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Effect of Pretreatment Conditions of Si–CuCl Mixtures on the Rate and Selectivity in the Reaction of Silicon with Methanol Using Copper(I) Chloride Catalyst

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The reaction of silicon with methanol was carried out in a fixed-bed flow reactor using copper(I) chloride as a catalyst. The rate of the reaction and the selectivity for trimethoxysilane greatly depends on the preheating conditions of the Si–CuCl mixture prior to feeding methanol. When the preheating temperature was above 623 K, trimethoxysilane was formed with selectivities around 65%, the remainder being tetramethoxysilane. The XRD and EPMA studies revealed that the Cu_3Si phase was scattered on the silicon surface upon heating the Si–CuCl mixture above 623 K. When the preheating temperature was below 553 K, the rate of the reaction was faster than that for higher preheating temperatures, and the selectivity for trimethoxysilane was very high (>98%). In this case, however, no evidence for the Cu_3Si phase was obtained. Pits on the silicon surface are formed upon the reaction with methanol. When the pretreatment temperature is high (723 K), the number of pits is close to that of the Cu_3Si patches which were present before starting the reaction. The number does not change with reaction time. This indicates that silicon atoms are consumed only around the areas where the Cu_3Si patches are located. The number of pits was far greater in the reaction with lower preheating temperatures (<513 K) compared with that with higher preheating. The kinetics of the reaction also depended on the preheating temperature of the Si–CuCl mixtures.

INTRODUCTION

Trimethoxysilane is one of the important chemicals from which various organosilicon compounds can be derived. Trimethoxysilane can be synthesized by the reaction of metallic silicon with methanol using copper compounds as catalyst. In previous works, Suzuki and Ono (*1*, *2*) reported the vapor-phase synthesis of trimethoxysilane with copper(I) chloride catalyst. The rate of silicon consumption and selectivity for trimethoxysilane were greatly influenced by the temperature of preheating of the silicon–copper(I) chloride mixture prior to the reaction. Thus, when the preheating temperature was below 573 K, the reaction at 513 K started only after an induction period and the reaction stopped at a low silicon conversion, the selectivity for trimethoxysilane being very high (>96%). On the other hand, when the preheating temperature was above 623 K, the induction period was eliminated and almost complete conversion of silicon was attained, though the selectivity for trimethoxysilane was low (70–80%). Formation of the Cu_3Si phase was observed after the pretreatment. In these works, silicon stored in ambient conditions was used.

A later work (*3*), however, has shown that silicon grains stored in ambient conditions have SiO_2-overlayers on the surface and that the removal of the SiO_2-overlayers by treating the silicon grains with an aqueous HF solution greatly improves the reactivity of the silicon towards methanol. Viale *et al.*

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have also noted that the formation of Cu_3Si by the reaction of silicon with CuCl vapor is greatly promoted by removing SiO_2-overlayers (*4*). Therefore, we have reexamined the vapor-phase reaction of methanol with silicon grains which are washed with an aqueous HF solution.

In this paper, the effects of the preheating conditions for the silicon–copper(I) chloride mixture and the reaction conditions are reported. It is shown that the preheating conditions, especially the preheating temperature, greatly alter the rate of silicon consumption as well as the selectivity for trimethoxysilane. The formation of Cu_3Si phase on the silicon surface and the number and the size of the pits, which are formed on the silicon surface, were examined by EPMA and SEM. The kinetics of the reaction is also described.

EXPERIMENTAL

Silicon grains obtained from Soekawa Chemical Co., Ltd., were 99.9% in purity and contained Fe as a major impurity. They were sieved into grains of 45–63 μm and washed with an aqueous hydrogen fluoride solution to remove the SiO_2-overlayers. A 2-g portion of the grains was mildly agitated in 20 cm^3 of 46% HF solution at room temperature for 1 h. After the liquid was filtered off, the grains were rinsed with water several times, dried in an evaporator at 323 K under a reduced pressure, and stored under a nitrogen atmosphere. The silicon grains thus treated have SiO_2-overlayers with 0.23 nm in thickness, as determined by ESCA (*3*).

Optically polished silicon wafers with (100) crystallographic orientation, containing ca. 0.01 ppm of P as a doped atom, were obtained from Toshiba Ceramics Co., Ltd. and washed with 46% HF solution. Copper(I) chloride (Kanto Chemical Co., Inc.) was sieved into grains of 45–63 μm.

The reaction of the silicon with methanol was carried out in a fixed-bed flow reactor. A 0.168-g (6.00-mmol) portion of the silicon grains was mixed with the copper(I) chloride ($Cu/(Cu + Si) = 0.01–0.1$ by weight) in a vial. The mixture was loaded in a reactor of silica tubing (10-mm i.d.) placed in an infrared furnace and then heated under a helium stream (49 mmol h^{-1}) at 513–723 K for 10 min–12 h prior to feeding methanol. In the experiments where the silicon wafer was used, a small piece of the wafer (4.5 × 4.5 mm) was embedded in the mixture of silicon and copper(I) chloride grains. This method was used to place a wafer and grains under the same preheating and reaction conditions.

Methanol, dehydrated over molecular sieve 3A, was fed by a motor-driven syringe into the preheating zone of the reactor. The partial pressure of methanol was 59 kPa, the total flow rate of methanol plus helium being 71 mmol h^{-1}. The effluent gas was analyzed automatically every 3.5 min with a gas chromatograph equipped with a 2-m-long SE-30 column and a thermal conduction detector. In the pressure- and temperature-jump experiments, the flow rate of methanol and the reaction temperature shifted to a new steady state after 3 min and 45 s, respectively (*5*).

Scanning electron micrographs (SEM) of the samples were taken using a Hitachi S-510 instrument operating at 15 kV. Electron probe microanalysis (EPMA) of the samples was carried out using a JEOL JSM-35CF equipped with EDX facility, operating at 25 kV. X-ray diffraction (XRD) patterns were recorded on a Rigaku Geigerflex 2013, operating at 30 kV and 20 mA.

RESULTS AND DISCUSSION

Effect of Preheating Temperature

As described above, in the reaction of methanol with silicon having thick SiO_2-overlayers, the temperature of preheating a silicon-catalyst mixture had a great effect on the reactivity of silicon and the selectivity for trimethoxysilane (*1*). Here, the effect of the temperature of preheating of the mixture on the reactivity of the silicon washed with a HF solution was examined.

After the silicon–copper(I) chloride mixture (Cu = 10 wt%) was preheated at a given

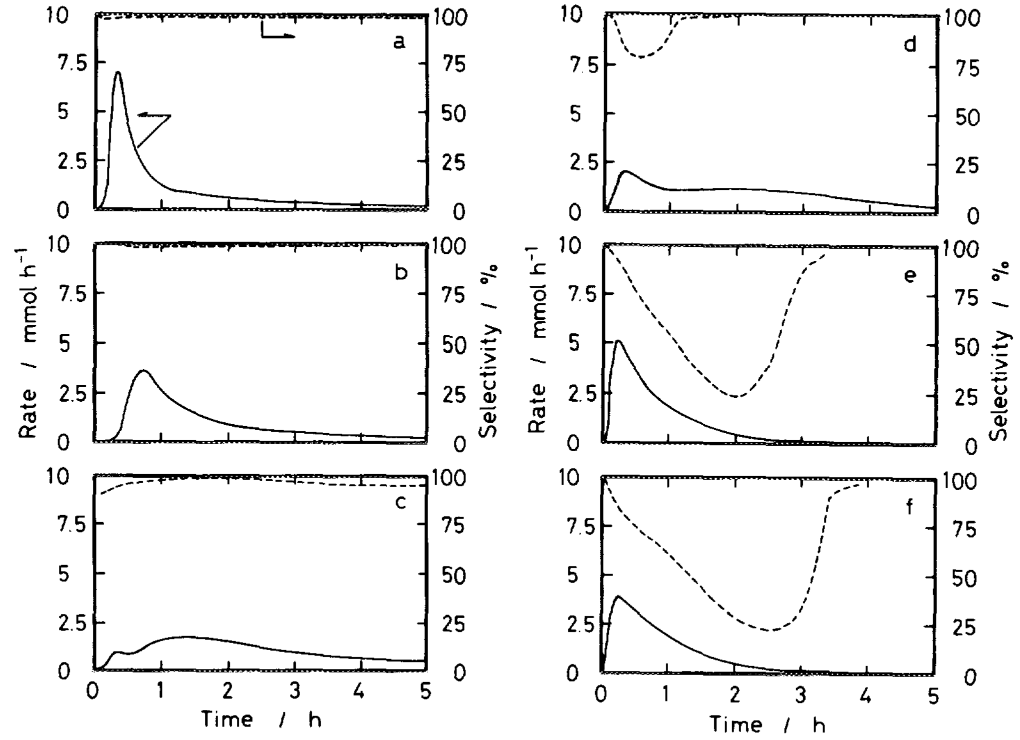

FIG. 1. Effect of the preheating temperature on the change in the rate of methoxysilanes ($(CH_3O)_3SiH$ and $(CH_3O)_4Si$) formation and the selectivity for trimethoxysilane with time. Preheating temperature = 513 K (a), 553 K (b), 603 K (c), 623 K (d), 673 K (e), and 723 K (f); preheating time = 1 h; Cu = 10 wt%. Reaction temperature = 513 K; CH_3OH = 59 kPa. Solid and dashed lines represent the rate of methoxysilane formation and the selectivity for trimethoxysilane, respectively.

temperature for 1 h, methanol (59 kPa) was fed to the reactor at 513 K. Figure 1 shows the changes in the rate of methoxysilane ($(CH_3O)_3SiH$ and $(CH_3O)_4Si$) formation and in the selectivity for trimethoxysilane with reaction time. When the preheating temperature was 513 K (Fig. 1a), the rate increased just after starting a methanol feed and, beyond a maximum, it decreased. At the preheating temperature of 553 K (Fig. 1b), an induction period in the rate curve became apparent, and the position of the rate maximum shifted to later reaction time. With the low preheating temperatures, trimethoxysilane was formed with high selectivity (>98%) throughout the reaction.

At the preheating temperature of 603 K (Fig. 1c), the rate maximum shifted further to a later reaction time of 1.2 h, with an earlier and lower rate maximum appearing at 0.25 h. At 623-K preheating, the later maximum shifted further to an even later reaction time, while the earlier maximum at 0.25 h became more evident (Fig. 1d). The later maximum seems to correspond to the one formed at lower preheating temperature. The shift of the rate maximum to a later reaction time indicates that the surface state changes with preheating temperature. The appearance of the earlier maximum suggests the development of a new type of the reactive surface.

