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# Mechanism of Active-Site Formation in Copper-Catalyzed Synthesis of Trimethoxysilane by the Reaction of Silicon with Methanol

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The direct synthesis of trimethoxysilane was carried out by feeding methanol at 513 K to a mixture of silicon and copper(I) chloride which had been heat-treated under a helium stream in a fixed-bed reactor at 533–773 K for 3 h. Silicon conversion increased, but selectivity toward trimethoxysilane decreased with increasing temperature of the heat treatment. Maximum yield was obtained after the treatment at 723 K with a silicon conversion of 98% and a selectivity of 82% in 3 h. When the heat-treatment is carried out above 623 K, the formation of trimethoxysilane starts just after the feed of methanol, while an induction period is observed when the temperature of the heat-treatment is below 573 K. In the former case, the surface of silicon is exposed to copper(I) chloride vapor or the melt to give an intermetallic phase, $Cu_3Si$. In the latter case, methanol takes part in the formation of the intermetallic phase. Upon the silicon–methanol reaction, pits are formed on the silicon surface. Their size increases with increasing silicon conversion.

## INTRODUCTION

The copper-catalyzed reaction of silicon with methyl chloride to give methylchlorosilanes was discovered by Rochow (*1*, *2*) in 1945. The direct synthesis is a key step in the synthesis of silicon-containing materials such as silicone polymers and numerous organosilicon chemicals (*3*).

Silicon is known to react also with methanol. Thus, in 1948, Rochow (*4*) reported that tetramethoxysilane was obtained when silicon fused with copper was brought into contact with methanol vapor at 553 K in a fixed-bed reactor. Both tri- and tetramethoxysilanes were obtained when methanol was fed at 553 K slowly into silicone oil containing silicon fused with copper, although the reaction stopped at a silicon conversion of 33% (*5*).

Many efforts have been made to obtain trimethoxysilane with high selectivity, since trimethoxysilane is an important intermediate in the synthesis of various organosilicon compounds. A high selectivity for trimethoxysilane has been attained by using silicon and copper(I) chloride. Thus, a 90% selectivity for trimethoxysilane together with a high silicon conversion was obtained when methanol was fed dropwise into a suspension of silicon and copper(I) chloride in, e.g., dodecylbenzene or diundecylbenzene at 493–513 K for 5.5–10 h (*6–9*). However, when the reaction was conducted in a fluidized bed reactor at 618 K using a silicon–copper(I) chloride–zinc mixture which had been preheated at 623 K prior to the contact with methanol vapor, trimethoxysilane was obtained with a selectivity of 84% and a silicon conversion of 26% after a reaction time of 7 h (*10*). The factors determining the rate of reaction of silicon with methanol, the selectivity for trimethoxysilane, and the entire reaction mechanism have not yet been clarified.

The present work concerns the direct synthesis of trimethoxysilane in the system silicon–copper(I) chloride–methanol and aims at advancing the knowledge of the mechanism of active-site formation over silicon grains. The consumption rate of silicon was determined for reactions proceeding in a

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continuous flow reactor by monitoring the rate of the formation of methoxysilanes. Electron microscopy was used to study the change in morphology of silicon grains during the heat treatment with copper(I) chloride and also during the reaction with methanol. X-ray powder diffraction measurement and electron probe microanalysis of the silicon grains were also carried out.

## EXPERIMENTAL

Silicon obtained from Soekawa Chemical Co., Ltd., was used without any pretreatment. Its purity was 99.5%, with Fe as a major impurity. The silicon and copper(I) chloride (Kanto Chemical Co., Inc.; guaranteed reagent grade) were sieved into grains of 45–63 $\mu$m. The sieved materials were mixed without any cleaning of their surfaces in a glass sample tube with vigorous vibration. The reactions were carried out in a fixed-bed flow reactor operating under atmospheric pressure. A 0.5-g portion of the mixture of 15 mmol of silicon and 0.79 mmol of copper(I) chloride (Cu/Si, 1/9, wt/wt), was packed in a reactor of silica tubing (10 mm i.d.), placed in a vertical furnace, and then heated under a helium stream at a given temperature for 3 h. Methanol (Kanto Chemical Co., Inc.; guaranteed reagent grade), dehydrated over molecular sieve 3 Å, was fed by a motor-driven syringe into the preheating zone of the reactor. Partial pressure of methanol (25–99 kPa) was adjusted by feeding helium through a flow meter, the total flow rate of methanol and helium being 87 mmol $h^{-1}$. The effluent gas was analyzed automatically every 2.5 min with a gas chromatograph equipped with a 2-m-long SE-30 column and a thermal conduction detector.

X-ray diffraction (XRD) patterns of samples were recorded on a Philips PW 1700 diffractometer using monochromatic Cu$K\alpha$ radiation, operating at 40 kV and 30 mA.

Scanning electron micrographs (SEM) were taken using a Hitachi S-510 instrument, operating at 25 kV. Electron probe microanalysis (EPMA) of the samples was carried out using JEOL JXA-733 and JSM-35CF equipped with EDX facility, operating at 25 kV.

