論文 / 著書情報
Article / Book Information

題目(和文)	
Title(English)	Synthesis of Trimethoxysilane by the Reaction of Silicon with Methanol Using Copper(I) Chloride as the Catalyst
著者(和文)	岡本昌樹
Author(English)	MASAKI OKAMOTO
出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第2735号, 授与年月日:1994年3月26日, 学位の種別:課程博士, 審査員:
Citation(English)	Degree:Doctor of Engineering, Conferring organization: , Report number:甲第2735号, Conferred date:1994/3/26, Degree Type:Course doctor, Examiner:
学位種別(和文)	博士論文
Type(English)	Doctoral Thesis

941143 /

Synthesis of Trimethoxysilane by the Reaction of Silicon with Methanol Using Copper(I) Chloride as the Catalyst

Masaki Okamoto
Ono - Suzuki Laboratory
Tokyo Institute of Technology
1994

Synthesis of Trimethoxysilane by the Reaction of Silicon with Methanol Using Copper(I) Chloride as the Catalyst

Chapter 3 Kinetics of the Formation of Methoxysilanes 60

Chapter 5 Direct Formation of Organosilicon Compounds by the Reaction of Silicon, Methanol and Alkenes 119

Chapter 6 Effect of Halide Ion of Copper(I) Halide Catalyst the Reaction of Silicon with Methanol 135

Chapter 1 INTRODUCTION

1-1 Synthesis of Organosilanes

1-1-1 Organosilanes

Organosilanes are the compounds containing Si-C bonds. No organosilanes exist in nature and all of organosilanes are synthesized artificially. The number of the kind of organosilanes is as large as that of organic compounds.

Organochlorosilanes ($R_{4-x}SiCl_x$) are the most important chemicals for producing silicones. Silicones are polymers including organosilicon groups linked by siloxane bonds (Si-O-Si). They are generally produced by hydrolysis and condensation of organochlorosilanes. Silicones are classified by their nature into three kinds: oils, rubbers and resins.

Organoalkoxysilanes are also important chemicals as silane-coupling reagents. Silane-coupling reagents consist of organic-functional and alkoxy groups, which can be bound to organic and inorganic materials, respectively. For example, they are used as adhesive reagents between glasses and resins.

In organic syntheses, organosilanes are in use as silylation reagents in order to protect functional groups of the organic compounds and to improve their solubilities for solvents and their heat-resistance. Active hydrogens of hydroxy, carboxy, amino and mercapt groups in organic compounds are replaced by triorganosilyl group.

1-1-2 Synthesis of Organosilanes

Organosilanes have been studied since 1800's. In 1863, Friedel and Crafts synthesized tetraethylsilane by the reaction of tetrachlorosilane with alkyl zinc. In 1944, Rochow discovered the direct synthesis of organohalosilanes [1], establishing the silicon chemistry as industry.

Rochow reported the formation of methylchlorosilanes by the silicon-methyl chloride reaction using copper catalyst [1]. The synthesis of various silicon compounds from metallic silicon is called direct synthesis. Various organic halides, alcohols, phenols, ethers and dimethylamine directly react with silicon. However, only the reactions of methyl chloride and chlorobenzene with silicon are carried out industrially. The silicon-methyl chloride reaction at 250-350^{o}C gives methylchlorosilanes, $(CH_3)_2SiCl_2$ being a major product. Chlorobenzene reacts above 400^{o}C to give phenylchlorosilanes such as Ph_2SiCl_2, the main product.

The direct syntheses of silicon compounds to form Si-OR and $Si-NR_2$ bonds were also reported.

The selective synthesis of trialkoxysilane by the reaction of silicon with alcohols was reported and noted for a part of new route of organosilane synthesis. Trialkoxysilanes are alkylated to give various organosilanes. For instance, organotrialkoxysilanes are obtained by the hydrosilylation of trialkoxysilane with alkenes.

The reaction of silicon with dimethylamine to form Si-N bond was also reported [2]. The products consist of tris- and tetrakisdimethylaminosilane, their yields being very low.

The exothermic reactions of silicon with chlorine and hydrogen chloride occur at 200-300 ^{o}C to form tetrachlorosilane and trichlorosilane, respectively.

$$Si + Cl_2 \longrightarrow SiCl_4$$
$$Si + HCl \longrightarrow HSiCl_3 + SiCl_4$$

Alkoxysilanes can be synthesized by the reactions of chlorosilanes with alcohols.

The synthesis methods of organosilanes other than direct synthesis are summarized as follows:

In 1952, Kautsky reported the formation of "active silicon" [Si] by removing calcium with antimony trichloride from calcium disilicide [3].

$$3\ CaSi_2 + 2\ SbCl_2 \longrightarrow 6\ [Si] + 2\ Sb + 3\ CaCl_2$$

Bonitz showed the formation of "active silicon" [Si] by the reaction of calcium silicide with chlorine in tetrachloromethane or tetrachlorosilane at room temperature.

$$CaSi_2 + Cl_2 \longrightarrow 2\ [Si] + CaCl_2$$

"Active silicon" is so reactive that it reacts with methanol, chlorine and methyl chloride at gentle reaction conditions (20-60 ^{o}C) to give tetramethoxysilane, polychlorosilanes and methylchlorosilanes, respectively.

$$[Si] + 4\ CH_3OH \longrightarrow Si(OCH_3)_4 + 2\ H_2$$

$$n\ [Si] + m\ Cl_2 \longrightarrow Si_nCl_{2m}$$

$$[Si] + n\ CH_3Cl \longrightarrow (CH_3)_nSiCl_{4-n}$$

Boudin et al. reported the synthesis of organosilanes from silica [6]. They obtained organosilanes by the reaction of Grignard agent and six-coordinated silicon compound formed from silica and catechol. The merit of this reaction is the absence of the the reduction process of silica to form metallic silicon.

1-1-3 Metallic Silicon

Metallic silicon utilized for the synthesis of methylchlorosilanes is formed by reducing silica (SiO_2) with cokes as a reducing agent in an electric furnace.

$$SiO_2 + 2\ C \longrightarrow Si + 2\ CO$$

The electric power to obtain 1 t of metallic silicon is so high (14,000 kWh) that the production of metallic silicon in Japan was stopped in 1987 and all of metallic silicon is imported.

1-1-4 Direct Synthesis of Methylchlorosilanes

In direct synthesis of methylchlorosilanes, copper catalyst is prepared by various methods, for example, by heating the mixture of silicon and copper above 1,050 ^{o}C in reductive atmosphere to form Si-Cu alloy [7] or by pretreating the silicon-copper(I) chloride at 260-300 ^{o}C prior to the reaction [8]. Copper(I) chloride reacts with silicon to give copper-silicon intermetallic compounds (Cu_xSi_y) on silicon surface.

$$CuCl + Si \longrightarrow Cu_xSi_y + SiCl_4$$

The Cu-Si alloy adhered to silicon-grains is very reactive.

In methylchlorosilanes synthesis, dimethyldichlorosilane is much in demand. However, various methylchlorosilanes except dimethyldichlorosilane are formed as by-products. Much effort has been made to improve the selectivity for dimethyldichlorosilane by addition of promoters.

Addition of zinc and tin to the copper catalyst resulted in the improvement of both the selectivity for dimethyldichlorosilane and the reaction rate [9,10].

Many reports have been made to obtain selectively for methylchlorosilane other than dimethyldichlorosilane.

Addition of aluminum gave higher selectivity for trimethylchlorosilane (10-20%) than that in the absence of aluminum (3-5%) [11]. Zinc and magnesium have the same effect as aluminum [12].

It was reported that high selectivity for methyltrichlorosilane was obtained by addition of iron, aluminum or tin chloride to the copper catalyst [13].

Effects of carrier gases during the reaction were reported. Use of nitrogen as a carrier gas improved the selectivity for dimethyldichlorosilane [7]. When hydrogen is fed to the silicon-catalyst mixture, the selectivity for silanes containing Si-H bonds, CH_3SiClH_2, increased [14]. In the reaction under a hydrogen chloride stream, the main product was CH_3SiCl_3 [15].