At higher preheating temperatures of 673 and 723 K (Figs. 1e and 1f), only one rate maximum appeared at 0.25 h. The selectivity for trimethoxysilane became very low with increasing reaction time except at the very end of the reaction.

These results indicate the presence of two types of reactive sites on the silicon surface. One appears at lower preheating temperatures and gives a high selectivity for trimethoxysilane. The other appears at higher preheating temperatures and gives a low selectivity for trimethoxysilane.

The silicon conversion at 5 h of reaction time, calculated by the integration of the rate curves in Fig. 1, was 88, 78, 75, 88, 74, and 74% for the mixtures preheated at 513, 553, 603, 623, 673, and 723 K, respectively. In this order of preheating temperature, the overall selectivity for trimethoxysilane during 5 h was 98, 99, 97, 96, 66, and 64%. As mentioned above, lower preheating temperature favors the high selectivity for trimethoxysilane.

Voorhoeve (*6, 7*) studied the effect of pretreatment of silicon copper(I) chloride mixture on the formation of Cu_3Si phase and concluded that pretreatment at 673 K is effective for obtaining high reactivity toward methyl chloride, since high temperature is advantageous to convert effectively copper into the Cu_3Si phase, which was supposed to be the active phase. The result in this study shows that this is not directly applicable to the reaction of silicon with methanol, since very high reactivity of silicon was attained by pretreatment as low as 513 K.

It must be pointed out that the effect of preheating has been studied only at greater than 620 K, since the reaction with methyl chloride was usually carried out only above 620 K.

Effect of Preheating Time

As mentioned in the preceding section, there seem to be two types of reactive sites on the silicon surface, as shown by two maxima in the rate–time curves. The ratio of the two types of reactive sites depended on the temperature of preheating the silicon–catalyst mixture. Time of preheating also affects the ratio of the two types of reactive sites.

The reaction was started by feeding methanol (59 kPa) to the silicon–catalyst mixture at 513 K after the mixture had been preheated for 0.17, 0.5, 1.0, 5.0, or 12 h at 603 K. An experiment without preheating was also carried out. Results are shown in Fig. 2.

When no pretreatment was carried out, the reaction occurred immediately upon feeding methanol (Fig. 2a). As shown in Figs. 2b and 2c, upon increasing the preheating time, the induction time became apparent with the shift of the rate maximum to later reaction time. When the preheating time was 1 h (Fig. 2d), two rate maxima were observed. When the preheating time was further prolonged, the rate curve had a single maxima at 0.25 h (Figs. 2e and 2f).

The silicon conversions after 5 h of the reaction at 513 K with preheating at 603 K for 0, 0.17, 0.5, 1.0, 5.0, and 12 h were 83, 91, 67, 75, 83, and 74%, respectively.

The selectivity for trimethoxysilane was very high (>98%) for silicon with preheating time of less than 1 h. On the other hand, the selectivity was depressed upon prolonged preheating.

These results show that the effect of increase in the pretreating time on the reaction was similar to that of the raising pretreatment temperature. Thus, low-severity treatment gives the reactive sites with high trimethoxysilane selectivity, while high-severity pretreatment gives those with low trimethoxysilane selectivity.

Surface Analysis of Silicon

In the reaction of silicon with methyl chloride, it is a usual practice to preheat silicon–catalyst mixtures at 620–670 K prior to the reaction (*6–9*). The preheating promotes the formation of silicon–copper alloys such as Cu_3Si, which are believed to be a prerequisite for the reaction to start (*6, 7*). It is rather surprising that the reaction of the HF-washed silicon with methanol starts with mild preheating or without any preheating.

The mixtures of copper(I) chloride and silicon grains, which had been washed with

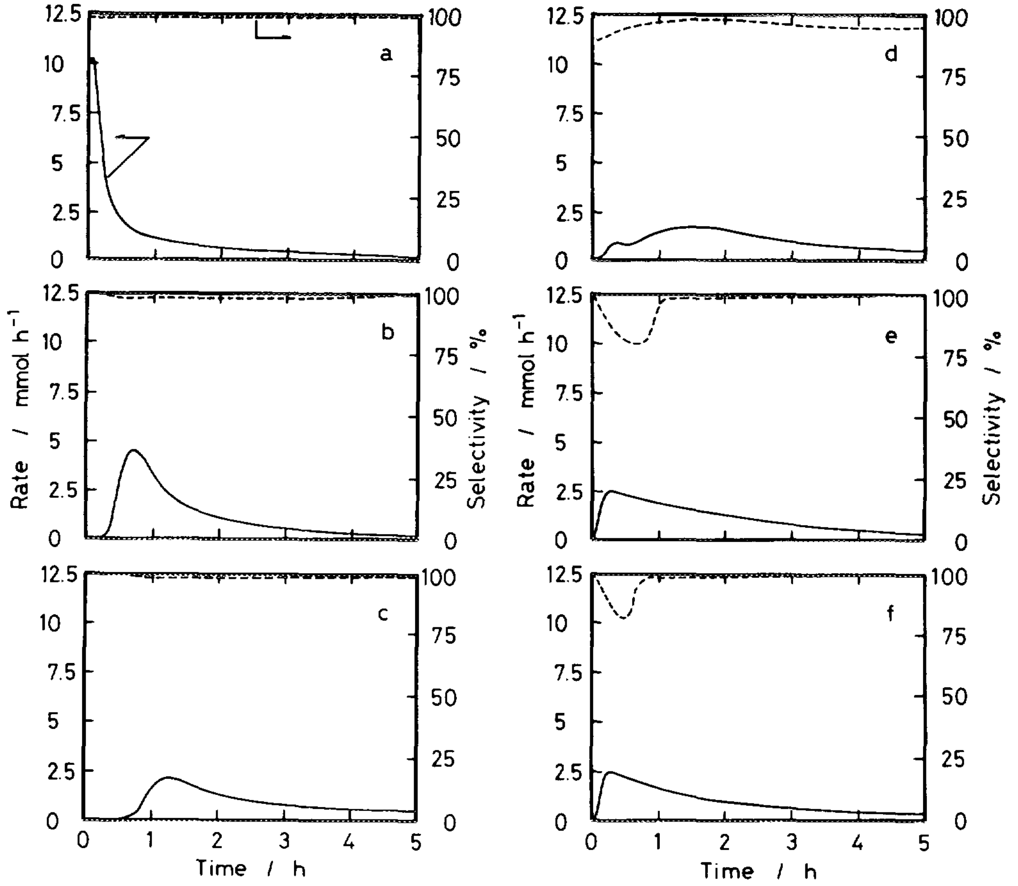

FIG. 2. Effect of the preheating time on the change in the rate of methoxysilanes ($(CH_3O)_3SiH$ and $(CH_3O)_4Si$) formation and the selectivity for trimethoxysilane with time. Preheating temperature = 603 K; preheating time = 0 h (a), 0.17 h (b), 0.5 h (c), 1 h (d), 5 h (e), and 12 h (f); Cu = 10 wt%. Reaction temperature = 513 K; CH_3OH = 59 kPa. Solid and dashed lines represent the rate of methoxysilane formation and the selectivity for trimethoxysilane, respectively.

HF, were examined by an X-ray diffraction (XRD) after heating the mixture at 513, 603, 623, and 723 K for 1 h. No new phases were observed from the mixtures heated at below 603 K (Fig. 3a). On the other hand, a Cu_3Si phase (d = 0.201 and 0.203 nm) was observed for the mixtures heated at 623 K (Fig. 3b). The diffraction peaks due to the Cu_3Si phase were more intense at the 723-K heating temperature (Fig. 3c). When heating time was prolonged to 12 h at 603 K, the Cu_3Si phase was observed (Fig. 3d), though it was not observed upon 1 or 5 h heating.

Weber *et al.* (*10*) reported that the Cu_3Si phase formed on the silicon surface can be washed away by a successive treatment with aqueous solutions of nitric acid and sodium hydroxide and that pits are formed on the silicon surface where the Cu_3Si phase was located. The formation of the Cu_3Si phase was examined using this technique. The method of Weber *et al.* (*10*) was slightly modified; the wafers were treated with aqueous ammonia before treating with nitric acid and then with sodium hydroxide, simply because photos with higher contrast were obtained in this way.

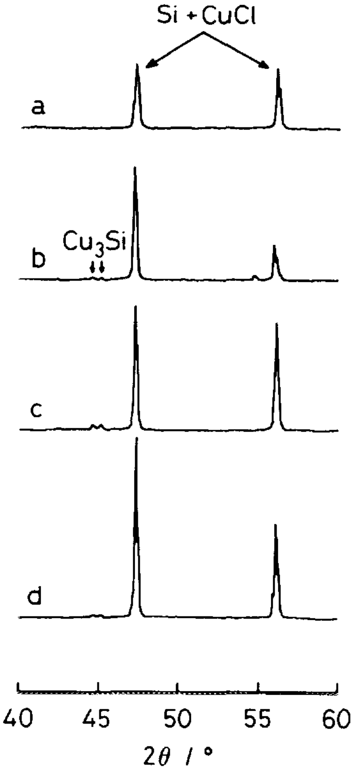

FIG. 3. XRD patterns of Si–CuCl mixtures heat-treated under various conditions. Heat-treatment conditions: (a) 603 K for 1 h, (b) 623 K for 1 h, (c) 723 K for 1 h, and (d) 603 K for 12 h. Cu = 10 wt%.

Silicon wafers were embedded in the silicon–copper(I) chloride mixture and heated in a helium stream at 493, 623, and 723 K for 1 h. As shown in Fig. 4a, essentially no change in the morphology of silicon surface was observed upon heating the mixture at 493 K. On the other hand, when heating was carried out at 623 and 723 K, pits were observed on the silicon surface after the washing procedure, the number of pits being larger at higher heat treatment temperature (Figs. 4b and 4c). These results show that patches of a Cu–Si alloy phase are formed and scattered on the silicon surface by heat treatment of the silicon–catalyst mixture. As described above, the patches were not detected upon the treatment at 493 K. The change in the surface morphology conforms to the result of the XRD study. The scattered formation of Cu_3Si on the silicon surface upon reaction with copper(I) chloride above 695 K has been reported by Weber and co-workers (*10–12*).