## RESULTS AND DISCUSSION

### *1. Reactions of Methanol with Si–CuCl Mixture Preheated at Various Temperatures*

In the direct synthesis of methylchlorosilanes, silicon was pretreated with copper or a copper compound prior to the contact with methyl chloride (*11–17*). For example, silicon was fused with metallic copper at 1323 K (*11, 15*) or heated with copper(I) chloride at 623 K (*13, 14*). These treatments bring about the formation of a silicon–copper alloy, $Cu_3Si$, of which formation is believed to be the prerequisite for the reaction to occur (*12, 16*). Similar treatments were made also in the reaction of silicon with methanol (*4, 5, 10*).

The effect of temperature of pretreating a Si–CuCl mixture on the reactivity of silicon toward methanol was examined. Thus, the Si–CuCl mixture in the reactor was heated at 533–773 K for 3 h under a helium stream, and then methanol was fed into the reactor at 513 K. The rates of formation of methoxysilanes ($(CH_3O)_3SiH$ and $(CH_3O)_4Si$) with reaction time are shown in Fig. 1. These rates increase markedly with the temperature of the pretreatment. The rates pass through a maximum with time. A constant rate is attained below 623 K, while it decreases monotonously after the maximum above 673 K. Pretreatment at higher temperature (up to 723 K) brings about higher rates of methoxysilane formation, although there is little difference in the rates between the pretreatment temperatures of 723 and 773 K. An induction period of 20 min was observed for the pretreatment at 533 K.

Figure 2 shows the change in the cumulative silicon conversion with reaction time calculated from the data in Fig. 1. The silicon conversions at 5 h of reaction time were 21 and 28% for the samples pretreated at 533 and 623 K, respectively. For the sample

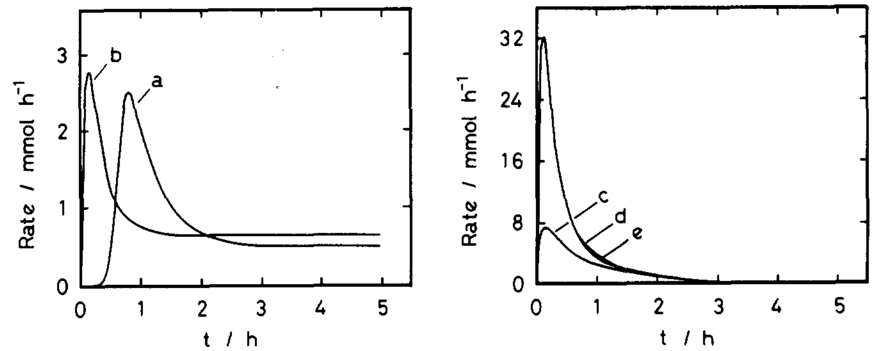

FIG. 1. Change in the rate of methoxysilanes ($(CH_3O)_3SiH$ and $(CH_3O)_4Si$) formation with reaction time. Pretreatment conditions: 533 K (a), 623 K (b), 673 K (c), 723 K (d), and 773 K (e) for 3 h. Reaction conditions: reaction temperature, 513 K; $CH_3OH$, 99 kPa (87 mmol h$^{-1}$).

pretreated at 673 K, the reaction stopped at the 46% level of silicon conversion. A conversion of 97–98% was attained in 3 h after the pretreatment at 723 and 773 K. Figure 2 also shows the change in the selectivity for trimethoxysilane with reaction time. A high selectivity of 98–99% is attained with samples pretreated at 533 and 623 K. However, for samples pretreated above 673 K, the selectivity greatly changes with reaction time in a wide range from 51 to 95%. The total selectivity for trimethoxysilane, averaged for 5 h of reaction time, was 98, 96, 80, 82, and 77% for the samples preheated at 533, 623, 673, 723, and 773 K, respectively.

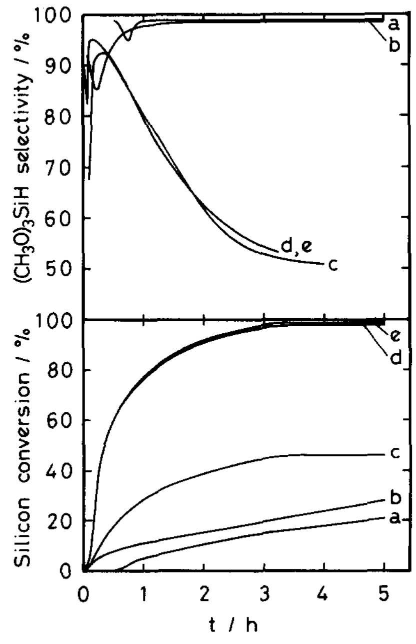

FIG. 2. Change in the cumulative silicon conversion and the selectivity for trimethoxysilane with reaction time. Pretreatment and reaction conditions are same as those in Fig. 1.