1-1-5 Role of Copper as a Catalyst in the Synthesis of Methylchlorosilanes

Cu_3Si phase is one of the stable phases of silicon - copper alloy, being formed by the dissolution of copper in silicon. The formation of Cu_3Si phase has been observed in silicon - copper mixtures treated in various manners. Trambouze reported that Cu_3Si phase is important in the formation of methylchlorosilanes [16]. Voorhoeve et al. also obtained the indication of Cu_3Si formation in all mixtures of silicon - catalyst, which were prepared by fusing copper with silicon or heating the mixture of silicon and copper(I) chloride [17,18]. Falconer et al. [19] reported that Cu_3Si phase provides an reactive surface for methylchlorosilanes formation and that, however, a clean surface of Cu_3Si is not catalytically active until the silicon is bound to chlorine.

Frank and Falconer proposed that the presence of copper results in the weakening of silicon bonding [20]. The silicon-copper bond energy was calculated to be ca. 126 kJ mol^{-1}, 84 kJ mol^{-1} less than the silicon-silicon bond [21].

Banholzer et al. determined the chemical composition of reactive surface [22]. They found that the ratio of Si/Cu is between < 0.5 to 2, almost part being about 1. This indicates that Cu_3Si is not present in the reacting region of the surface. Lewis et al. also concluded that the reactive surface is richer in silicon than Cu_3Si [21].

Gupta et al. determined the chemical state of copper on the silicon surface after the reaction by XPS. They reported that catalytic copper is two valence [23,24]. Owen et al. [25] and

Chen et al. [26] reported the zero and one valence of active copper, respectively. The chemical state of copper has not been completely clarified yet. However, it seems certain that the copper exists as the silicon-copper intermetallic compound during the reaction.

1-1-6 Mechanism of Formation of Methylchlorosilanes

Several mechanisms in the methylchlorosilanes formation have been proposed.

Rochow and Hurd proposed a radical mechanism in the reaction of silicon-copper alloy with methyl chloride [27].

$$2\ Cu + CH_3Cl \longrightarrow CuCl + CuCH_3$$
$$Si + CuCl \longrightarrow Cu + (Si{-}Cl)$$
$$(Si{-}Cl) + CuCH_3 \longrightarrow (CH_3SiCl) + Cu$$

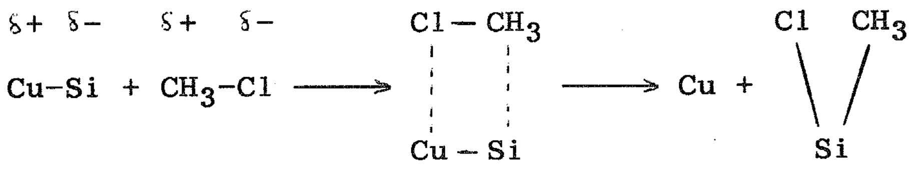
This mechanism was supported by the following experiment. A stream of methyl chloride was passed over finely divided copper at 250°C and led over a lead mirror. The lead mirror disappeared to form volatile $Pb(CH_3)_4$ by the reaction of $CH_3{}^{\cdot}$ and Pb.

$$CuCH_3 \longrightarrow Cu + CH_3{}^{\cdot}$$
$$4\ CH_3{}^{\cdot} + Pb \longrightarrow Pb(CH_3)_4$$

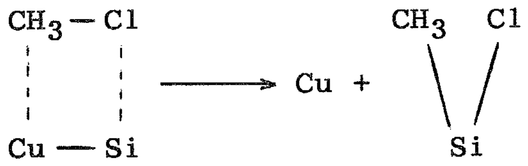
Methyl radical formed from $CuCH_3$ reacts with silicon to form Si-C bond. However, no evidence for the formation of $CuCH_3$ intermediate was obtained.

Klebansky et al. [6,28] and Bazant et al. [29] proposed the ionic mechanism.

Klebansky et al. considered that chlorine atoms migrate to silicon after dissociative adsorption of methyl chloride on silicon and copper, and that this was caused by polarization of methyl chloride by the lattice charge of Si-Cu bonds. In the reaction of methyl, ethyl, propyl, tert-butyl and vinyl chloride with silicon, the reactants having higher dipole moment reacts with silicon at lower temperatures.



In contrast to Klebansky's mechanism, Bazant et al. proposed that methyl group as an electrophile migrates to silicon after methyl and chlorine combine to copper and silicon, respectively. The reaction rate of methyl bromide instead of chloride increased. This shows that methyl group easily migrate to silicon since bromine is more electron-donative than chlorine.



Voorhoeve et al. [18,30,31] supported the ionic mechanism by the relationship between product selectivity and lattice charge in variation of silicon-metal alloy such as copper, calcium, chromium and iron. Their mechanism is shown in Fig. 1-1. On the alloy surface, copper and silicon charged with plus and minus, respectively. The physisorbed methyl chloride is polarized on the surface to charge methyl and chlorine with plus and minus, the Si-C bond formation involving C-Cl bond cleavage.

The intermediates of the reaction have been studied. Zubkov et al. found the formation of dichlorosilylene in the reaction of silicon with copper(I) chloride by mass spectroscopy [32]. They proposed that dichlorosilylene reacts with methyl chloride and copper to form dimethyldichlorosilane and copper(I) chloride.

$$:SiCl_2 + MeCl,\ Cu \longrightarrow Me_2SiCl_2 + CuCl$$

Lewis proposed the intermediacy of methylchlorosilylene (:SiMeCl) in dimethyldichlorosilane formation [21].

However, Clarke et al. concluded that silylenes (:SiXCl (X = Me, Cl)) in gas phase is not reaction intermediates [33]. When butadiene as a trapped reagent of silylene was added to methyl chloride feed, very low yields of butadiene-trapped products were obtained, indicating that silylenes are not involved in the reaction mechanism.

Podgornyi et al. concluded that the chlorinated surface silicon is the reaction intermediate since high reaction rate was caused by chlorination of silicon by chlorine before the reaction [34,35]. Chlorinated silicon reacts with two molecules of methyl chloride to give dimethyldichlorosilane (Fig. 1-2). Falconer and coworkers also reported that the reactive site in

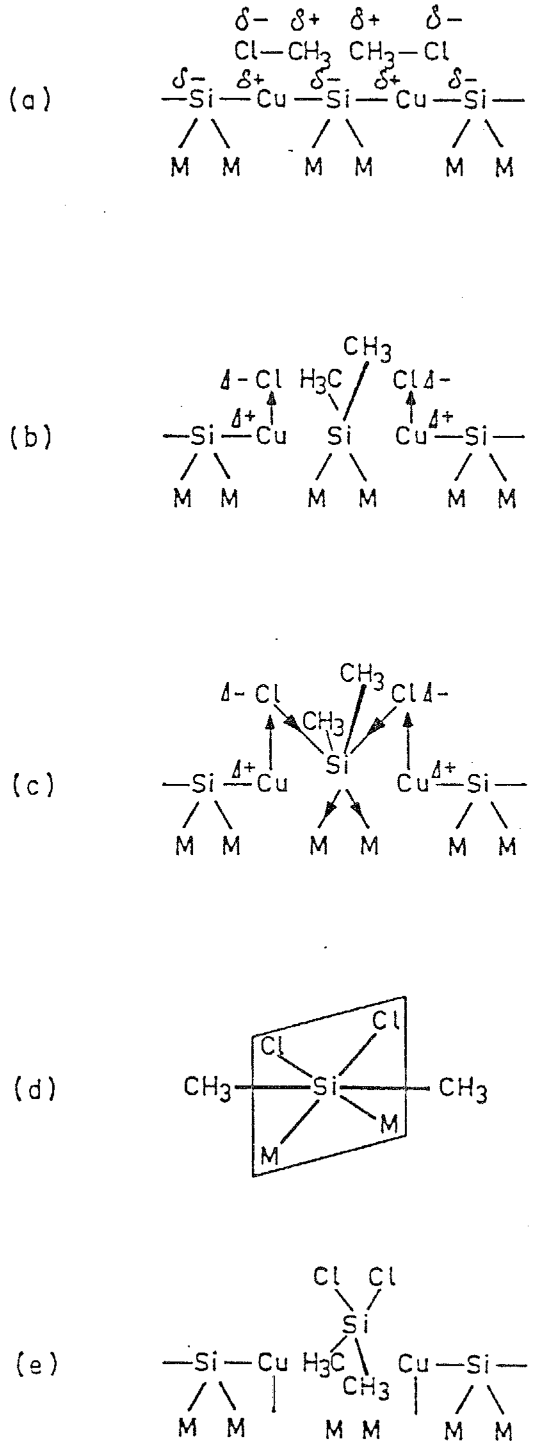


Figure 1-1 Voorhoeve's mechanism of dimethyldichlorosilane formation.