The microanalysis of the surface of silicon wafers heated in a bed of copper(I) chloride–silicon mixture under a severe (723 K) or mild (493 K) condition was made by an electron probe microanalysis (EPMA). Figure 5a shows an electron micrograph of silicon wafer heated at 723 K for 1 h. Patches are scattered on the surface. The size of the patches varied in the range 10–200 μm. The EPMA pattern from the area without the patches showed no signals other than silicon, as shown in Fig. 5b. Examples of EPMA patterns from the patches are shown in Figs. 5c and 5d. In the case of Fig. 5c, the pattern mainly consists of signals of copper and chlorine. The atomic ratio Cu/Cl, estimated from the relative signal intensity and relative sensitivity, was close to unity, indicating that some of the patches mainly consist of CuCl deposited on the silicon surface. In the case of Fig. 5d, the EPMA pattern consists of signals of silicon and copper, no chlorine signal being observed. This indicates that the reaction between silicon and copper(I) chloride occurs on the silicon surface to form Si–Cu alloy at 723 K, in accordance with the XRD results.

Figure 6a shows an electron micrograph of silicon wafer heated with copper(I) chloride at 493 K. In contrast to the wafer heated at 723 K, the presence of patches is not evident. Inspection by EPMA for the areas designated as (1) and (2) in Fig. 6a gave the signal patterns shown in Figs. 6b and 6c, respectively. Both patterns did not give any indication of the presence of copper or chlorine atoms on the silicon surface beyond the background level. In other words, the amount of copper and chlorine on the surface is extremely small and below the detection limit of EPMA. However, the reaction of silicon with methanol proceeds even after preheating at 493 K, indicating that a chemical interac-

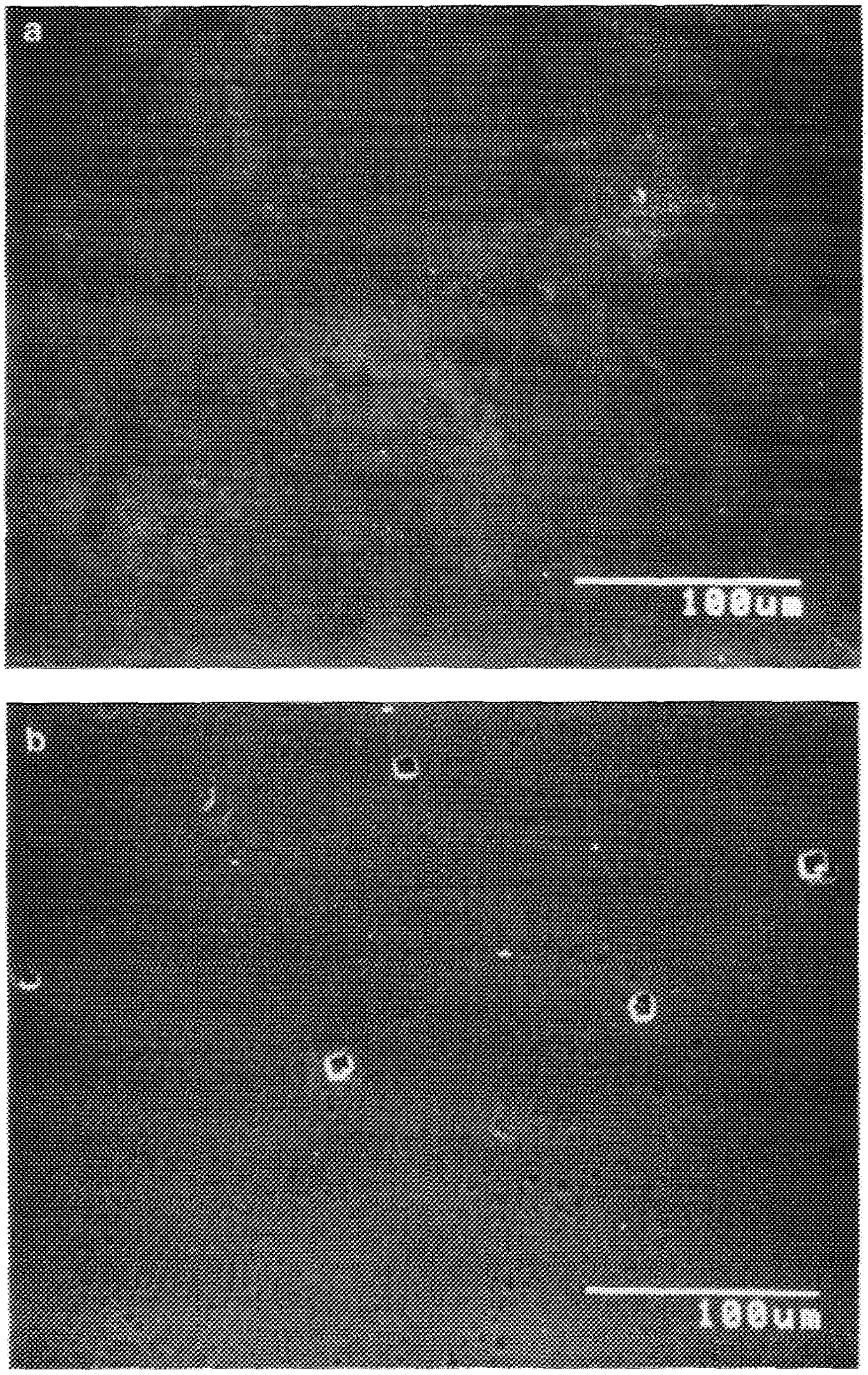

FIG. 4. Scanning electron micrograph of the silicon wafers after the preheating. Preheating temperature = 493 K (a), 623 K (b), and 723 K (c). Preheating time = 1 h; Cu = 10 wt%. The wafers were washed successively with aqueous solutions of ammonia for 15 min, nitric acid (11 mol dm^{-3}) for 1 h, and sodium hydroxide (1 mol dm^{-3}) for 1 h at room temperature. Micrographs were taken at magnification ×300.

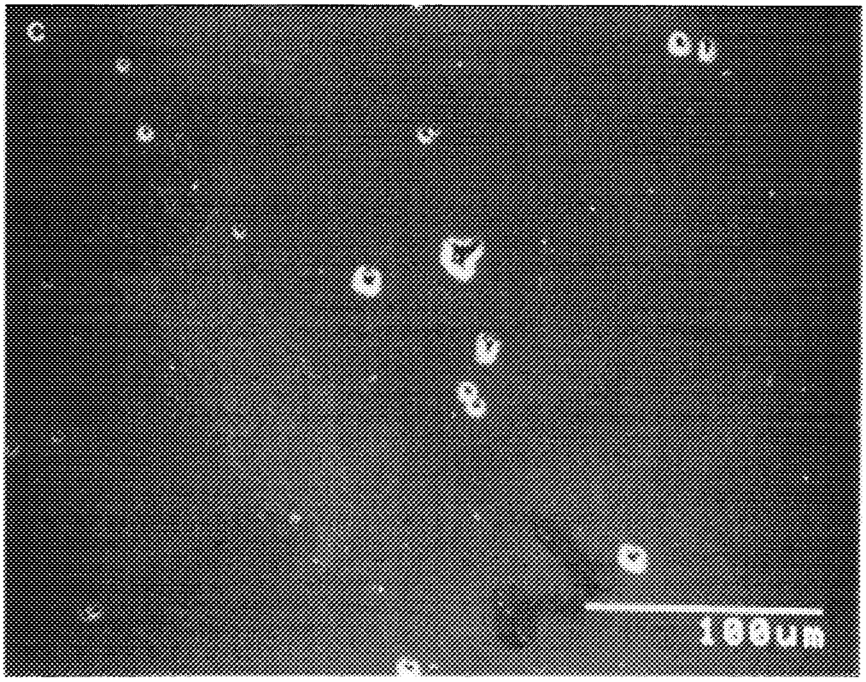

FIG. 4—*Continued*

tion exists between the silicon surface and copper(I) chloride. It is concluded that the size of the alloy formed under mild preheating conditions is too small to be detected by XRD or EPMA.

The results described above clearly show that the preheating conditions of silicon–copper(I) chloride mixtures, especially preheating temperature, affect the rate and the selectivity of the reaction and the surface state of the silicon. Therefore, we examined the details of the reactions with the mixture preheated mainly at two temperatures (723 and 513 K), which represent the preheating under high- and low-severity conditions, respectively.

Reaction Sites on Silicon Surface

In the direct synthesis of methylchlorosilanes from silicon and methyl chloride using copper(I) chloride catalyst, pits are formed on the surface of silicon upon a reaction with methyl chloride (*8*). We observed the formation of the pits in the copper(I) chloride-catalyzed reaction of methanol with silicon with SiO_2-overlayers (*1*).

As described above, the patches of the Cu_3Si phase are formed on the silicon surface after the high-temperature treatment of a silicon–copper(I) chloride mixture. On the other hand, we could not obtain any positive evidence for the formation of the alloy phase after the low-temperature pretreatment by XRD or EPMA.

Here, we examined with a scanning electron microscope how the state of the silicon surface changes upon the reaction with methanol. A silicon wafer was embedded in a mixture of silicon grains and copper(I) chloride, preheated at 723 or 493 K, and subjected to the reaction with methanol (16 kPa) at 493 K. After the reaction, the wafer was separated from the grains, and scanning electron microscopic measurements were made for the grains and the wafer.