## 2. *XRD Patterns of Si–CuCl Mixture Heat-Treated at Various Temperatures*

To determine the effect of heat-treatment on the state of the silicon–copper(I) chloride mixture, XRD measurements of the samples were carried out. Figure 3 shows the XRD patterns of the Si–CuCl mixtures heated at various temperatures together with that of the pristine Si–CuCl mixture. As shown in Fig. 3a, the Si–CuCl mixture gave three intense peaks at $2\theta = 28.4$, 47.3, and 56.1°, all of which were ascribed to crystals of Si and CuCl, since silicon and copper(I) chloride have the same lattice structure and almost the same lattice constants as each other. A diffuse peak at $2\theta = 33.0°$ is characteristic of CuCl.

An XRD pattern of the mixture heated at 533 K (Fig. 3b) was completely superimposed on that of the pristine Si–CuCl mixture (Fig. 3a). Two new diffraction peaks assignable to $Cu_3Si$ alloy appeared at $2\theta =$ 44.6 and 45.1° when the sample was heated

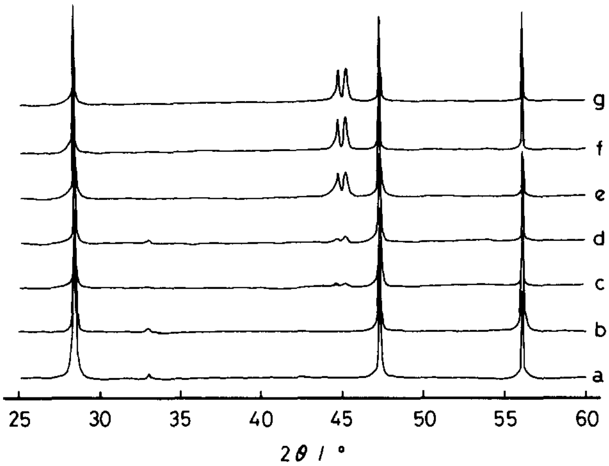

FIG. 3. X-ray powder diffraction patterns of the Si–CuCl mixtures heated at various temperatures. Pristine Si–CuCl mixture (a) and the mixture heated at 533 K (b), 623 K (d), 673 K (e), 723 K (f), and 773 K (g). The pattern (c) was obtained for the mixture heated at 533 K for 3 h and subsequently kept in contact with methanol vapor (99 kPa) at 513 K for 20 min.

above 623 K, as shown in Figs. 3d–3g. The intensity of the $Cu_3Si$ peaks developed with increasing pretreatment temperature up to 723 K, while little difference was observed in the intensities of samples heated at 723 and 773 K. A peak at $2\theta = 33.0°$ assignable to CuCl became more diffuse upon pretreatment at 623 K (Fig. 3d) and undetectable upon pretreatment above 673 K (Figs. 3e and 3f).

The changes in the intensity of peaks due to the $Cu_3Si$ alloy with the temperature of heating of the Si–CuCl mixture seem to be correlated with the rate of methoxysilane formation. Thus, the mixture heated at 533 K gave no peaks due to $Cu_3Si$; methoxysilane was formed only after the induction period of 20 min. The intensities of the peaks as well as the initial rates increased with increasing pretreatment temperature up to 723 K. This suggests that the formation of $Cu_3Si$ alloy is essential to the silicon–methanol reaction.

After the sample heated at 533 K was kept in contact with methanol vapor for 20 min, corresponding to the end of the induction period in Fig. 1a, the sample gave the XRD pattern of Fig. 3c, in which diffuse peaks due to the $Cu_3Si$ alloy were observed at $2\theta = 44.6$ and $45.1°$. These results also support the conclusion that the formation of the $Cu_3Si$ alloy is essential to the reaction of silicon with methanol.

### 3. *Grain Morphologies of Heat-Treated Si–CuCl Mixtures*

As described in the preceding section, an XRD study revealed that the $Cu_3Si$ phase appears in the samples heated above 623 K. In this section, the change in the grain morphologies of the samples upon heat-treatment will be described. Figure 4 shows the SEM images of samples pretreated at various temperatures. The starting mixture contains two kinds of grains with different morphologies (Fig. 4a). Thus, each silicon grain consists of a single particle, while copper(I) chloride grains look like an agglomerate and have more irregular outlines than those of the silicon grains. Heating the mixture at 533 K caused no change in the grain morphologies of either silicon or copper(I) chloride. Upon treatment at 623 K, however, some silicon grains are partly covered with deposits (Fig. 4b). Treatment above 673 K gave two striking changes in the grain morphologies (Fig. 4c). One is the disappearance of the grains of CuCl. The other is