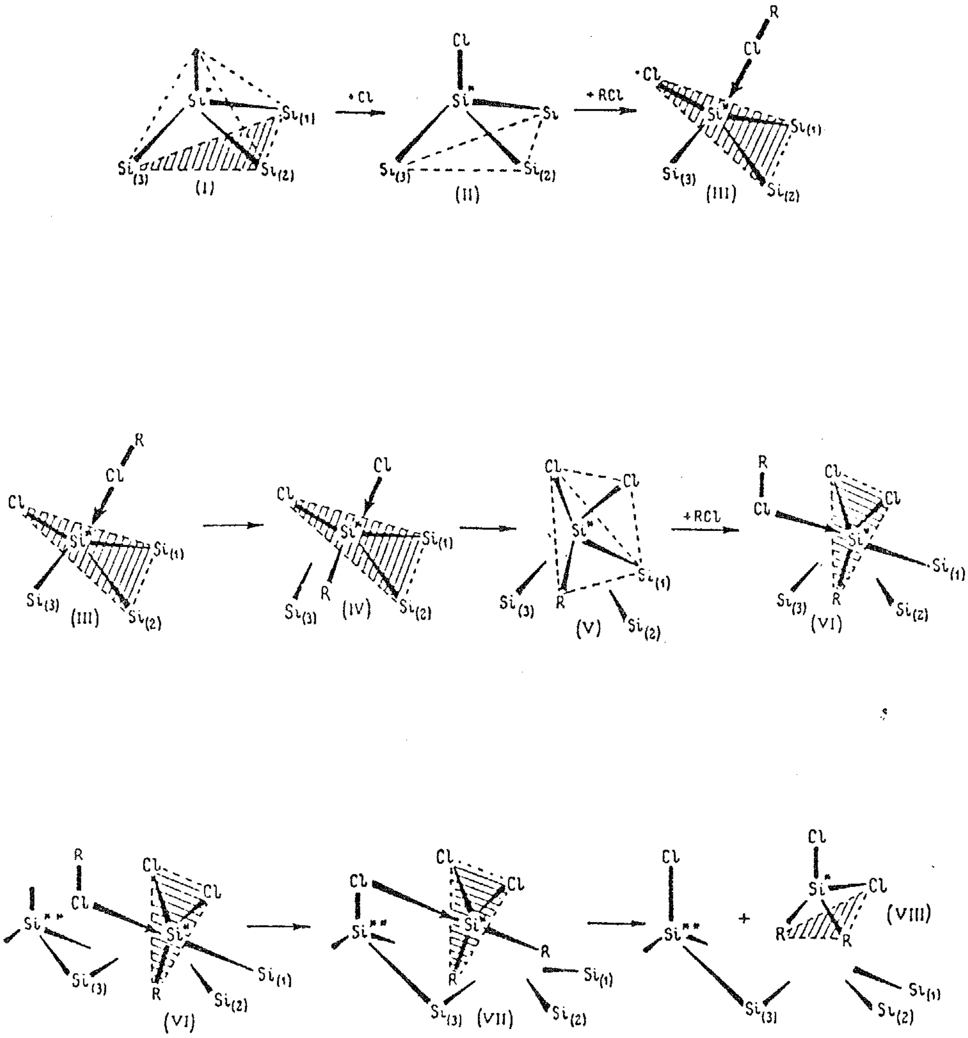


Figure 1-2 Podgornyi's mechanism of dimethyldichlorosilane formation.

the formation of dimethyldichlorosilane was chlorinated silicon species, using AES [19,36]. The silicon (LVV) Auger transition gave evidence for the formation of Si–Cl bond on the silicon surface at the induction period.

As described above, many reaction mechanisms have been proposed. However, the mechanism consistent with all experimental results has not been found yet.

1-2 Synthesis of Alkoxysilanes

1-2-1 Alkoxysilanes

Organoalkoxysilanes contain alkoxy groups, which are readily hydrolyzed, and hydrophobic organogroups. Alkoxy groups are condensed with the surface of inorganic materials (M–OH) to form Si–O–M bond. When the silane has functional groups such as vinyl group, the silane is used as silane-coupling agent for combining between organic and inorganic materials. For example, organoalkoxysilanes are applied to the modification of organic-inorganic complex materials and the improvement of their mechanical strength and their water resistance.

Organoalkoxysilanes are industrially synthesized by the alkoxylation of organochlorosilanes.

$$R_xSiCl_{4-x} + (4-x)\ R'OH \longrightarrow R_xSi(OR')_{4-x} + (4-x)\ HCl$$

In this reaction, a special reactor resistant to acids is required since corrosive hydrogen chloride gas is formed as a by-product.

Another synthesis method of organoalkoxysilanes is the hydrosilylation of trialkoxysilanes.

$$HSi(OR')_3 + RCH{=}CH_2 \longrightarrow RCH_2CH_2Si(OR')_3$$

In this reaction, the ordinary reactor can be used because no corrosive gases are formed. This reaction will be expected as a part of a new route of organoalkoxysilanes synthesis, if easier synthesis of trialkoxysilanes is developed.

At present, however, trialkoxysilanes are produced by the reaction of trichlorosilane and alcohols in spite of the formation of hydrogen chloride. Thus, the procedures of organoalkoxysilanes production will be simplified if trialkoxysilanes are directly formed from metallic silicon without using any halides.

Trialkoxysilanes are very reactive. Si-H bond adds to alkenes or alkynes (hydrosilylation), and is alkylated by organic lithium (reductive silylation), leading the formation of organosilanes with various functions. The disproportionation of trimethoxysilane gives silane [37,38].

$$4\ HSi(OCH_3)_3 \longrightarrow SiH_4 + 3\ Si(OCH_3)_4$$

Silane is industrially formed by the disproportionation of trichlorosilane. The method of trimethoxysilane disproportionation does not involve the formation of hydrogen chloride, having the merit of non-corrosivity of the reactors.

As mentioned above, it is expected that trimethoxysilane could be used as a raw material for organosilanes and silane, if the method of direct synthesis of trimethoxysilane is established.

1-2-2 Synthesis of Alkoxysilanes

Rochow synthesized methoxysilanes from silicon with methanol in vapor phase [39]. The mixture of metallic silicon (90 wt%) and copper (10 wt%) was pretreated at 1,050 ^{o}C for 1 h under a hydrogen stream, and then was exposed to methanol at 250-300 ^{o}C to give tetramethoxysilane as a main product.

Rochow et al. demonstrated the liquid phase synthesis of alkoxysilanes [40]. In the reaction of methanol, silicon conversion was 33% and products consisted of trimethoxysilane and tetramethoxysilane, the selectivity for trimethoxysilane being 87%. Furthermore, they carried out the reactions of silicon with higher alcohols such as ethanol, 1-propanol and isobutyl alcohol to give alkoxysilanes especially trialkoxysilanes, silicon conversions being low at 15.5, 4.8, and 8.3%, respectively. n-Butyl, secondary and tertiary alcohols, such as isopropyl, sec-butyl and tert-butyl alcohol, did not react with silicon.

There have been many efforts to improve the selectivity for trimethoxysilane, which is of greater value than tetramethoxysilane. Many patents about liquid-phase synthesis of trimethoxysilane have been reported and discussed about the effect of solvents [41]. The mixture of silicon and copper(I) chloride was heated in the solvent such as dodecylbenzene, dibenzyltoluene, octylbenzene and liquid paraffin, and reacted with methanol at 200-240 ^{o}C. The selectivity for trimethoxysilane was high at 85-90%, silicon conversion being 80-92% in 8-10.5 h.

The method of trimethoxysilane synthesis using fluidized reactor was reported in a patent [42]. The silicon-copper(I) chloride mixture was pretreated at 350^{o}C and reacted with methanol under a hydrogen stream, products consisting of tetra-, tri- and dimethoxysilane. At 325 ^{o}C of reaction temperature, the selectivities for tetra-, tri- and dimethoxysilane were 6, 68 and 14 wt%, respectively. The point of this patent is the formation of dimethoxysilane. In the absence of hydrogen, tetra-, tri- and dimethoxysilane were obtained at 42, 45 and 2 wt% of the selectivities, respectively. These facts shows that the presence of hydrogen gave an increased yield of products having Si-H. This indicates hydrogen affects the selectivity.

The selective synthesis of trimethoxysilane in the presence of alkyl halide was reported [43]. The high selectivity for trimethoxysilane was obtained by the addition of alkyl chloride (1/90 of methanol) in an alkylbenzene solvent.