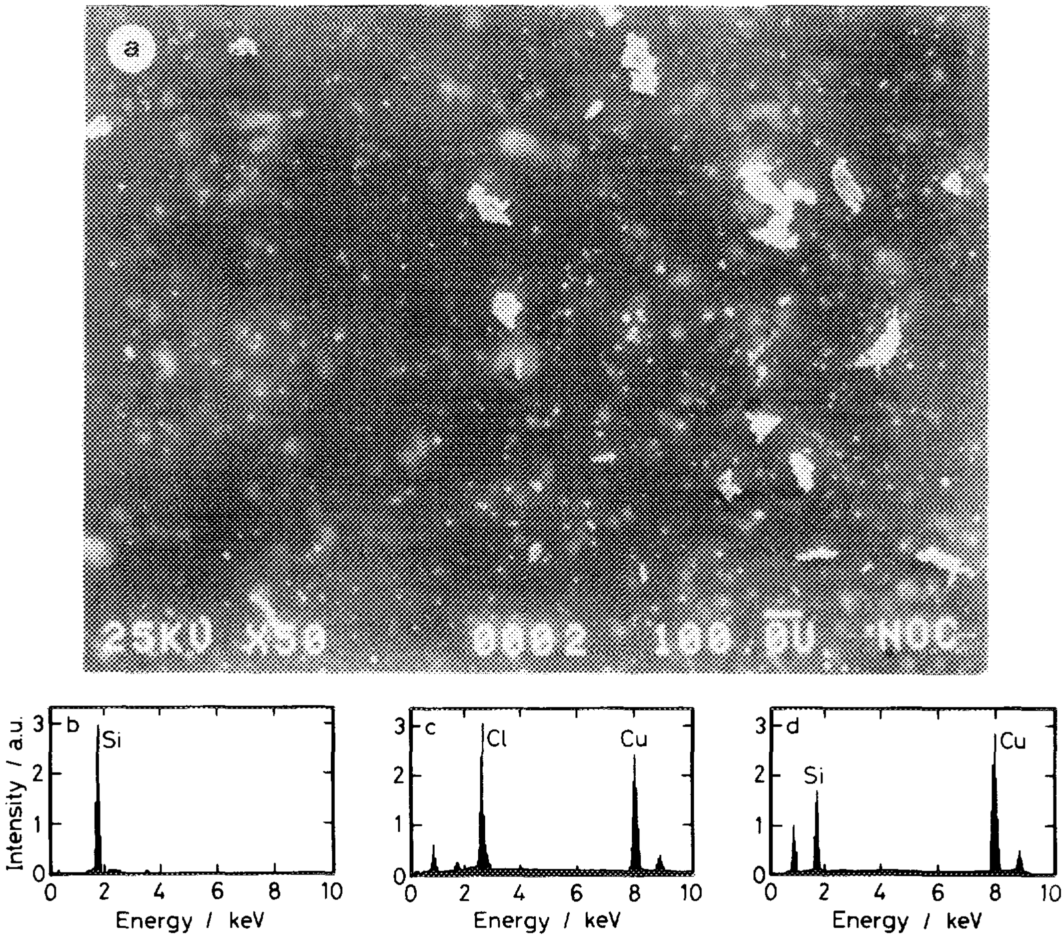

FIG. 5. Electron probe microanalysis (EPMA) of the silicon wafer preheated at 723 K. The silicon was heated with copper(I) chloride at 723 K for 1 h. (a) Electron micrograph at magnification × 50. (b) EPMA signals from the area without patches. (c) and (d) EPMA signals from the area in a patch.

(*a*) *The reaction after preheating at 723 K.* Figure 7 shows the SEM photographs of the grains and the wafer, after reaction for 183 min, when the silicon conversion reached 30%. Pits are formed both on the grains and the wafer. The shape and size of the pits on the grains and on the wafer are quite similar, indicating that the chemistry occurring on the surface is essentially the same in the two types of silicon materials.

The distribution of the size and the number of the pits on the silicon wafer was examined at various silicon conversions. Reactions were carried out at 493 K with 16 kPa of methanol pressure. The reaction was stopped at 36, 58, 91, 183, and 303 min, and the wafers were subjected to scanning electron microscopic investigation. For these reaction times, silicon conversions of the grains were 1, 5, 10, 30, and 45%, respectively. Scanning electron micrographs of the samples are shown in Fig. 8. The size of the pits increases with reaction time. At 45% conversion, some of the pits come into contact each other.

Though the size of the pits increases, the number of the pits does not change appre-

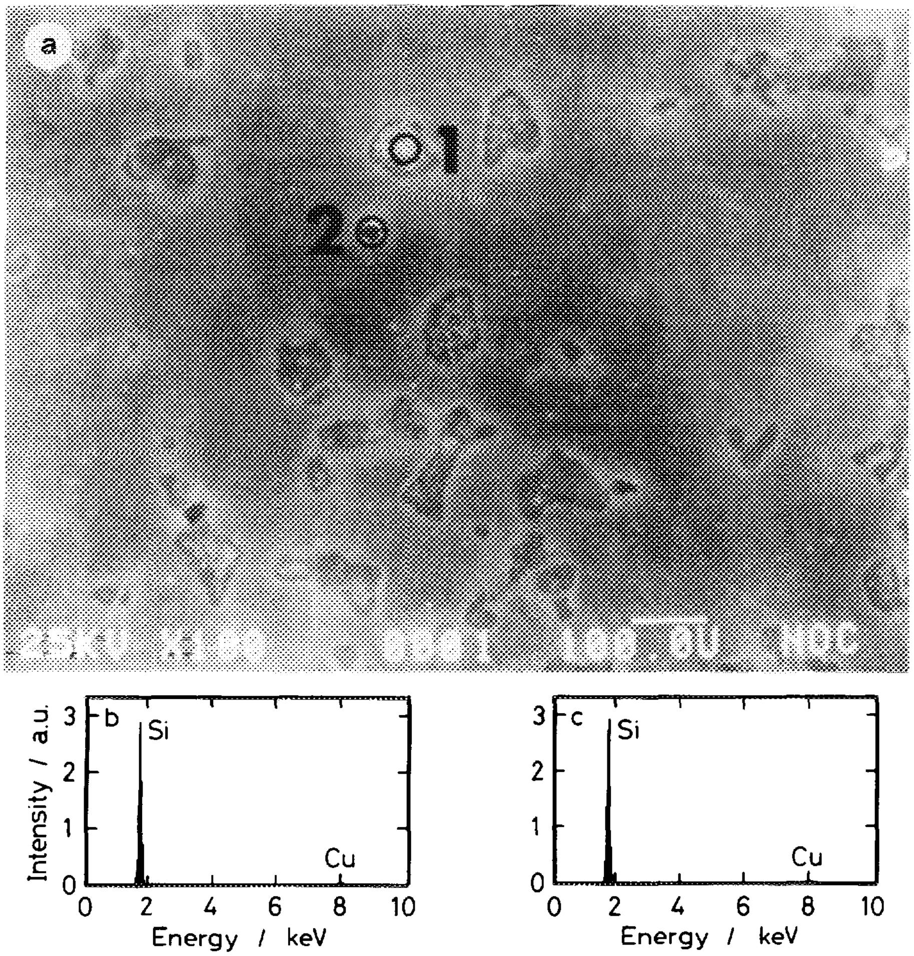

FIG. 6. Electron probe microanalysis (EPMA) of the silicon wafer preheated at 493 K. The silicon was heated with copper(I) chloride at 493 K for 1 h. (a) Electron micrograph at magnification × 100. (b) and (c) EPMA signals from the areas designated as (1) and (2) in (a), respectively.

ciably with reaction time. Thus, the number of the pits per unit area of the wafer surface was 110, 97, 109, 101, and 104 per mm^2 at silicon conversion of 1, 5, 10, 30, and 45%, respectively. This indicates that the reaction starts at a discrete area on the surface and that the silicon atoms are consumed around the area.

Distribution of the size of the pits is shown in Fig. 9. It is clear that the average size of the pits increases with reaction time and that the distribution becomes broader as reaction time increases. This indicates that part of the pits stop growing, probably due to the formation of metallic copper particles. The formation of metallic copper may be related to the decrease in the rate of silicon consumption and ultimately a low conversion of silicon. The formation of metallic copper during the reaction was confirmed by XRD. The metallic copper may also be related to lowering of the selectivity for trimethoxysilane with reaction time. We have confirmed that metallic copper functions as a catalyst for the reaction of trimethoxysilane with methanol. This point will be discussed in a forthcoming paper (*14*).

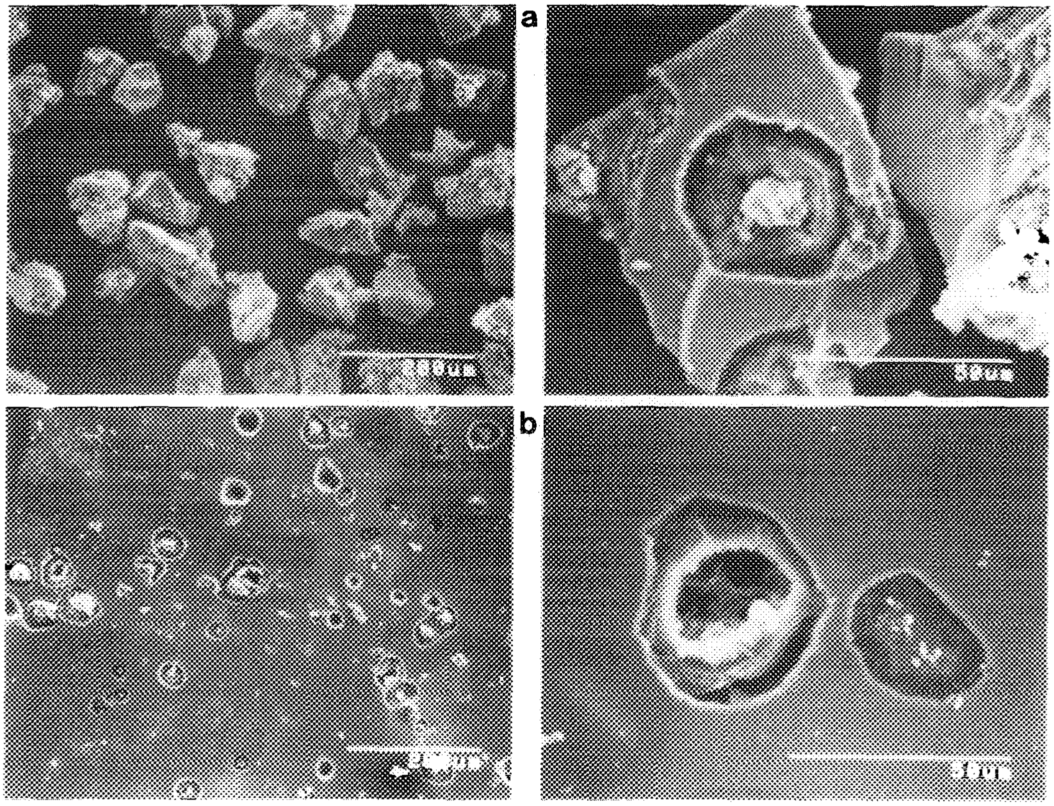

FIG. 7. Surface morphology of silicon grains (a) and silicon wafer (b) upon reaction with methanol after preheating at 723 K. Reaction temperature = 493 K; CH_3OH = 16 kPa. Si conversion = 30%. The left and the right plates were obtained at magnification ×90 and ×600, respectively.