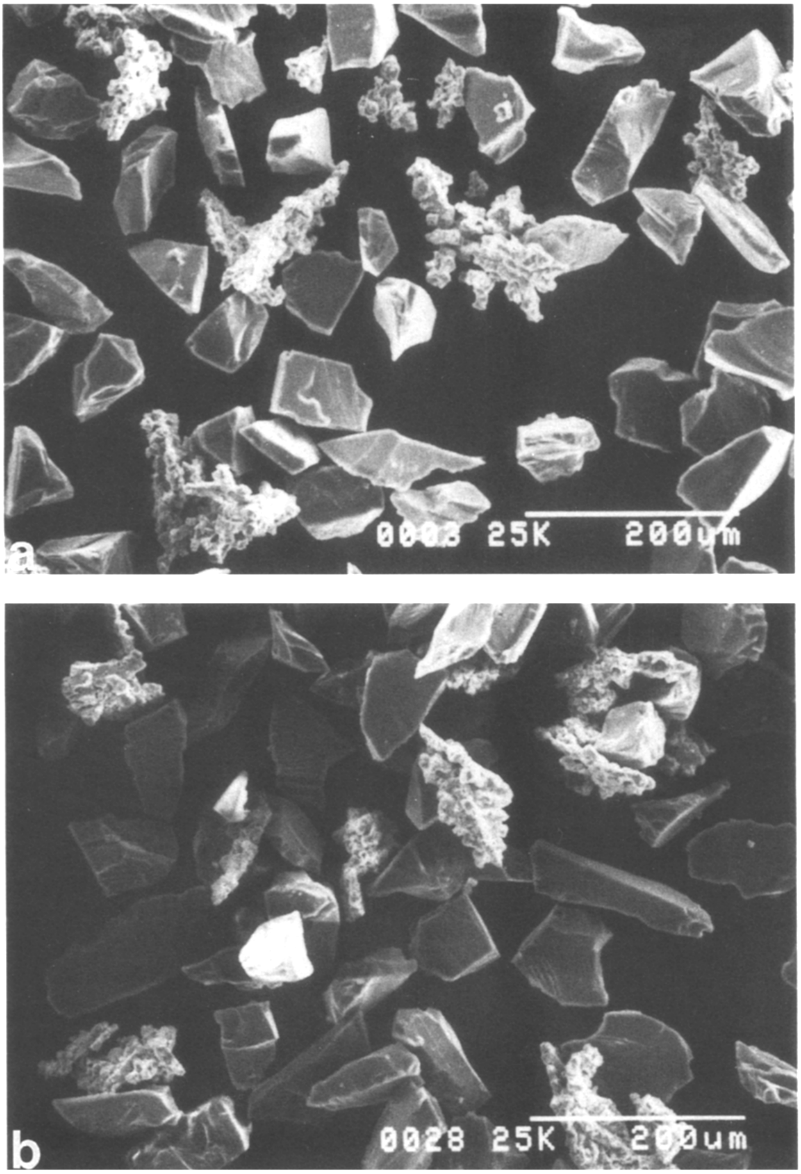

FIG. 4. Scanning electron micrographs of the Si–CuCl mixtures heated at various temperatures. Pristine Si–CuCl mixture (a) and the mixture heated at 623 K (b) and 723 K (c) (150×). The magnified image (1000×) of the completely covered silicon grain is shown in (d).

an increase in the number of grains partly covered with the deposits and the appearance of grains even completely covered with the deposits. A magnified image of the silicon grain completely covered with the deposits is shown in Fig. 4d. The presence of Cu and Cl on the silicon surface after pretreatment of the Si–CuCl mixture was confirmed by EPMA (electron probe microanalysis).

As described above, the formation of the $Cu_3Si$ alloy upon heat-treating the Si–CuCl