Suzuki et al. carried out the reaction in the fixed-bed flow reactor [44]. The mixture of silicon (with oxide overlayers) and copper(I) chloride heated under a helium stream at 723 K for 1 h before the reaction with methanol at 513 K. The silicon conversion reached 98% in 3 h, the selectivity for trimethoxysilane being 82%. High silicon conversion was obtained after high-temperature pretreatment (>623 K). The Cu_3Si phase was observed on the surface by the silicon-copper(I) chloride reaction above 623 K at the pretreatment stage. It is transformed into reactive sites once the reaction started.

We studied the effect of the oxide-layers covering the silicon surface on the reaction [45]. When the oxide overlayers were removed by washing silicon grains with a HF solution, a high silicon conversion was obtained even after low-temperature pretreatment (513 K), the selectivity for trimethoxysilane being almost 100%.

The preparation of the silicon-catalyst mixture was studied in order to improve the reaction rate. In the study of Kamata et al., copper(I) chloride was supported on the silicon surface to attempt to increase the number of reactive sites [46]. Silicon covered with oxide overlayers hardly reacted at 513 K of reaction temperature after the physical mixture of silicon and copper(I) chloride (2.5 wt%) was pretreated at 533 K. When the reaction of the copper(I) chloride-supported silicon with methanol was carried out, the silicon conversion reached 15%. Supporting copper(II) chloride on the silicon gave high silicon conversion [47]. When the supported silicon was reduced in a hydrogen stream at 553 K and reacted with methanol, silicon conversion and the selectivity were 100% and 89% in 5.5 h, respectively.

A catalyst other than copper compounds was reported [48]. Using sodium methoxide as a catalyst, the silicon reacted with methanol in tetramethoxysilane solvent at 140^{o}C in an autoclave reactor. However, tetramethoxysilane was only produced in this reaction, the reaction rate being slower than that using a copper catalyst.

The novel method of tetraalkoxysilanes formation from silica instead of metallic silicon was reported by Ono et al. [49]. The silica gel reacted with dialkyl carbonate to form tetraalkoxysilane. When dimethyl carbonate vapor was fed to silica gel loaded with alkali (or alkali earth) metal hydroxides or salts as catalysts, a 100% yield of tetramethoxysilane was obtained. They demonstrated that the reaction of rice hull ash can be used as a source of silica with dimethyl carbonate [50].

As described above, many studies of direct synthesis from metallic silicon and methanol were reported. However, there were a few reports of the reaction mechanism.

1-3 Aims of This Thesis

The synthesis of trimethoxysilane from silicon and methanol is important as a new route of synthesis of organosilanes. As mentioned in the previous section, Rochow discovered the reaction of silicon with methanol in vapor phase, a product being tetramethoxysilane [39]. Rochow et al. also reported the liquid-phase synthesis, tri- and tetramethoxysilane being formed [40]. Up to date, many patents for selective synthesis of trimethoxysilane were reported. In most of these patents, tedious operations for separation of the product from the solvent may be needed due to the liquid-phase reactions.

Suzuki et al. performed the gas-phase reaction of methanol and silicon covered with oxide layers in a fixed-bed flow reactor [44]. The silicon conversion and the selectivity for trimethoxysilane greatly depended on the conditions of the pretreatment of the silicon-copper(I) chloride mixture. Thus, a high silicon conversion with a high selectivity was obtained after the pretreatment of the silicon-copper(I) chloride mixture above 623 K. We reported the removal of oxide overlayers greatly improves the reactivity of silicon toward methanol [45].

The aims of this thesis are to determine the pretreatment and reaction conditions for obtaining a high yield of trimethoxysilane and to examine the mechanism for methoxysilane formation in the genuine reaction of pure silicon without oxide overlayers with methanol.

In order to obtain a high yield of trimethoxysilane, the pretreatment and reaction conditions was determined. In particular, the effect of the pretreatment conditions on the rate of methoxysilanes formation and the selectivity for trimethoxysilane was examined.

In the reaction of silicon with methanol using copper(I) chloride as a catalyst, copper(I) chloride reacts with silicon to form the precursor, Cu-Si alloy, of reactive sites on the silicon surface. The formation of reactive site was examined during the time course of the rate of methoxysilanes formation. In order to examine the nature of reactive sites, the kinetics of the reaction was examined.

The silicon-methanol reaction gives tri- and tetramethoxysilane. The factor determining the selectivity has not been clarified yet. It was reported that tetramethoxysilane is formed upon the reaction of trimethoxysilane with methanol catalyzed by metallic copper [17]. In the silicon-methanol reaction, metallic copper is formed during the reaction. It was determined whether tetramethoxysilane is a primary product or is formed by the secondary reaction of trimethoxysilane and methanol by the action of metallic copper. Poisoning of metallic copper by a proper additive to give selective formation of trimethoxysilane was carried out.

Several mechanisms for methylchlorosilane formation has been proposed, calling for further discussion. One of the aims in this thesis is to clarify the mechanism of methoxysilane formation. On the base of the reaction pathway of formation of methoxysilanes, the mechanism of methoxysilane formation and the intermediate of the reaction will be proposed. To obtain further evidence for the intermediate of the silicon-methanol reaction, the experiment of trapping the intermediate is attempted.

Organosilanes are produced by the reaction of silicon with alkyl chloride such as methyl chloride. On the base of the proposed mechanism, a new synthesis of organosilanes without the use of any alkyl halides is pursued.

The formation of Cu-Si intermetallic compound, which is the precursor of reactive sites, includes the transport of copper(I) chloride onto the silicon surface and the reaction of silicon with copper(I) chloride at the pretreatment stage. The vapor pressure of copper(I) halide and the reactivity of copper(I) halide toward methanol changes with the kind of the halide ion. To examine the role of halide ions in the formation of reactive sites, the reactions of silicon with methanol using various copper(I) halides were carried out. If the halide ion is involved in the reactive sites, the reaction order with respect to methanol pressure and the activation energy might change with the kind of the halide ion. The kinetics of the reaction with the three halides are examined and the results is discussed.

1-4 Outline of This Thesis

This thesis consists of following seven chapters.

In Chapter 1, I started with reviewing the direct syntheses of organosilanes and alkoxysilanes. The aims and outline of this thesis are stated.

In Chapter 2, the effect of the pretreatment conditions of the silicon-copper(I) chloride mixture on the rate of methoxysilanes formation and on the selectivity for trimethoxysilane is described. The time courses of the reaction rate and the selectivity after pretreating the mixtures at various temperatures and for various time were examined. To examine the surface state of the pretreated or reacting mixtures, the mixtures after the pretreatment were analyzed by XRD and EPMA and the reacting silicon surface were examined by SEM.

In Chapter 3, the kinetics of methoxysilanes formation is described. The effect of pretreatment conditions on the nature of reactive sites was examined from the dependences of methanol pressure and reaction temperature on the reaction rate.

In Chapter 4, the reaction pathway of methoxysilanes formation are examined. The method of the selective synthesis of trimethoxysilane is established and will be proposed the mechanism of trimethoxysilane formation.

In Chapter 5, a new synthesis of method of organosilanes will be presented. This offers supporting evidence for the reaction mechanism proposed in a previous chapter.

In Chapter 6, the silicon-methanol reactions using copper(I) bromide and iodide instead of the chloride as catalysts are described. The effect of the halide ion on the rate of methoxysilanes formation, the formation of reactive site and the nature of reactive sites is examined.

In Chapter 7, the content of this thesis is summarized and the remaining problems and future possibilities of direct synthesis will be discussed.

References

1) E.G. Rochow, J. Am. Chem. Soc., 67, 963 (1945).

2) Japan Tokkyo Koho 61-11957 (1986).

3) H. Kautsky, Z. Naturforsch., 7b, 174 (1952).

4) E. Bonitz, Chem. Ber., 94, 220 (1961).

5) E. Bonitz, Angew. Chem. Internat. Edit., 5, 462 (1966).

6) A. Boudin, G. Cerrean, C. Chuit, R.J.P. Corriu and C. Reye, Organometallics, 7, 1165 (1988).

7) A.L. Klebansky and V.S. Fikhtengolts, J. Gen. Chem. USSR, 26, 2795 (1956).

8) T.Araki and Y. Takami, Rept. Govt. Chem. Ind. Res. Inst. Tokyo, 45, 113 (1950).