As described above, the patches of the Cu_3Si phase are formed on the silicon surface during the preheating of the silicon-catalyst mixtures. The number of Cu_3Si patches was estimated to be 120–130 per mm^2, which is close to the number of pits formed upon the silicon–methanol reaction, indicating that the reaction starts at the Cu_3Si phase and that silicon atoms are consumed only from the surrounding area.

The Cu_3Si phase was detected by XRD after preheating at 723 K, while the rate curve had an acceleration period. There was no similarity between the change in the amount of the Cu_3Si phase with reaction time and the change in the rate curve. This shows that Cu_3Si may not be a reactive intermediate once the reaction with methanol starts. This suggests that the reaction intermediate is probably an intermetallic compound of Si and Cu, but that the Cu_3Si phase formed during the preheating is merely a source of Cu for the real reactive intermediate. Banholzer and Burrell (9) studied the surface of silicon in the silicon–methyl chloride reaction by Auger spectroscopy. The estimated value of the Cu/Si ratio in the active region varied from <0.5 to 2, with the majority of the values near 1. From this, they questioned the hypothesis that Cu_3Si is the active species in the silicon–methyl chloride reaction.

An electron probe microanalysis was made of pits on the silicon surface. An image (1300 ×) of an area where the small pits are located is shown in Fig. 10a. The EPMA

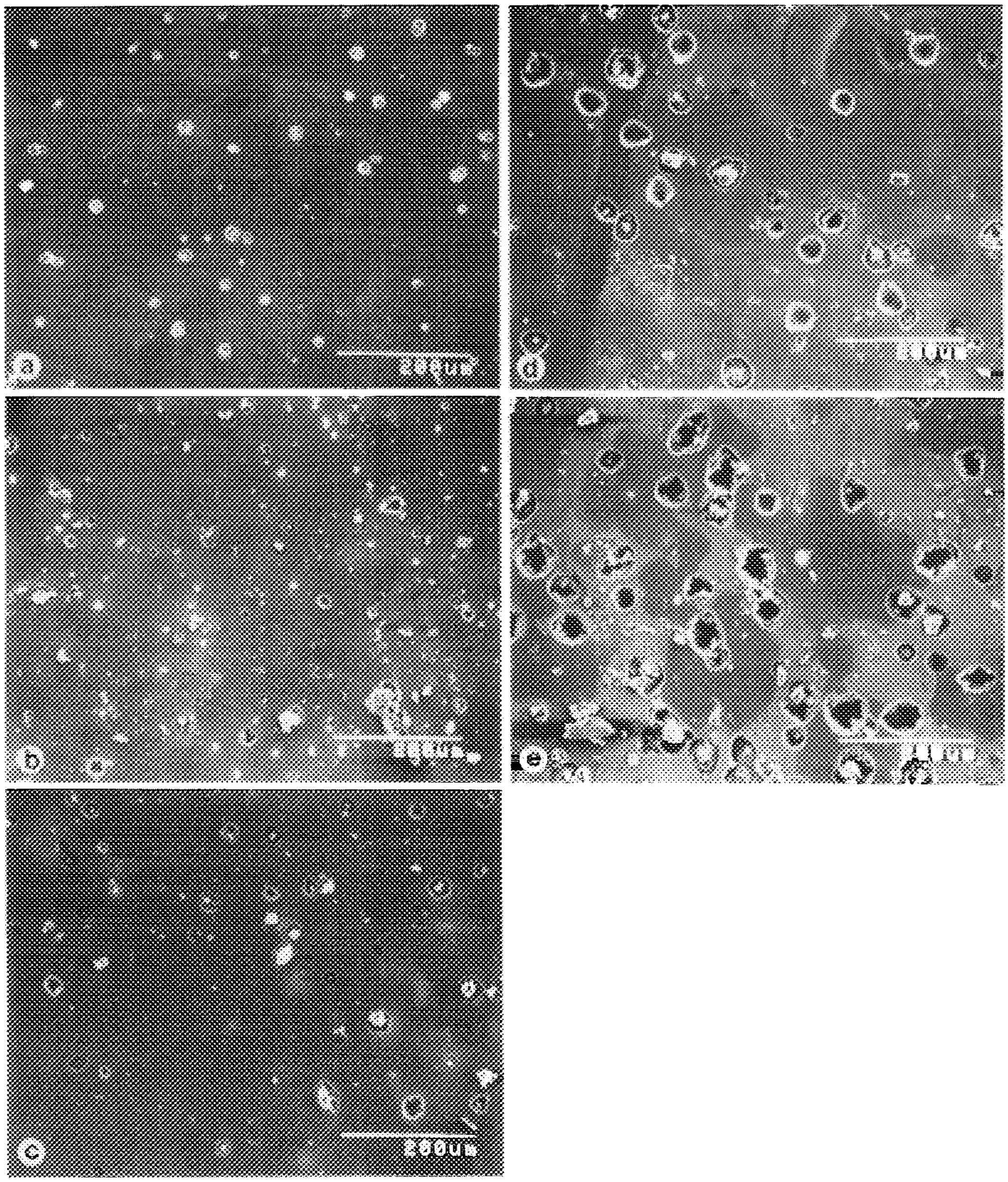

FIG. 8. Change in the distribution of pits on the surface of silicon wafer with silicon conversion. Reaction conditions are the same as those in Fig. 7. Silicon conversion = 1% (a), 5% (b), 10% (c), 30% (d), and 45% (e). The plates were obtained at magnification ×90.

signals from the center of the pits are shown in Figs. 10b and 10c. Both of the spectra consist of Cu and Si signals. A Cl signal was not detected at all. The signal due to copper atoms were not detected at the flat part of the surface. These results conform with the idea that the reaction starts around the area where the Cu_3Si phase is located.

The formation of the alloy phase by a transport of copper(I) chloride onto silicon

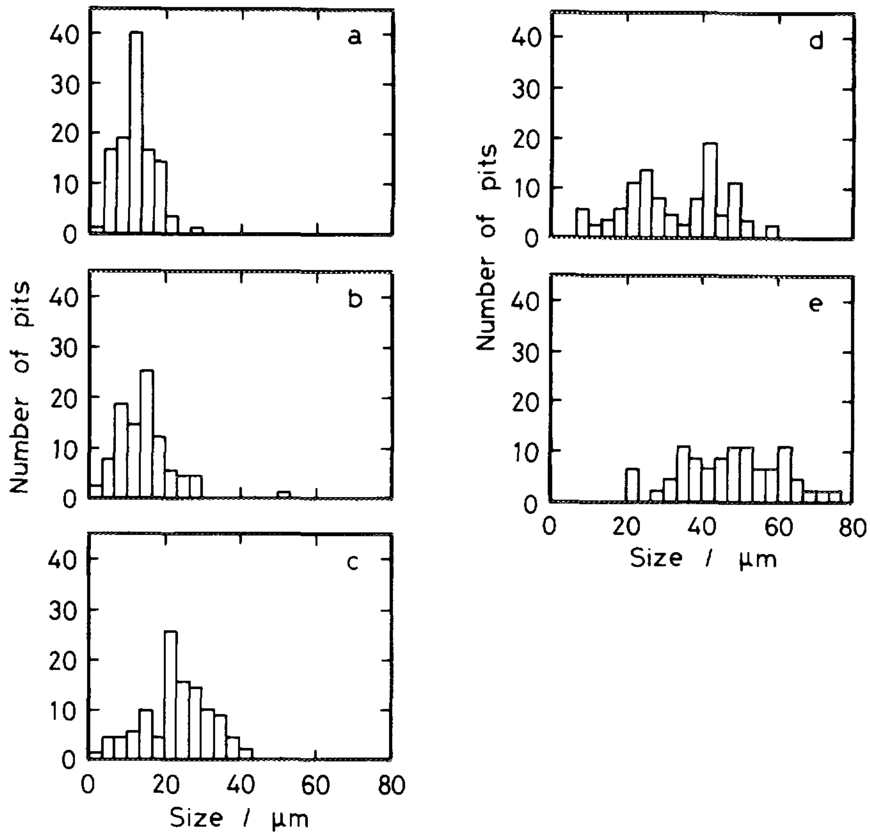

FIG. 9. Size distribution of pits on the silicon surface during the silicon–methanol reaction. Experimental conditions and notation (a)–(e) are the same as those in Fig. 8.

surface from the vapor phase has been reported (*4, 10, 13*). To confirm the transfer of copper(I) chloride through the gas phase in the present system, the following experiment was carried out. Copper(I) chloride was placed at 1.2 cm upstream from the bed of silicon grains and heated in a helium stream at 723 K for 1 h. Then, methanol 55 kPa was fed at 513 K. The reaction proceeded. When the reaction was stopped at a 10% conversion of silicon, the formation of pits was observed. The number and the size of the pits are close to those in the reaction where a mixture of silicon and copper(I) chloride was subjected to the reaction.

(*b*) *The reaction after preheating at 493 K.* A mixture of silicon grains, a silicon wafer, and copper(I) chloride grains was packed in a fixed-bed reactor. The mixture was preheated at 493 K and methanol was fed at the same temperature. The reaction was stopped when the silicon conversion reached a certain value.

Figure 11 shows the micrographs of the silicon wafers at silicon conversions of 0.01, 0.4, 0.7, 4.8, 15.1, and 43.5%. These conversions correspond to the reaction for 24.5, 38.5, 42, 52.5, 80.5, and 301 min, respectively.