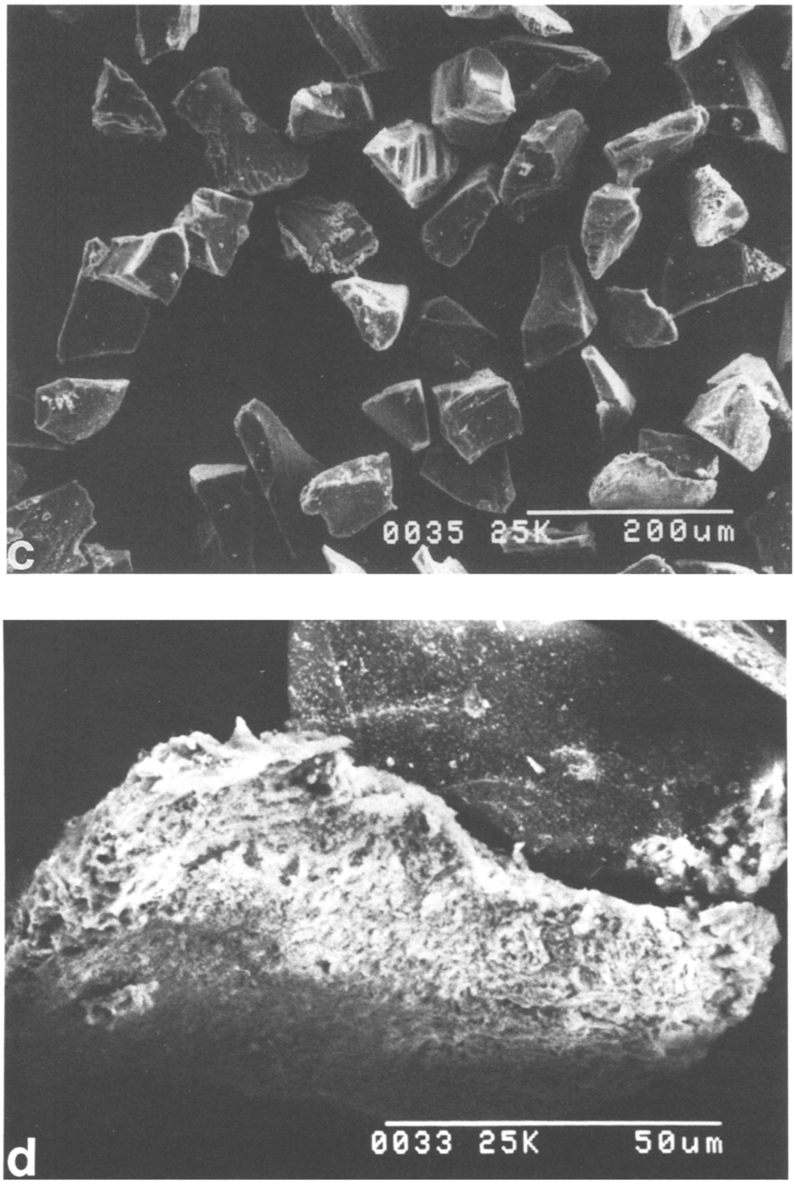

FIG. 4—*Continued.*

mixture above 623 K was revealed by an XRD measurement. During the heat treatment, the vapor or the melt of CuCl (mp 695 K) reaches the surface of silicon grains to react with silicon. Reaction of CuCl vapor or the melt with solid silicon is known to give $Cu_3Si$ alloy (*18, 19*).

### *4. Induction Period and Active-Site Formation*

As described in the first section, the change in the rate with reaction time depends greatly on the temperature of preheating of the Si–CuCl mixture. In this section, the change in the rate with reaction time is discussed in relation to the formation and the deactivation of active sites.

As shown in Fig. 1a, an induction period of 20 min was observed in the reaction using the Si–CuCl mixture pretreated at 533 K for 3 h. Longer helium pretreatments at 533 K (200 min) did not reduce the induction period of 20 min and the time course of the rate was completely superimposed on Fig. 1a. This indicates that contact of the Si–CuCl mixture with methanol is essential to the formation of active sites for the reaction of silicon with methanol at this pretreatment temperature.

The dependence of the induction period on the heat-treatment temperature and on the reaction temperature was studied. The Si–CuCl mixture was pretreated in the reactor at a given temperature (493–573 K) for 1 h, and then the reaction was carried out at temperatures lower than the pretreatment temperature. The induction period did not depend on the pretreatment temperature, but changed greatly with the reaction temperature. As shown in Fig. 5, the reciprocal of the induction period, which is taken as the rate of active-site formation, showed an Arrhenius-type dependence on the reaction temperature, the activation energy being 74 kJ $\text{mol}^{-1}$. The induction period was also a function of the partial pressure of methanol. Thus, as shown in Fig. 6, the reciprocal of the induction period depended greatly on methanol pressure. These results suggest that the reaction of methanol with the Si–CuCl mixture is essential to the formation of active sites for mixtures with pretreatment temperatures below 573 K. Indeed, the $Cu_3Si$ phase was detected by XRD measurement (Fig. 3c) for a sample pretreated at 533 K and exposed to methanol at 513 K for 20 min. When the Si–CuCl mixture was heated at temperatures higher than 623 K, no induction period was observed in the rate curves, as shown in Figs. 1b–1e. The disappearance of the induction period may be due to the formation of $Cu_3Si$ by the direct reaction of copper(I) chloride with silicon surface in the pretreatment stage.

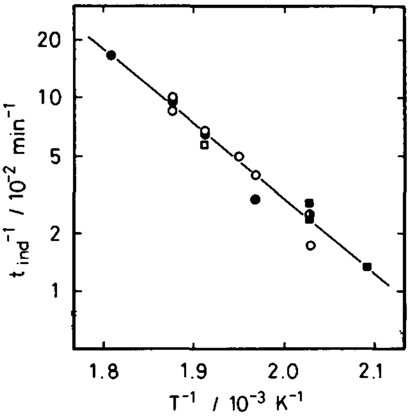

FIG. 5. Arrhenius plot for the reciprocal of the induction period. Pretreatment conditions: 493 K (■), 523 K (◑), 533 K (○), 553 K (●), and 573 K (□) for 1 h. Reaction condition: $CH_3OH$, 99 kPa (87 mmol $h^{-1}$).