9) L.D. Gasper-Galvin, D.M. Sevenich, H.B. Friedrich, and D.G. Rethwisch, J. Catal., 128, 468 (1991).

10) J.P. Kim, and D.G. Rethwisch, J. Catal., 134, 168 (1992).

11) British Patent 622516 (1949): M. Sekino, S. Miyakawa, H. Hani, K. Imamuro and W. Ichikawa, Rept. Res. Lab. Asahi Glass Co. Ltd., 2, 78 (1952).

12) British Patent 680953 (1952).

13) Japanese Patent 74 (1953).

14) U.S. Patent 2380998 (1945): British Patent 575674 (1946): British Patent 6255191 (1949).

15) U.S. Patent 2466429 (1949).

16) P. Trambouze, Bill. Soc. Chim. France, 1756 (1956).

17) R.J.H. Voorhoeve, "Organohalosilanes: Precusor to Silicones," Elsevier, Amstrdam (1967).

18) R.J.H. Voorhoeve, J.A. Lips, and J.C. Vlugter, J. Catal., 3, 414 (1964).

19) T.C. Frank, K.B. Kester, and J.L. Falconer, J.Catal., 91, 44 (1985).

20) T.C. Frank, and J.L. Falconer, Appl. Surf. Sci., 14, 359 (1982-83).

21) K.M. Lewis, D. McLeod, and B. Kanner, Stud. Surf. Sci. Catal., Catalysis, 38, 415 (1987).

22) W.F. Banholzer, and M.C. Burrell, J. Catal., 114, 259 (1988).

23) A.K. Sharma and S.K. Gupta, J.Catal., 93, 68 (1985).

24) S.K. Gupta and A.K. Sharma, J. Catal., 103, 263 (1987).

25) T.M. Gentle and M.J. Owen, J. Catal., 103, 232 (1987).

26) C. Chen, S. Li and B. Kang, Hecheng Xiangiiao Gongye, 7, 146 (1984).

27) D.T. Hurd and E.G. Rochow, J. Am. Chem. Soc., 67, 1057 (1945).

28) V.S. Fikhtengolts and A.L.Klebansky, J. Gen. Chem. USSR, 27, 2535 (1956).

29) J. Joklik, M. Kraus and V. Bazant, Coll. Czech. Chem. Comm., 27, 974 (1962).

30) R.J.H. Voorhoeve, J.A. Lips and J.C. Vlugter, J. Catal., 4, 220 (1965).

31) R.J.H. Voorhoeve and J.C. Vlugter, J. Catal., 4, 123 (1965).

32) V.I. Zubkov, M.V. Trikhomirov, K.A. Andrianov, and Golubtsuv, Dokl. Akad. Nauk SSSR, 159, 1221 (1964).

33) M.P. Clarke, and I.M.T. Davidson, J. Organomet. Chem., 408, 149 (1991).

34) I.M. Podgornyi, S.A. Golubtsov, K.A. Andrianov, and E.G. Mangalin, J. Gen. Chem. USSR, 44, 739 (1974).

35) I.M. Podgornyi, S.A. Golubtsov, K.A. Andrianov, and E.G. Mangalin, J. Gen. Chem. USSR, 44, 745 (1974).

36) T.C. Frank, and J.L. Falconer, Langmuir, 1 104 (1985).

37) Eur. Patent Appl., 201919 (1986).

38) E. Suzuki, M. Okamoto and Y. Ono, Chem. Lett., 1487 (1989).

39) E.J. Rochow, J. Am. Chem. Soc., 70, 2170 (1948).

40) W.E. Newton and E.G. Rochow, Inorg. Chem., 9, 1071 (1970).

41) Japan Tokkyo Kokai Koho 55-28928 (1980): Japan Tokkyo Kokai Koho 57-108094 (1982): Japan Tokkyo Kokai Koho 57-99593 (1982).

42) German Patent 1127338 (1960).

43) Eur. Patent 280517 (1988).

44) E. Suzuki and Y. Ono, J. Catal., 125, 390 (1990).

45) E. Suzuki, M. Okamoto, and Y. Ono, Solid State Ionics, 47, 97 (1991).

46) T. Kamata, Master Thesis, Tokyo Institute of Technology, (1989).

47) E. Suzuki, T. Kamata, and Y. Ono, Bull. Chem. Soc. Jpn., 64, 3445 (1991).

48) Kokai Tokkyo Koho 63-41482 (1988).

49) Y. Ono, M. Akiyama, and E. Suzuki, Chem. Mater., 5, 442 (1993).

50) M. Akiyama, E. Suzuki, and Y. Ono, Inorg. Chim. Acta, 207, 259 (1993).

Chapter 2 Effect of the Pretreatment on the Rate of Methoxysilanes Formation and the Selectivity for Trimethoxysilane

2-1 Introduction

Trimethoxysilane is one of the important chemicals from which various organosilicon compounds can be derived.

Rochow discovered the vapor-phase synthesis of tetramethoxysilane from methanol and silicon fused with copper as a catalyst [1]. Rochow et al. reported the liquid-phase synthesis of methoxysilanes, the products being of tri- and tetramethoxysilane [2].

Many efforts have been made to obtain trimethoxysilane with a high selectivity [3]. When the reaction of silicon with methanol using copper(I) chloride as a catalyst was carried out in the solvent such as dodecylbenzene and diundecylbenzene, a 90% selectivity with a high silicon conversion was obtained.

Suzuki et al. studied the reaction of methanol and silicon covered with oxide-layers [4,5]. They reported that the reaction rate and the selectivity for trimethoxysilane were greatly influenced by the conditions of the pretreatment of the silicon-copper(I) chloride mixture prior to feeding methanol as well as the reaction conditions. Thus, when the pretreatment 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, though the selectivity for trimethoxysilane was very high (>96%). On the other hand, when the pretreatment temperature was above 623 K, the induction period was eliminated and almost complete conversion of silicon was attained, though the selectivity for the trimethoxysilane was low (70-80%). Formation of the Cu_3Si phase was observed after the pretreatment.

We have shown that silicon grains stored in ambient conditions have SiO_2-overlayers and that the treatment of the silicon grains with an aqueous HF solution greatly improves the reactivity of the silicon towards methanol [6]. Viale et al. have also noted that the formation of Cu_3Si by the reaction of silicon with copper(I) chloride vapor is greatly promoted by removing SiO_2-overlayers [7].

It is very important to use silicon grains without oxide overlayers for understanding the mechanism of the reaction. Therefore, I examined the vapor-phase reaction of methanol with silicon grains which had been washed with an aqueous HF solution.

In this chapter, in order to determine the pretreatment and reaction conditions for obtaining a high conversion with a high selectivity for trimethoxysilane, the effects of the pretreatment of the silicon-copper(I) chloride mixture and the reaction conditions, especially pretreatment temperature are examined. To examine the effect of the pretreatment temperature on the formation of Cu-Si intermetallic compounds by the reaction of silicon and copper(I) chloride, the mixtures of silicon and copper(I) chloride pretreated at various temperatures were analyzed by XRD, SEM and EPMA.

2-2 Experimental

2-2-1 Reagents

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 (46%) at room temperature for 1 h to remove the SiO_2-overlayers. The silicon grains thus treated have SiO_2-overlayers with 0.23 nm in thickness, as determined by ESCA [6].

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 a 46% HF solution for 1 h.

Copper(I) chloride grains (Wako Pure Chemical Industries, Ltd.) were 99.9% in purity. They were sieved into grains of 45-63 μm.

Methanol and heptane (Kanto Chemical Co., Ltd.: guaranteed reagent grade) were dehydrated over molecular sieve 3A.

2-2-2 Reaction Procedures and Analysis of the Products

The reaction of silicon with methanol was carried out in a fixed-bed reactor. A 0.168 g (6.00 mmol) portion of the silicon grains was mixed with the copper(I) chloride grains (Cu/(Cu+Si) = 0.01-0.1 by weight) in a vial. The mixture was loaded in a reactor of silica quartz tube (10 mm i.d.) placed in an infrared furnace and then heated under a helium stream (30 cc h^{-1}) at 513-723 K for 0-12 h prior to feeding methanol. In the experiments where the silicon wafer was used, a small piece of the wafer (4.5 x 4.5 mm) was embedded in the mixture of silicon and copper(I) chloride grains.

Methanol at various pressures between 12–98 kPa was fed to the reactor at 493–553 K. The total flow rate of methanol and helium was 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.