As shown in Fig. 11, pits were observed even at a conversion of 0.01%. Upon increasing the conversion to 0.4%, the number of pits sharply increased (Fig. 11b), indicating that the reaction sites were newly formed after feeding methanol. The number

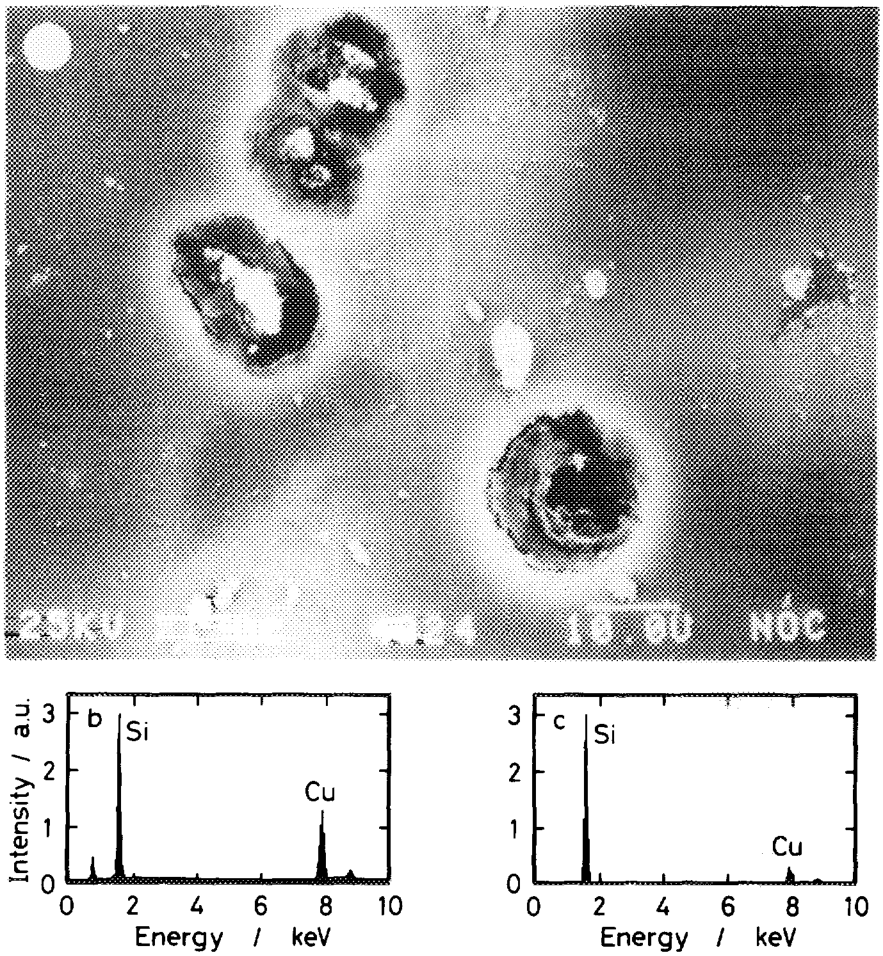

FIG. 10. Electron probe microanalysis of the silicon wafer preheated at 723 K and exposed to methanol. Reaction temperature = 493 K; CH_3OH = 18 kPa. Si conversion = 0.3%. (a) Electron micrograph at magnification × 1300. (b) and (c) EPMA signal patterns from the center of pits.

of pits per unit surface is far greater than that of the reaction after high-temperature pretreatment. The pits grew in size as the conversion increased to 0.7% (Fig. 11c), and pits merged with each other. As a result, most of the surface area became reactive. This is also a very sharp difference from the reaction after the high-temperature treatment, where the reactive areas are scattered on the surface.

As the conversion increased (Figs. 11d and 11e), the number of smaller pit decreased and the surface became more flat, except for the area of large pits. At 15.1% conversion, a skin of the silicon wafer was reacted away in parts of the wafer (not shown in Fig. 11e). At 43.5% conversion (Fig. 11f), the surface became very rough, probably because of a repeated irregular stripping of the skin of the wafer.

The high density of small pits on silicon surface formed upon the reaction with methanol indicates that the Si–Cu colony existed on the surface even at low pretreatment temperature. The reason that the alloy phase was not observed by EPMA is probably due to smallness of the phase. The reaction with methanol magnifies the small patches into

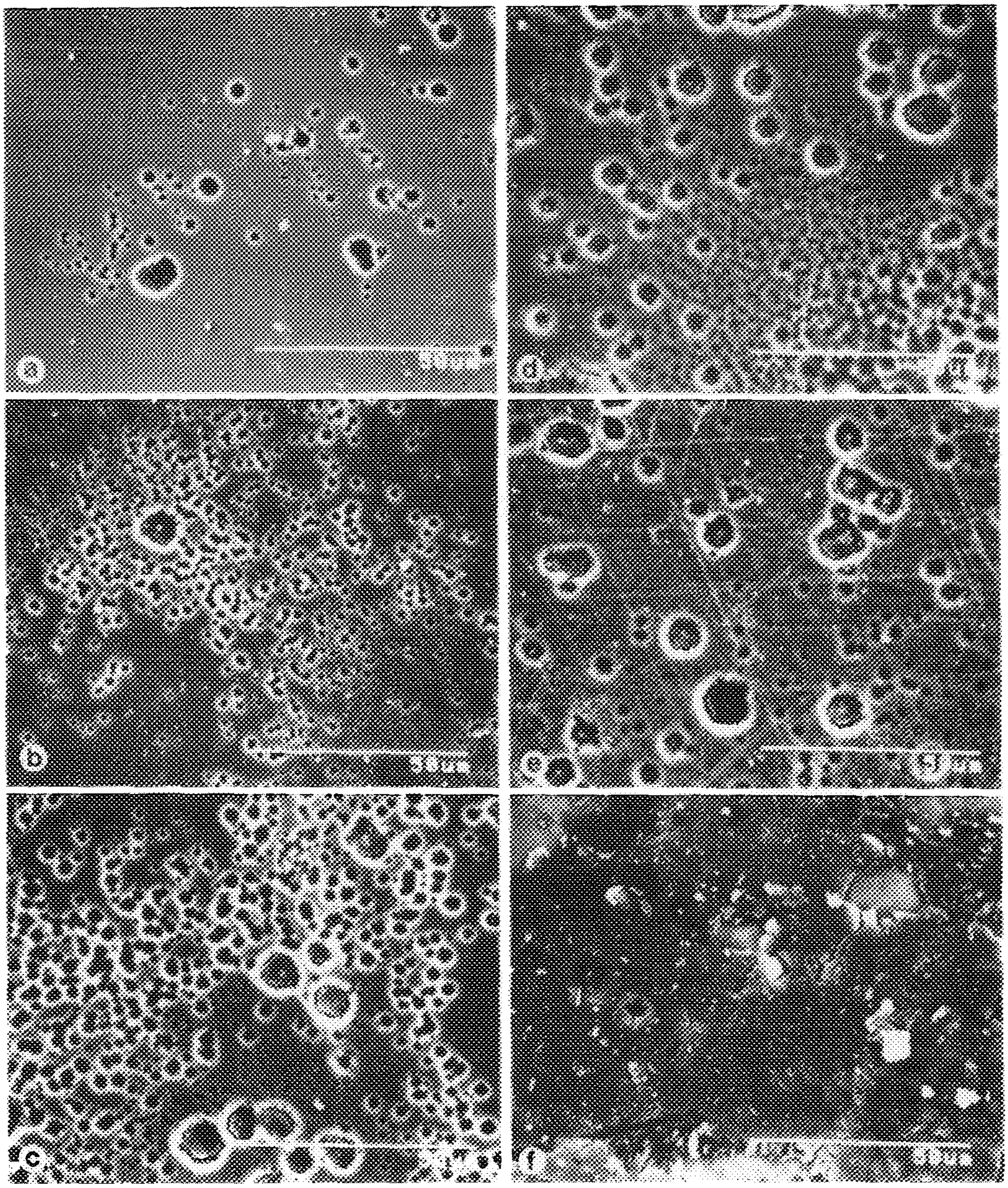

FIG. 11. Scanning electron micrographs of silicon wafers reacted with methanol up to various silicon conversions after preheating at 493 K. Preheating temperature = 493 K; Cu = 10 wt%. Reaction temperature = 493 K; CH_3OH = 27 kPa. Silicon conversion = 0.01% (a), 0.4% (b), 0.7% (c), 4.8% (d), 15.1% (e), and 43.5% (f). The plates were obtained at magnification ×600.

pits with observable size due to the consumption of silicon atoms around the patches. The micrographs of the silicon grains are shown in Fig. 12. Though the number and size of pits on the grains changes from grain to grain, the micrograph of a typical grain was selected for a conversion level.

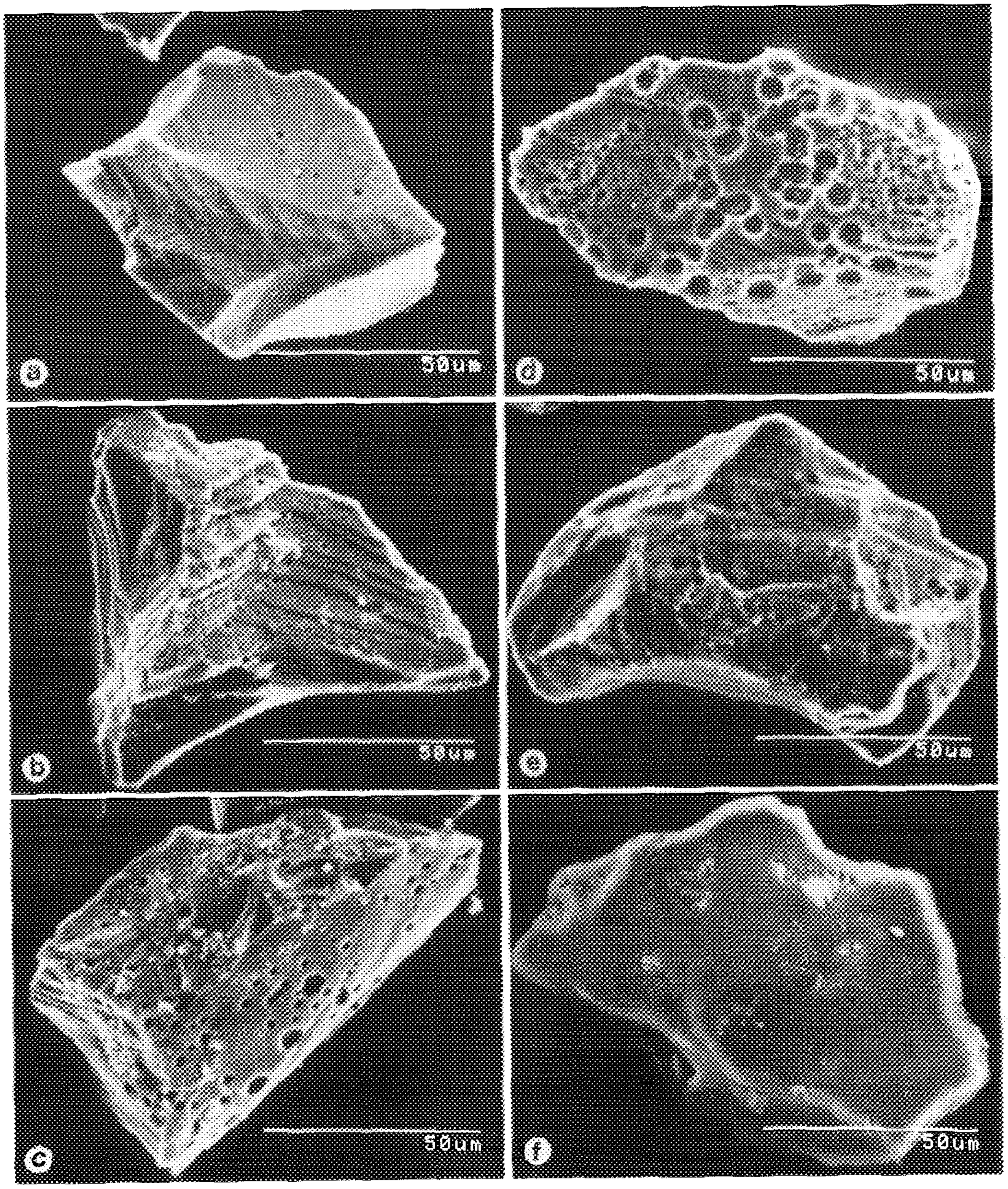

FIG. 12. Scanning electron micrographs of silicon grains reacted with methanol up to various silicon conversions after preheating at 493 K. Conditions of sample preparation and silicon conversions are same as those in Fig. 11. The plates were obtained at magnification ×600.