In the direct synthesis of methylchlorosilanes from silicon and methyl chloride using copper(I) chloride as a catalyst, the bulk of copper is present as $Cu_3Si$ and the "active" surface phase is enriched in Si ($Cu_xSi$, $x$ = ca. 1) (*20, 21*). As mentioned before, in also the trimethoxysilane synthesis, the formation of the $Cu_3Si$ alloy is assumed to be essential to the reaction of silicon with methanol. The observation that the rate increased sharply at the beginning of the reaction indicates that even if $Cu_3Si$ is formed on the

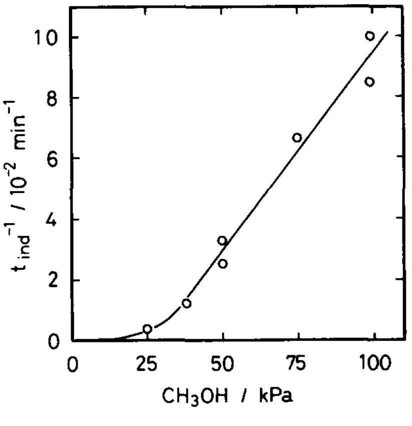

FIG. 6. Dependence of the reciprocal of the induction period on the partial pressure of methanol. Pretreatment conditions: 533 K for 1 h. Reaction conditions: reaction temperature, 533 K; $CH_3OH$ + He, 87 mmol $h^{-1}$.

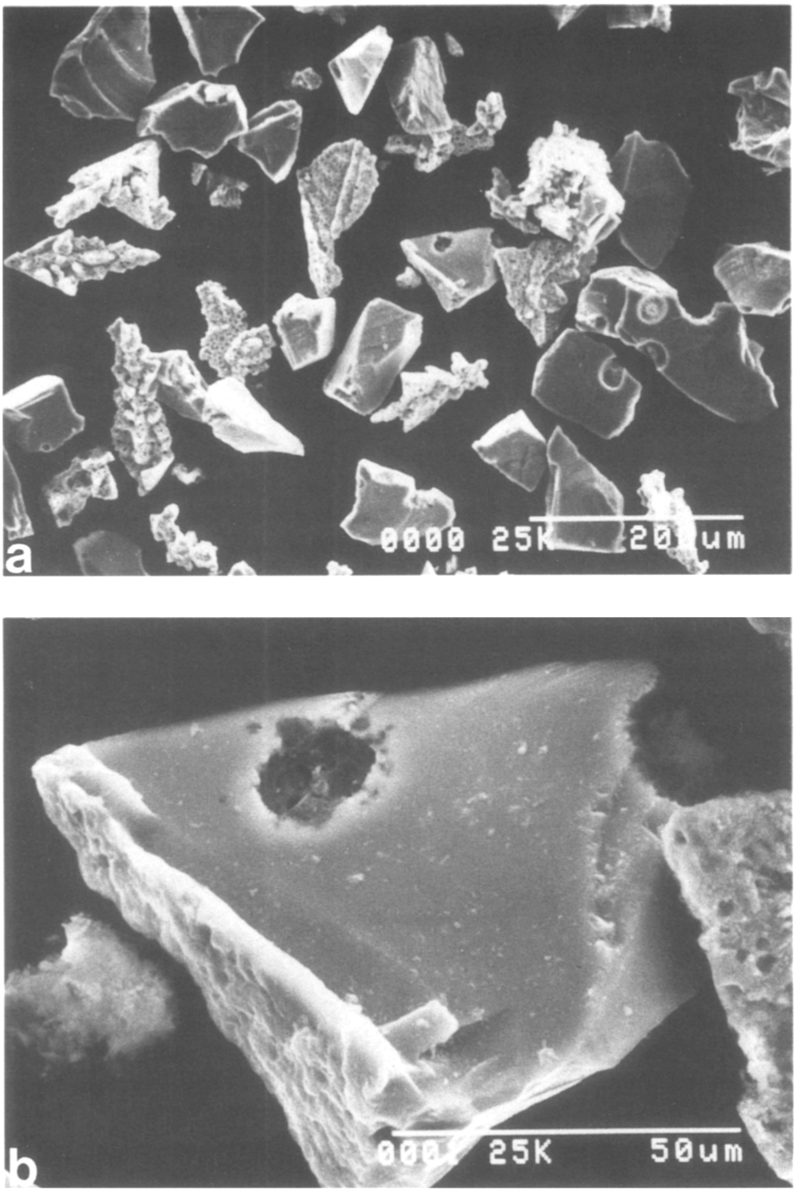

FIG. 7. Scanning electron micrographs of reacting silicon grains with various levels of silicon conversion. Pretreatment conditions: 623 K for 3 h. Reaction conditions: $CH_3OH$, 99 kPa (87 mmol $h^{-1}$); 533 K for 40 min (a,b), 2 h (c,d), and 5 h (e,f).

surface of silicon grains, this cannot be the true active site for the reaction of silicon with methanol. The $Cu_3Si$ alloy may be transformed into more reactive species once the reaction starts. Actually, no $Cu_3Si$ phase was detected in the mixtures after partial conversion of silicon.