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.

2-3 Effect of the Pretreatment on the Rate of Methoxysilanes Formation

2-3-1 Effect of the Pretreatment Temperature

As described above, in the reaction of methanol with silicon having thick SiO_2-overlayers, the temperature of pretreating a silicon-catalyst mixture had a great effect on the reactivity of silicon and the selectivity for trimethoxysilane [4]. Here, the effect of the pretreatment temperature 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 pretreated at a given temperature for 1 h, methanol (59 kPa) was fed to the reactor at 513 K. Figure 2-1 shows the changes

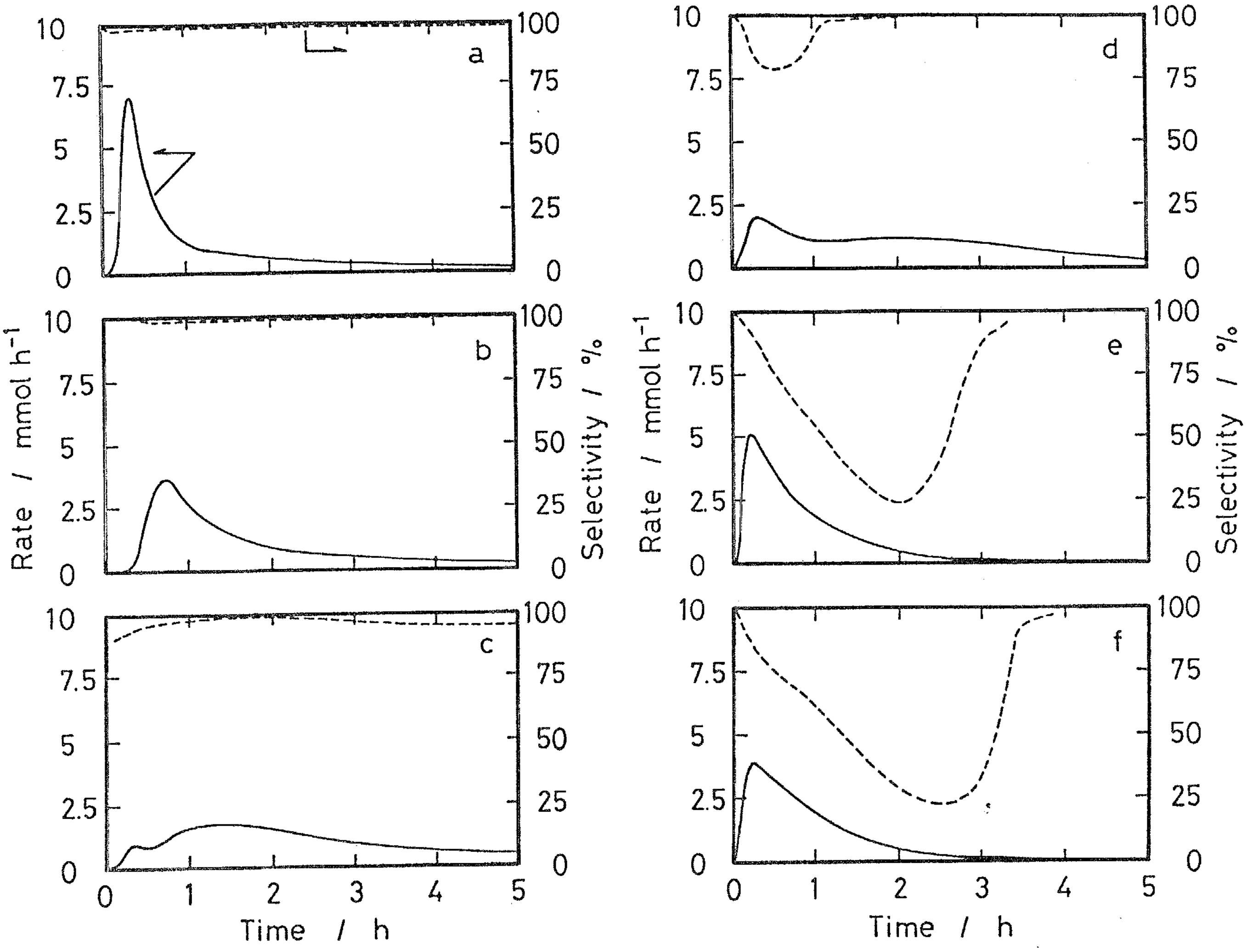


Figure 2-1 Effect of the pretreatment temperature on the change in the rate of methoxysilanes formation and the selectivity for trimethoxysilane with time.
Preheating temperature= 513(a), 553(b), 603(c), 623(d), 673(e), and 723 K(f), pretreatment time= 1 h, Cu= 10 wt%.
Reaction temperature= 513 K, CH_3OH= 59 kPa.
Solid and dashed lines represent the rate of methoxysilanes formation and the selectivity for trimethoxysilane, respectively.

in the rate of methoxysilanes ($(CH_3O)_3SiH$ and $(CH_3O)_4Si$) formation and in the selectivity for trimethoxysilane with reaction time. When the pretreatment temperature was 513 K (Fig. 2-1a), the rate increased just after starting a methanol feed and, beyond a maximum, it decreased. At the pretreatment temperature of 553 K (Fig. 2-1b), an induction period in the rate curve became apparent, and the position of the rate maximum shifted to a later reaction time. With the low pretreatment temperatures, trimethoxysilane was formed with a high selectivity (> 98%) throughout the reaction.

At the pretreatment temperature of 603 K (Fig. 2-1c), 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-pretreatment, the later maximum shifted further to an even later reaction time, while the earlier maximum at 0.25 h became more evident (Fig. 2-1d). The later maximum seems to correspond to the one formed at lower pretreatment temperature. The shift of the rate maximum to a later reaction time indicates that the surface state changes with pretreatment temperature. The appearance of the earlier maximum suggests the development of a new type of the reactive surface.

At higher pretreatment temperatures of 673 and 723 K (Figs. 2-1e and f), only one rate maximum appeared at 0.25 h. The selectivity for trimethoxysilane became very low with increasing reaction time except 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 pretreatment temperatures and gives a high selectivity for trimethoxysilane.

The other appears at higher pretreatment 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. 2-1, was 88, 78, 75, 88, 74, and 74% for the mixtures pretreated at 513, 553, 603, 623, 673, and 723 K, respectively. In this order of pretreatment temperature, the overall selectivity for trimethoxysilane during 5 h was 98, 99, 97, 96, 66, and 64%. As mentioned above, lower pretreatment temperature favors the high selectivity for trimethoxysilane.

Voorhoeve [9,10] studied the effect of pretreatment of a silicon-copper(I) chloride mixture on the formation of Cu_3Si phase and concluded that the pretreatment at 673 K is effective for obtaining high reactivity toward methyl chloride, since high temperature is advantageous to effectively convert copper into Cu_3Si phase, which was supposed to be the active phase. The result in this study shows that this does not directly applicable to the reaction of silicon with methanol, since very high reactivity of silicon was attained by the pretreatment as low as 513 K.

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

2-3-2 Effect of the Pretreatment 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 pretreating the silicon-catalyst mixture. Time of pretreatment 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 pretreated for 0.17, 0.5, 1.0, 5.0, or 12 h at 603 K. An experiment without pretreatment was also carried out. Results are shown in Fig. 2-2.

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

The silicon conversions after 5 h of the reaction at 603 K with pretreating at 513 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 pretreatment time of less than 1 h. On the other hand, the selectivity was depressed upon prolonged pretreatment.