At conversion of 0.01%, the formation of small pits are seen (Fig. 12a). As seen in Fig. 12b, the number of pits increased when the conversion increased to 0.4%. The size of the pits increased with increasing silicon conversion (Figs. 12c and 12d). At conversion of 4.8%, every part of the surface became a reacting area (Fig. 12d). This tendency is more clearly seen at higher conversion levels (Fig. 12e). As the result, the number of pits decreases and the surface becomes smooth. When the conversion was increased to 43.5%, most of the pits disappeared and the surface became very smooth (Fig. 12f). This means that silicon atoms are consumed homogeneously at all areas of the surface at this stage. This change in the surface morphology of the grains with silicon conversion is very similar to that found on the surface of the water, except for the stripping of surface skins found only on the wafers.

As described above, it is shown that copper(I) chloride is easily transferred onto the silicon surface through the gas phase during the high-temperature pretreatment. In order to know if this is the case also for the low pretreatment conditions where the vapor pressure of copper(I) chloride is very low, the following experiments were carried out. A bed of copper(I) chloride (0.200 g) was placed at 1.2 cm upstream from a bed of silicon grains (0.168 g) in the reactor. The beds were heated at 513 K for 1 h under a helium stream and then methanol (55 kPa) was fed to the reactor at 513 K. Silicon did not react with methanol at all. As described earlier, when a mixture of copper(I) chloride and silicon grains was placed in the reactor, silicon reacted with methanol up to an almost complete conversion under the same reaction conditions. These results show that a long-range vapor-phase transport of copper(I) chloride onto the silicon surface does not occur in this temperature range and that silicon grains and copper(I) chloride grains must be present in close proximity to each other for the formation of the reaction sites. Since the concentration of pits formed is greater than the estimated concentration of the contact points of the two kinds of grains, most of reactive sites are not formed by a direct contact of the grains. The actual mechanism of copper transport from copper(I)-chloride grains to the silicon surface is not clear at this moment. Since the induction period depends on methanol pressure and the number of pits increases with reaction time, it is plausible that adsorbed methanol facilitates the transport of copper species. At 0.3% conversion, the pits were examined by an electron probe microanalysis. Copper atoms were not detected by this technique, indicating that the size of the chemical species containing copper is still too small to be detected.

Kinetics of the Reaction

As described above, the state of the silicon surface sharply depends on the preheating temperature of the Si–CuCl mixtures. We examined the kinetics of the reactions with preheating temperatures at 723 and 513 K to see if the change in the surface state is reflected on the reaction kinetics.

(*a*) *The reaction after preheating at 723 K.* After preheating a silicon–copper(I) chloride mixture at 723 K, methanol (16, 29, 59, and 87 kPa) was fed to the reactor at 513 K. Figure 13 shows the change in the rate of methoxysilanes formation with reaction time for each methanol pressure. At 87 and 59 kPa methanol pressure, the rate increased immediately after methanol was fed (Figs. 13a and 13b). When methanol pressure was reduced (Figs. 13c and 13d), the initial rate increase slowed and a short induction period appeared. This shows that methanol participates in the formation of reactive sites. The lower the methanol pressure, the lower the overall conversion of silicon.

At every methanol pressure, the selectivity for trimethoxysilane was 100% only at the beginning and decreased sharply as the silicon conversion increased, indicating that the state of the catalyst changes as the reaction proceeds. The selectivity increased in the final stage of the conversion.

The rate of silicon consumption may be a product of the number of the reactive sites and the rate of reaction per reactive site. Since the number of the reactive sites (or area) changes with reaction time, kinetics for the rate per reactive site cannot be obtained under ordinary reaction conditions. In order to eliminate the effect of the change in the reactive sites, a pressure-jump

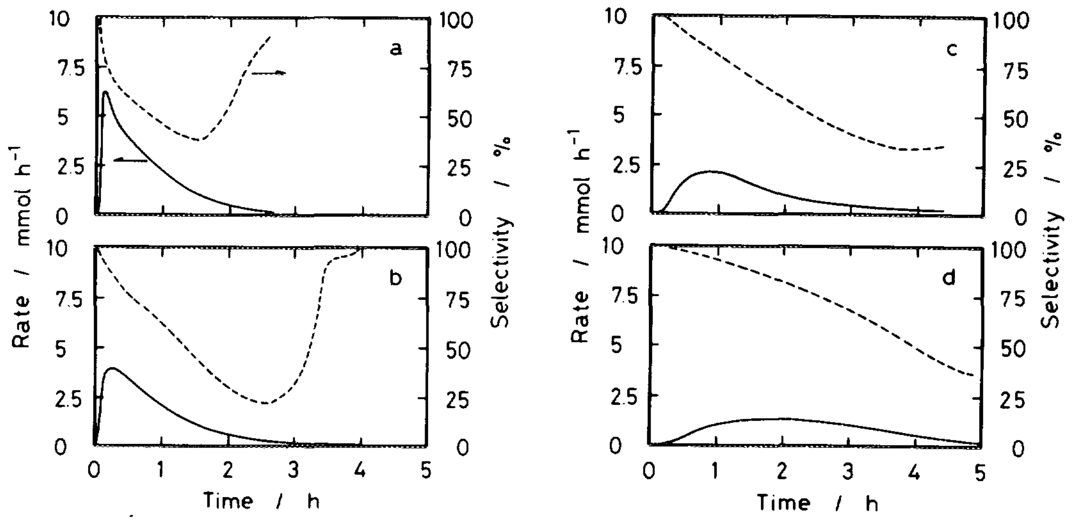

Fig. 13. Change in the rate of methoxysilanes formation and the selectivity with time at various methanol pressures. Preheating temperature = 723 K; Cu = 10 wt%. Reaction temperature = 513 K; CH_3OH = 87 kPa (a), 59 kPa (b), 29 kPa (c), and 16 kPa (d).

method was employed. The partial pressure of methanol was quickly changed during a run. The rate change just before and after the pressure change may be ascribed to the pressure dependence of the reaction rate per reactive site, since the number of reactive sites (or area) does not change immediately after the pressure jump. The reaction was started at methanol pressure of 57 kPa, and during the run methanol pressure was changed stepwise to another pressure (P_1). After a certain time, the pressure was again changed stepwise back to 57 kPa. A typical experimental run is shown in Fig. 14, where P_1 is 85 kPa. The rate changed sharply upon the stepwise change of methanol pressure. The pressure P_1 was varied and the time at which the pressure was jumped was also changed. The logarithmic ratio of the rates before and after the pressure jump (relative rate) was plotted against the logarithm of pressure P_1 (Fig. 15). The reaction order with respect to methanol was estimated to be 1.4. This indicates that the reaction rate is determined by a chemical process involving methanol and that neither the diffusion of silicon atoms to the reaction sites nor the formation of a silicon–copper intermetallic species is a rate-determining step in this gas–solid reaction.

The temperature dependence of the reaction rate was also measured by a temperature-jump method. An example is shown in Fig. 16. The logarithm of the relative rate was plotted against the reciprocal of the re-

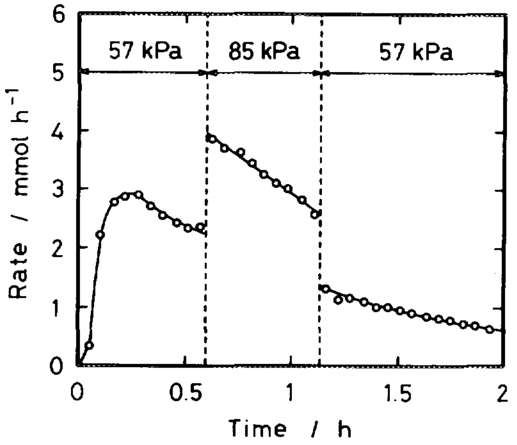

Fig. 14. Effect of stepwise change in methanol pressure on the reaction rate. Reaction temperature = 513 K; reaction was started at 57 kPa of methanol pressure and the pressure was changed stepwise to 85 kPa and afterwards back to 57 kPa.

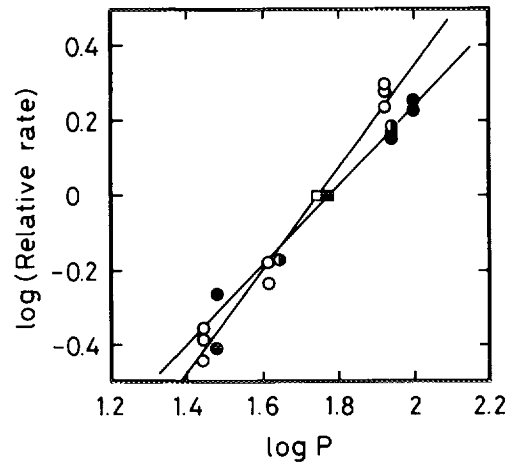

FIG. 15. Dependence of the relative rate on methanol pressure. (○) preheating at 723 K and reaction at 513 K, (●) preheating at 493 K and reaction at 493 K, and (◑) no preheating and reaction at 463 K. Rates at 57 kPa (□) are taken as unity for the reaction with 723-K preheating, and those at 59 kPa (■) for the reactions with the 493-K preheating and without the preheating.

action temperature. The activation energy thus determined was 44 kJ mol^{-1}, when the pretreatment was done at 723 K.