### 5. *Morphologies of Reacting Silicon*

The change in the morphology of reacting silicon grains with various levels of silicon conversion was examined. The Si–CuCl mixture was pretreated at 623 K for 3 h and brought into contact with methanol at 533 K for 40 min, 2 h, and 5 h, the silicon conver-

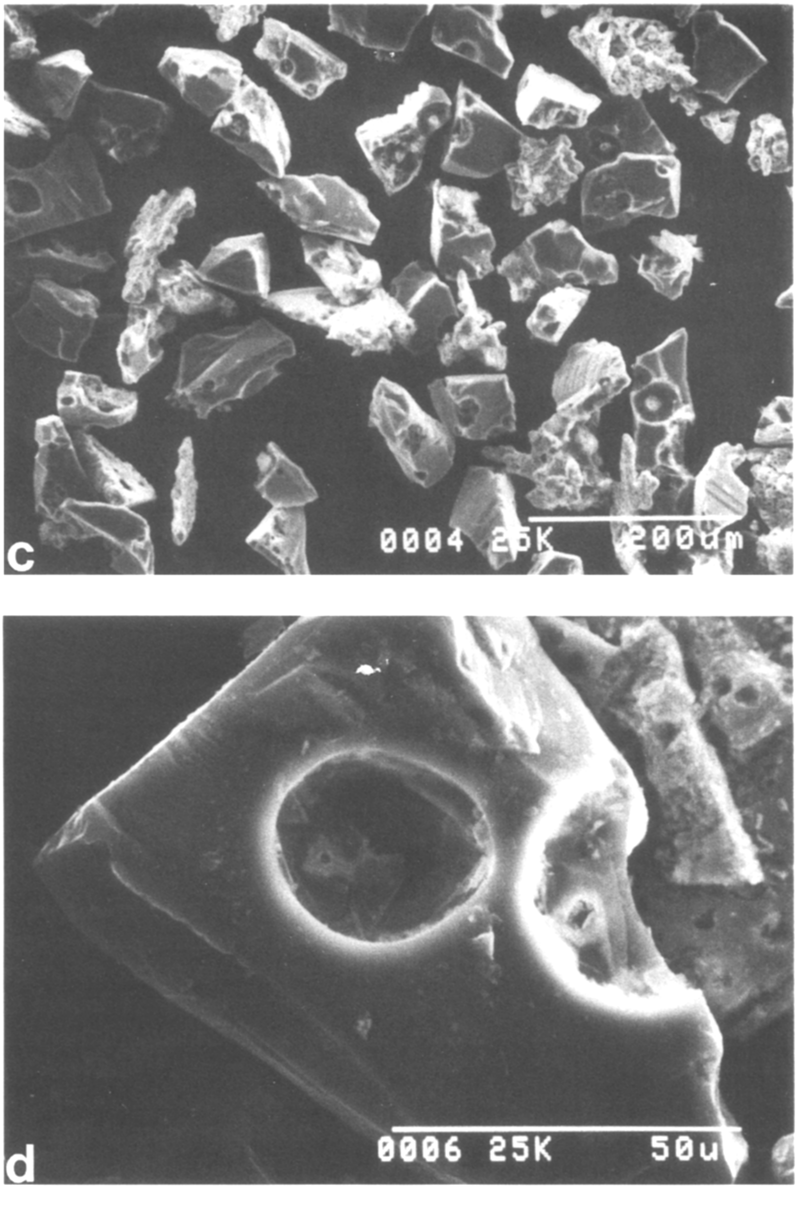

FIG. 7—*Continued.*

sion being 9.8, 47, and 91%, respectively. The SEM images of the samples are shown in Fig. 7. A striking change in the morphology of silicon grains upon exposure to methanol can be seen when the sample was subjected to reaction with methanol for 40 min (Fig. 7a). Thus, some silicon grains have pits on their surfaces. The magnified image of the grain is shown in Fig. 7b; the pits are shaped like craters.

With the increase in the silicon conversion to 47%, the number of silicon grains having detectable pits increased and the size of the pits increased (Fig. 7c). The magnified image (Fig. 7d) clearly shows the hollow structure of the pits and a bright spot in the center of the pit. The EPMA (Cu and Cl) signals from the bright spot were intense, while the intensities were very low from the spherical wall of the pits and from the silicon