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

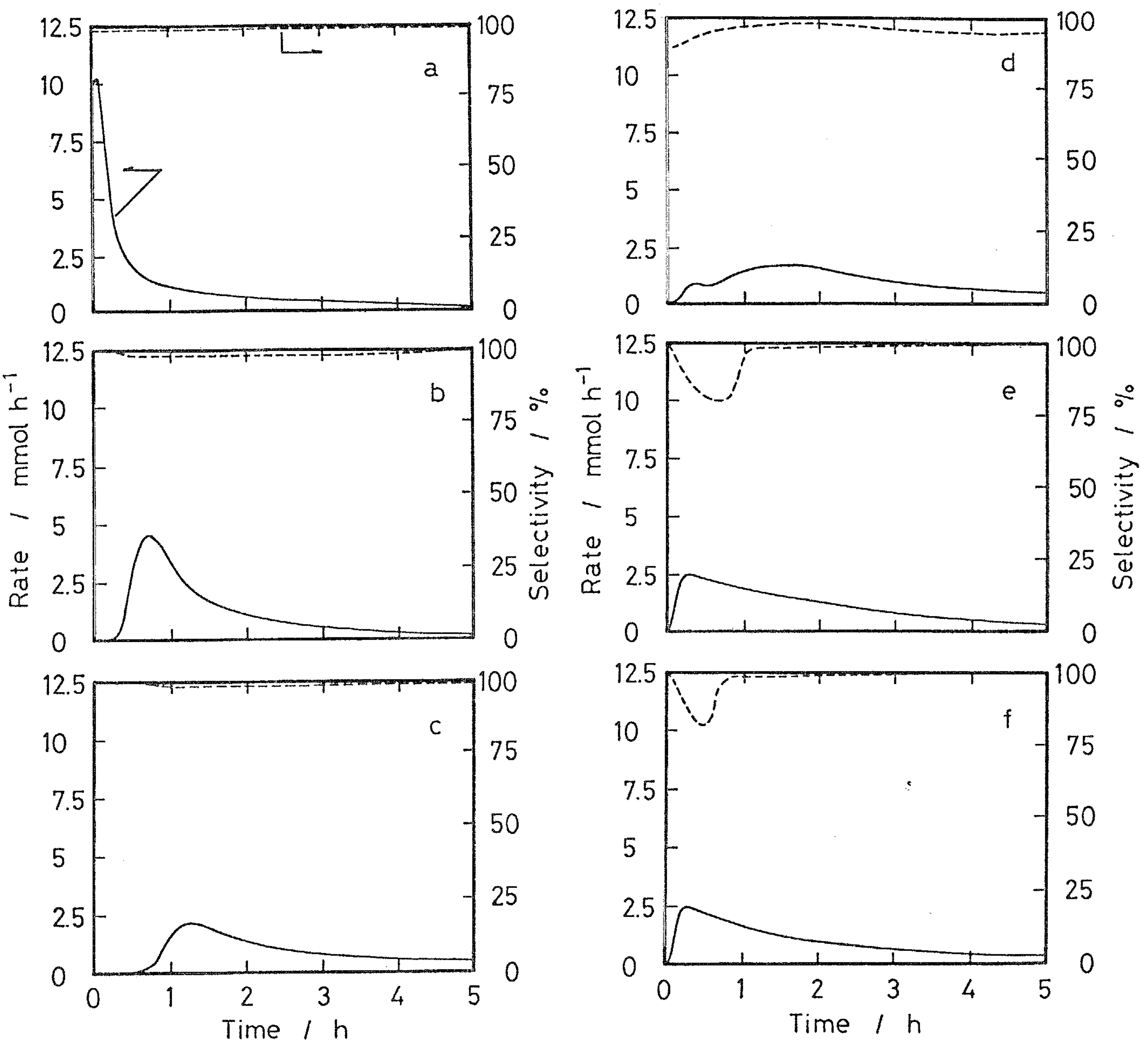


Figure 2-2 Effect of the pretreatment time on the change in the rate of methoxysilanes formation and the selectivity for trimethoxysilane with time.
Preheating temperature= 603 K, pretreatment time= 0(a), 0.17(b), 0.5(c), 1(d), 5(e), and 12 h(f), Cu= 10 wt%.
Reaction Temperature= 513 K, CH_3OH= 59 kPa.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

while high-severity pretreatment gives those with low trimethoxysilane selectivity.

2-3-3 Analysis of the Silicon-Copper(I) Chloride Mixture after the Pretreatment

In the reaction of silicon with methyl chloride, it is a usual practice to pretreat silicon-catalyst mixtures at 620-670 K prior to the reaction [5-11]. The pretreatment promotes the formation of silicon-copper alloys such as Cu_3Si, which are believed to be a prerequisite for the reaction to start [8,9]. It is rather surprising that the reaction of silicon with methanol starts with mild pretreatment or without any pretreatment.

The mixtures of copper(I) chloride and silicon grains 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. 2-3a). 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. 2-3b). The diffraction peaks due to the Cu_3Si phase was more intense at 723 K of the heating temperature (Fig. 2-3c). When heating time was prolonged to 12 h at 603 K, the Cu_3Si phase was observed (Fig. 2-3d), though it was not observed upon 1 h or 5 h-heating.

2-3-4 Analysis of the Silicon Surface after the Pretreatment

Weber et al. [12] 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

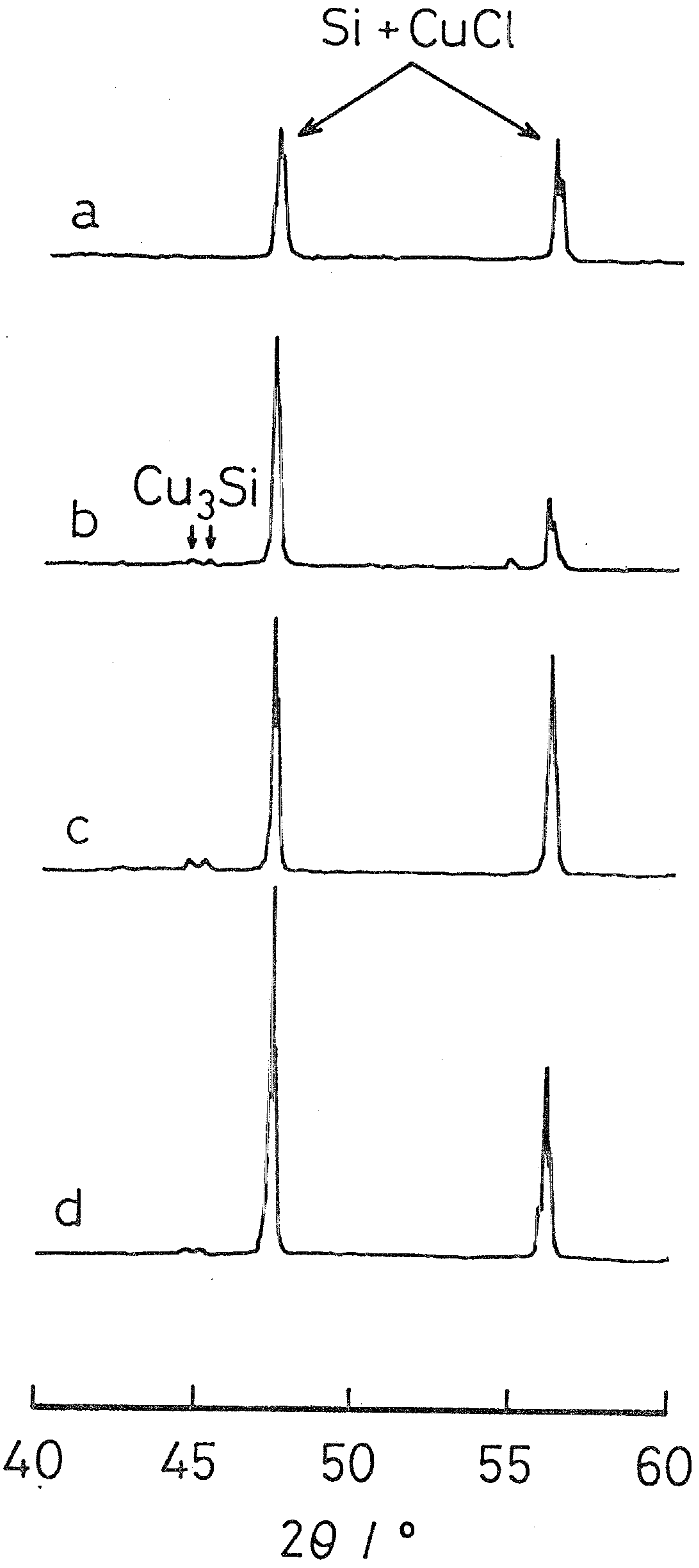


Figure 2-3 XRD patterns of Si-CuCl mixtures heat-treated under various conditions.
Heat-treatment conditions:(a) 603 K for 1 h, (b) 623 K for 1 h, (c) 723 K for 1 h, and (d) 603 K for 12 h.
Cu= 10 wt%.

that pits are formed on the silicon surface where the Cu_3Si phase has been located. The formation of the Cu_3Si phase was examined using this technique. The method by Weber et al. [12] was slightly modified; the wafers were treated with aqueous ammonia before treating with nitric acid and then with sodium hydroxide, simply because more contrasty photos were obtained in this way.

