the reaction. On the other hand, addition of acetaldehyde depressed the rate significantly, as is shown in Fig. 11. Without acetaldehyde, a silicon conversion of 95% was obtained. By adding 0.34 and 1.0 mol% of acetaldehyde to the ethanol feed, the overall conversion of silicon decreased to 85 and 32%, respectively. When 3.4 mol% of

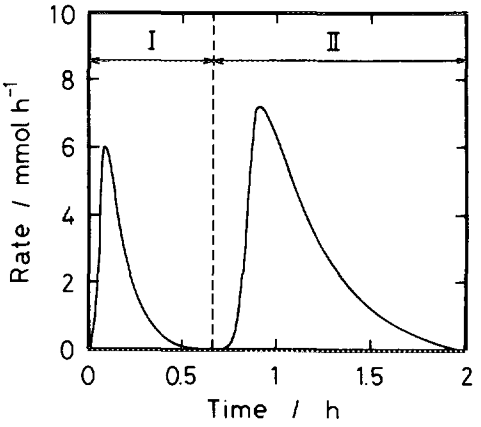


FIG. 10. Change in the reaction rate with time in the silicon–methanol reaction after the end of silicon–ethanol reaction. No preheating. Reaction conditions: reaction temperature = 553 K, (I) ethanol = 94 kPa, (II) methanol = 90 kPa.

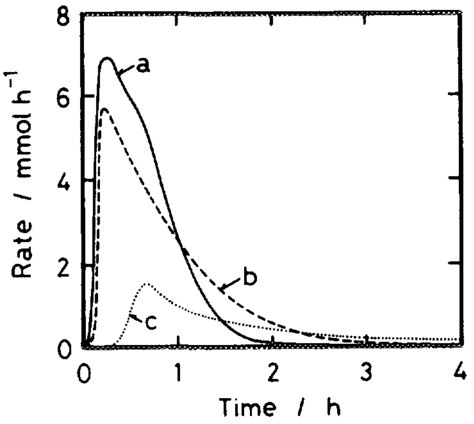


FIG. 11. Effect of acetaldehyde on the change in the rate of ethoxysilanes formation. No preheating. Reaction conditions: reaction temperature = 513 K, ethanol = 94 kPa, acetaldehyde = 0 (a), 0.34 (b), 1 mol% (c).

acetaldehyde was added, no reaction of ethanol with silicon was observed.

The effect of acetaldehyde on the reaction was reversible as shown in Fig. 12. The reaction was started with pure ethanol. At 0.7 h of the reaction, the feed was replaced by ethanol containing acetaldehyde (3.4 mol%). The reaction stopped completely. At 1.2 h, the feed was again switched back to pure ethanol. The reaction resumed.

In the reaction of silicon with 1-propanol, the formation of propanal was observed. When propanal (2 mol%) was added to the 1-propanol feed, no reaction occurred.

These results clearly show that poisoning by aldehydes formed as by-products is at least one of the reasons for the deactivation. The higher temperature seems to facilitate the aldehyde formation. This causes the sharp decay of the rate at higher temperatures.

Both of conversions and the selectivity values in Si-alcohol reactions far exceeded those found in literature (3, 4). This is probably due to the reaction conditions, which we could minimize the formation of aldehydes during the reactions. The other important factor may be the thickness of $SiO_2$-overlayers on the silicon surface (9).

### *Preventive Effect of Thiophene or Propyl Chloride on the Deactivation*

As described above, aldehydes cause the deactivation of the catalysis in Si–alcohol reactions. We presume that the dehydrogenation of starting alcohols is formed by the catalytic action of metallic copper, which is formed during the Si–alcohol reactions.

We have shown that metallic copper is formed during the Si–methanol reaction and the extent of the metallic copper formation is more extensive at higher pretreatment temperatures, where large $Cu_3Si$ patches are formed (8). This explains lower silicon conversion in the reactions with high temperature pretreatment of the Si–CuCl mixture.

We have also shown that metallic copper formed on the silicon surface catalyzes the secondary reaction of trimethoxysilane and methanol to lead to the lowering of the selectivity for trimethoxysilane (8). In the reactions of silicon with ethanol and 1-propanol, the low selectivity for trialkoxysilane was observed when the pretreatment temperature was high. In these cases too, the lower selectivity plausibly caused by the catalysis of the metallic copper to convert trialkoxysilane into tetraalkoxysilane.

We have further shown that the addition of thiophene or alkyl chloride depresses the catalytic activity of metallic copper and enhances the selectivity for trimethoxysilane (8).

We presume here that metallic copper catalyzes the formation of aldehydes from the starting alcohols. If this is the case, the addition of thiophene or alkyl chloride should prevent the deactivation.