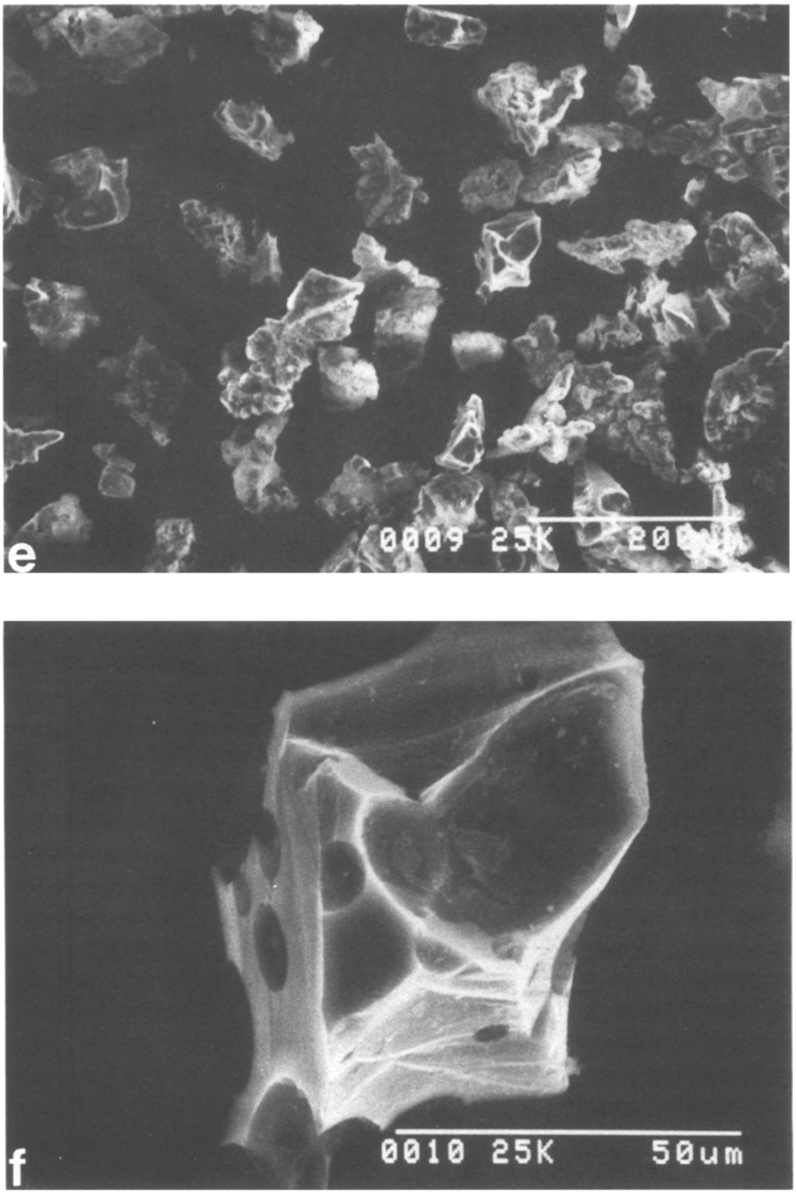

FIG. 7—*Continued.*

surfaces having no pits. The intensity ratio of Cu signals to Cl signals was 2.1, while that of neat CuCl was 1.1.

These observations clearly show that the reaction does not occur uniformly on the silicon surface, but starts at copper-containing areas scattered on the surface. Upon the reaction with methanol, the pits are formed in these areas, and the size of the pits increases with increasing silicon conversion. Banholzer *et al.* (*17, 20*) have reported that pits are formed on the silicon surface in methylchlorosilane synthesis; they ascribed the formation of the pits to the scattered formation of $Cu_3Si$. The observation of pits on silicon surfaces in this study is similar to that in methylchlorosilane synthesis. The scattered formation of a $Cu_3Si$ phase on the silicon surface upon reaction with CuCl has been reported by Weber *et al.* (*18, 19, 22*). They suggest that the deposition of CuCl and the subsequent reaction with silicon to form $Cu_3Si$ start at defects or pinholes in the $SiO_2$ layer covering the silicon surface. In fact, when the silicon surfaces were washed with aqueous HF solution before use, their activities toward methanol and the number of the pits on the silicon grains increased significantly (*23*).

At 91% of silicon conversion, the sample contained fewer silicon grains (Fig. 7e), as expected, most of the remaining grains being copper(I) chloride. The size of silicon grains is smaller than that of silicon grains at the lower silicon conversions. A magnified image (Fig. 7f) shows a large spherical surface (ca. 40 $\mu$m in diameter) of the silicon grain as a result of an enlargement of the hollow structure with increasing degree of the reaction.

## CONCLUSIONS

The direct synthesis of trimethoxysilane was carried out by feeding methanol at 513 K into a Si–CuCl mixture, which had been heat-treated under a helium stream in a fixed-bed reactor at 533–773 K for 3 h. Reactivity of silicon increased with increasing heat-treatment temperature up to 723 K, at which a 98% silicon conversion with an 82% selectivity for trimethoxysilane was obtained in 3 h of reaction time.

During pretreatment above 623 K, copper(I) chloride is transported onto the surface of silicon grains to give deposits. The deposits react with silicon to form an intermetallic copper–silicon phase, $Cu_3Si$, which is dispersed on the silicon surface. Upon reaction with methanol, pits are formed at the scattered areas; the size of pits grows with increasing silicon conversion.

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