The number of the pits formed on the silicon surface did not change with methanol pressure, though the time course drastically changes. This again shows that methanol does not change the number of reactive areas, but that it participates in converting the Cu_3Si phase to the reactive state.

(*b*) *The reaction after preheating at 493 K.* After the silicon–copper(I) chloride mixture was heated in a helium stream at 493 K, methanol was fed to the reactor at 493 K. Figure 17 shows the change in the rate of methoxysilane formation with reaction time at various methanol pressure. As in the case of high-temperature pretreatment, methanol pressure affects the induction time, but the effect is more significant at the lower pretreatment temperature. At 98 kPa methanol pressure, the rate increased immediately after methanol was fed (Fig. 17a). With decreasing methanol pressure (Figs. 17b–17f), the initial rate increase slowed and eventually a long induction period appeared. The reciprocal of the induction period may be a measure of the rate of reactive-site formation on the silicon surface. As shown in Fig. 18, the reciprocal of the induction period ($1/t_{ind}$) depended greatly on methanol pressure. These results show that methanol participates in the formation of reaction sites on the silicon surface.

The pressure-jump method revealed that the rate per reaction site is first-order with respect to methanol pressure, as shown in Fig. 15, in which are included the results of the reaction conducted at 493 K without preheating. The reaction order is different from that for the reaction after the high-temperature (723 K) pretreatment. This difference indicates that the nature of reactive sites depends on the pretreatment conditions of the silicon–catalyst mixture.

The silicon–methanol reactions were carried out at various temperatures after a silicon–catalyst mixture was heated in a helium stream at 513 K for 1 h. The results are shown in Fig. 19. The reaction rate was sharply increased just after methanol was fed to the reactor. Almost complete conversion of silicon was attained at 513 K. As the

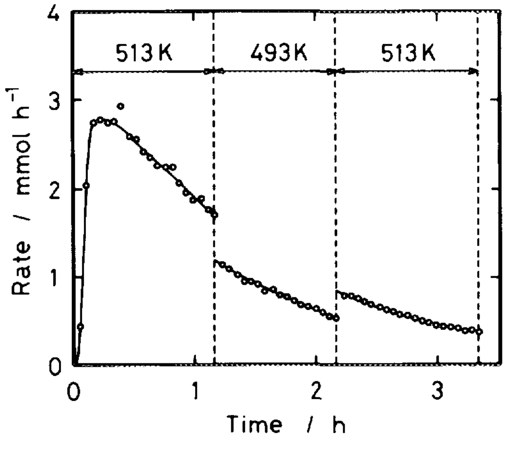

FIG. 16. Effect of stepwise change in reaction temperature on the time course of reaction rate. CH_3OH = 57 kPa; reaction was started at 513 K and the reaction temperature was changed stepwise to 493 K and afterwards back to 513 K.

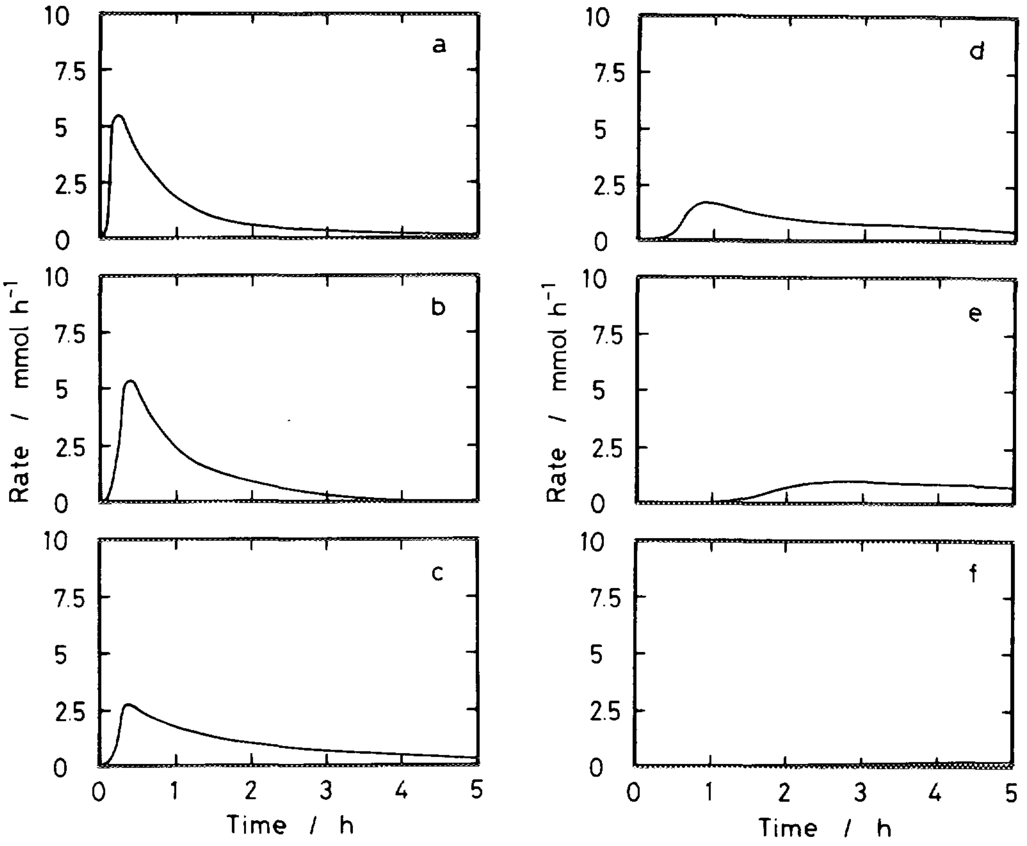

FIG. 17. Effect of methanol pressure on the change in the rate of methoxysilanes ($(CH_3O)_3SiH$ and $(CH_3O)_4Si$) formation with time. Preheating temperature = 493 K; Cu = 5 wt%. Reaction temperature = 493 K; CH_3OH = 98 kPa (a), 86 kPa (b), 59 kPa (c), 29 kPa (d), 18 kPa (e), and 12 kPa (f).

reaction temperature decreased, the induction period appeared and became longer. The selectivity for trimethoxysilane was always close to 100%.

The temperature dependence of the reaction rate per reaction site was determined by a temperature-jump method. The activation energy for the reaction was determined to be 88 kJ mol^{-1}, against 44 kJ mol^{-1} for the reaction with the high-temperature pretreatment.

CONCLUSION

The silicon–methanol reaction using copper(I) chloride catalyst proceeds at different reactive sites depending on the conditions of preheating of the silicon–catalyst mixture prior to feeding methanol. Thus, a low-severity preheating such as low temperature and short time results in a highly selective formation of trimethoxysilane, while a high-severity preheating results in a lower selectivity.

The XRD and EPMA revealed that the Cu_3Si phase is scattered on the surface of silicon after preheating under the high-severity conditions. The higher rate of copper(I)–chloride transfer and the easier migration of copper species on the silicon surface may favor the formation of large Cu_3Si patches during high-temperature pretreatment. By heating silicon–copper(I) chloride mixture at 723 K, copper(I) chloride is transported through the vapor phase onto

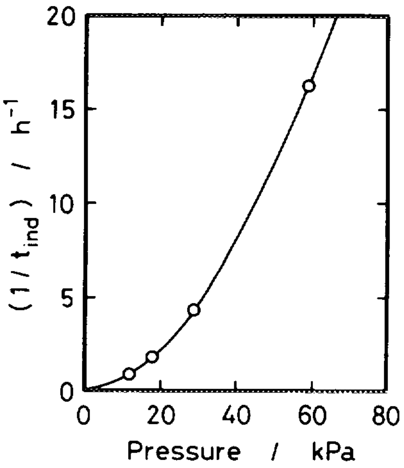

FIG. 18. Dependence of the reciprocal of induction period on methanol pressure. Experimental conditions are the same as those in Fig. 17.

the silicon surface to form patches of the Cu_3Si phase. The Cu_3Si phase is a precursor of the reactive sites. The presence of induction time in the reaction with methanol suggests that methanol participates in the formation of the reactive sites. Silicon is consumed around the area where the Cu_3Si phase is located, resulting in the formation of pits on the silicon surface.

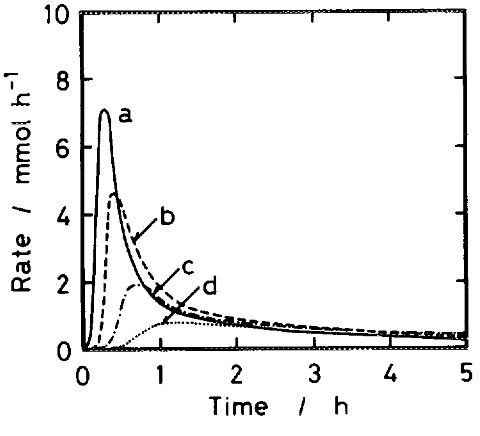

FIG. 19. Effect of reaction temperature on the change in the rate of methoxysilane formation with time. Preheating temperature = 513 K; Cu = 10 wt%. Reaction temperature = 513 K (a), 493 K (b), 483 K (c), and 473 K (d); CH_3OH = 56 kPa.

Upon a low-severity preheating, formation of the Cu_3Si phase was not confirmed, though the rate of the reaction was higher than that upon preheating under high-severity conditions. The formation of pits was observed on the silicon surface during the reaction with methanol also with low-temperature pretreatment. This indicates that the formation of an Si–Cu intermetallic compound on the silicon surface occurs even in the reaction with the low-temperature pretreatment of the silicon–catalyst mixture. The number of pits increased with reaction time and at low conversion, and with increasing methanol pressure. This indicates that methanol is involved in the reactive-site formation.

The failure to detect the alloy phase with XRD and EPMA may be attributed to the small size of each alloy ensemble. The high initial reaction rate following low-temperature pretreatment is due to the high number of reaction areas, though the size of each area is small. In the later stage of the reaction, most of the surface becomes reactive, resulting in a complete conversion of silicon by the reaction with methanol.

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