Figure 13 shows the effects of addition of thiophene and propyl chloride to the ethanol feed. The Si–catalyst mixture was pretreated at 723 K and the reaction temperature was 533 K. Under these conditions, the rate was low and the overall conversion in 5 h was 30% when pure ethanol was fed. The selectivity for triethoxysilane was also low (16%). When 1 mol% of thiophene was added to the feed ethanol, the rate significantly increased and the overall conversion of silicon reached 82%. The selectivity for triethoxysilane was also enhanced, the overall selectivity being 97%. The addition of propyl chloride gave similar effects. The rate was enhanced and the overall silicon conversion reached 92% and the overall selectivity for triethoxysilane enhanced to practically 100%.

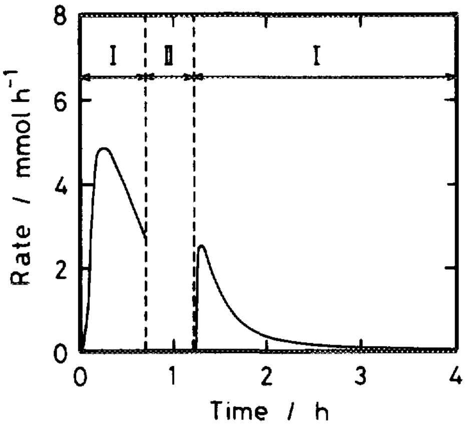


FIG. 12. Change in the rate of ethoxysilanes formation upon addition of acetaldehyde. Preheating condition: 513 K, 1 h. Reaction conditions: reaction temperature = 513 K, (I) ethanol = 94 kPa, (II) ethanol = 94 kPa and acetaldehyde = 3.2 kPa.

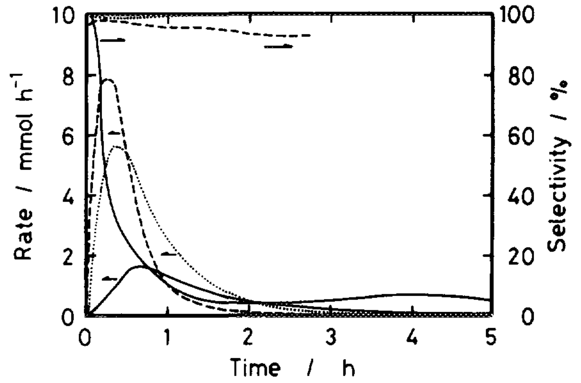


FIG. 13. Effect of thiophene or propyl chloride on the reaction rate and the selectivity for triethoxysilane. Preheating condition: 723 K, 1 h. Reaction conditions: reaction temperature = 533 K, ethanol = 94 kPa, no additive (solid lines), thiophene = 0.94 kPa (dashed lines), propyl chloride = 0.94 kPa (dotted lines).

These results were just as expected. Thiophene poisons the catalytic actions of metallic copper. The rate is increased by depressing the formation of acetaldehyde on copper and the selectivity is enhanced by depressing the reaction between triethoxysilane and ethanol on copper.

The effect of propyl chloride on the Si–1-propanol reaction was also studied. The Si–catalyst mixture was pretreated at 723 K and the reaction was carried out at 493 K. The overall conversion was very low (20%) and the overall selectivity for tripropoxysilane was 30% when pure 1-propanol was fed. When 1 mol% of propyl chloride was added to 1-propanol, the overall silicon conversion increased to 70% and the selectivity for tripropoxysilane increased to practically 100%.

## CONCLUSION

The reactions of silicon with ethanol, propanols, and butyl alcohols were studied. Only primary alcohols reacted with silicon, while secondary and tertiary alcohols did not.

The reaction rate and the selectivity for trialkoxysilane greatly depended on the temperature of pretreating the silicon catalyst mixture. The reactions with ethanol, 1-propanol, and n-butanol gave the silicon conversion of 95, 85, and 77%, respectively, the selectivities for trialkoxysilanes being about 100% when no pretreatment was carried out.

The rate and the silicon conversion sharply decreased upon high-temperature pretreatment, especially at high reaction temperatures, and this phenomenon also occurred at high reaction temperature without the pretreatment. Under these conditions, the formation of metallic copper was facilitated. The metallic copper catalyzes the dehydrogenation of alcohols to aldehydes, which is a poison for the Si–alcohol reactions.

Addition of thiophene or propyl chloride to the alcohol feed depresses the catalysis by metallic copper to give the high reaction rates and high silicon conversions. The addition also improves the selectivity for trialkoxysilane by preventing the reaction of trialkoxysilane and alcohol on metallic copper.

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