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. 2-4a, 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 temperature of the heat treatment (Figs. 2-4b and c). These results show that the patches of a Cu-Si alloy phase are formed and scattered on the silicon surface by the 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 silicon surface upon a reaction with copper(I) chloride above 695 K has been reported by Weber et al. [12-15].

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 2-5a 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 of

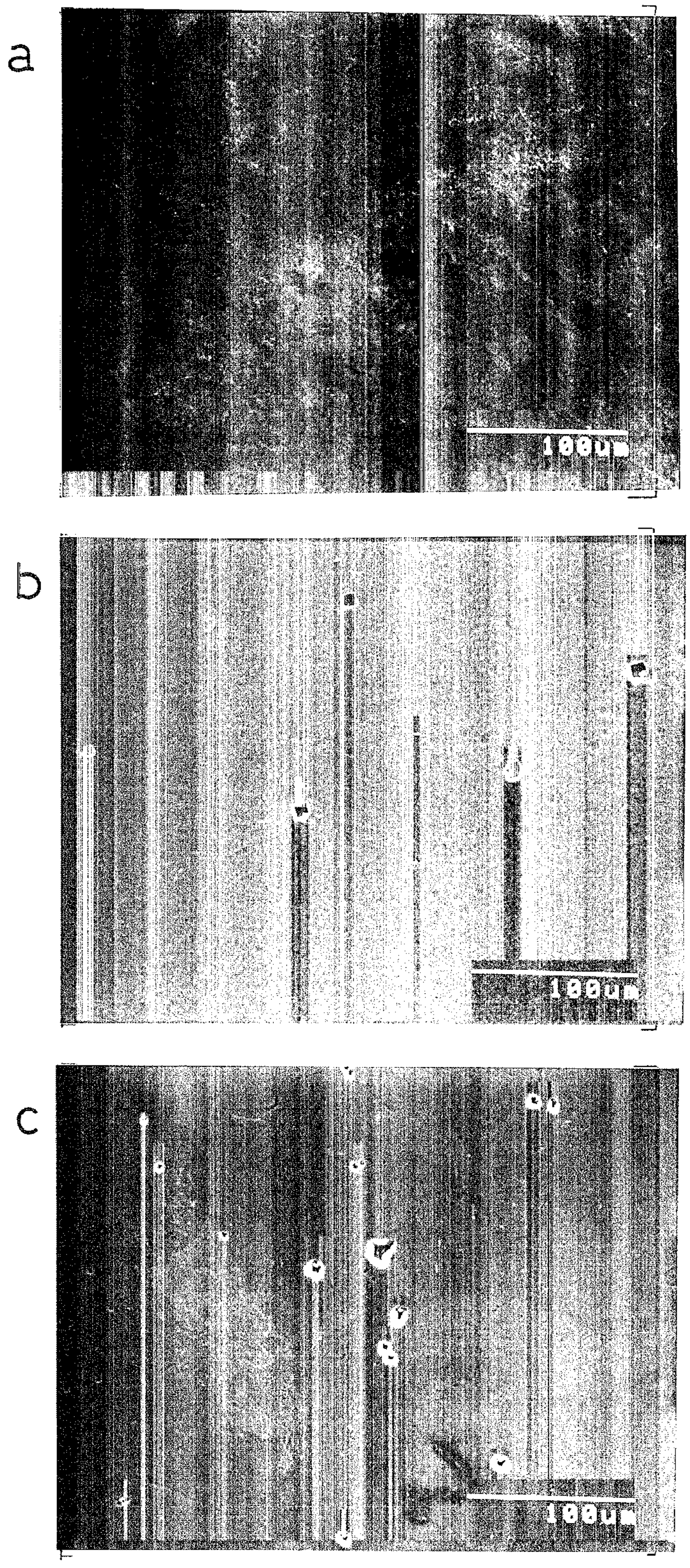


Figure 2-4 Scanning electron micrograph of the silicon wafers after the pretreatment.
Preheating temperature= 493(a), 623(b), and 723 K(c).
Preheating time= 1 h, Cu= 10 wt%.
The wafers were washed successively with aqueous solutions of ammonia for 15 min, nitric acid (11 mol dm^{-3}) for 1 h, and sodium hydroxide (1 mol dm^{-3}) for 1 h at room temperature. Micrographs were taken at 240 magnifications.

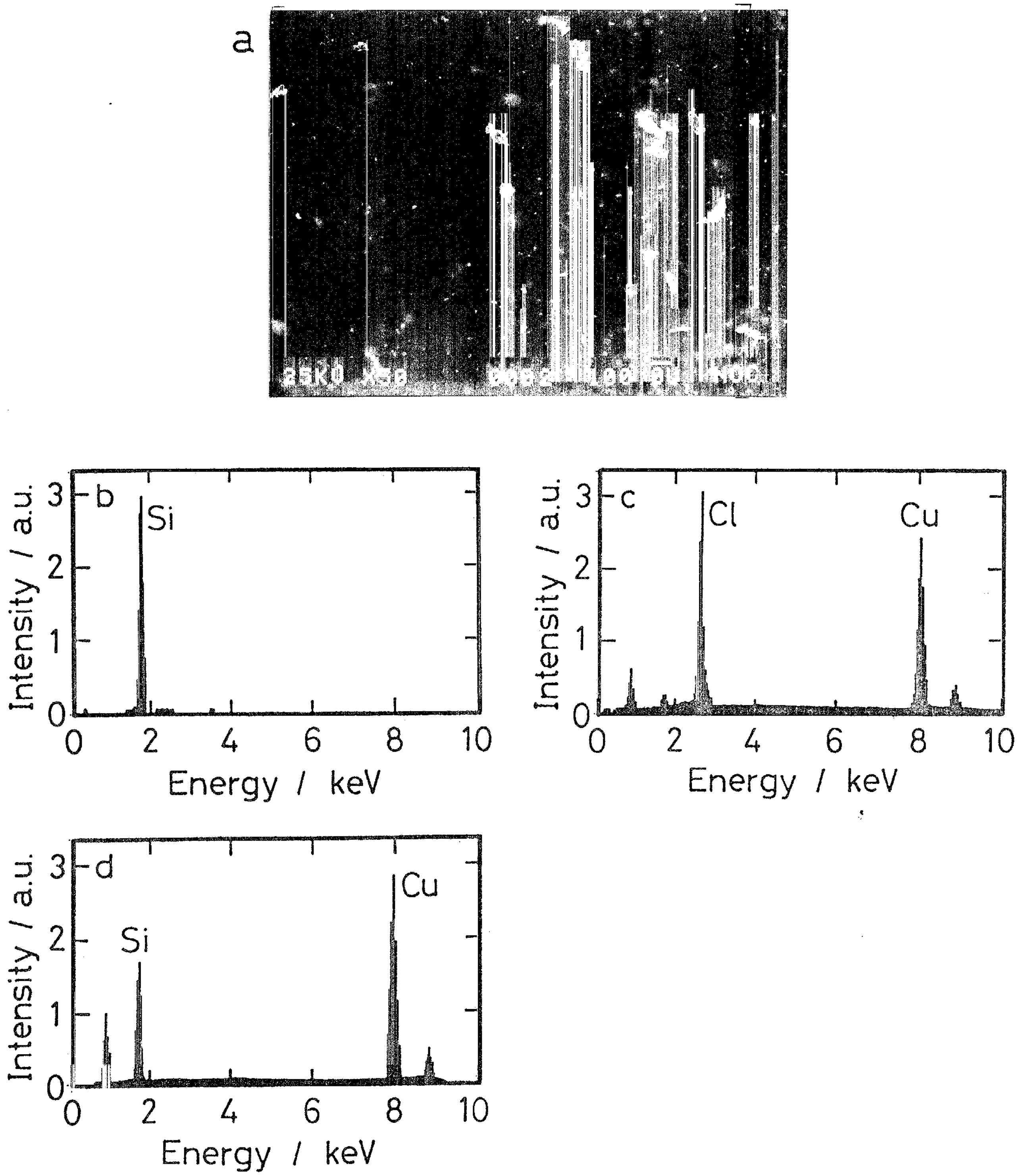


Figure 2–5　Electron probe microanalysis (EPMA) of the silicon wafer pretreated at 723 K.
The silicon was heated with copper(I) chloride at 723 K for 1 h.
(a) electron micrograph at 38 magnifications.
(b) EPMA signals from the area without patches.
(c) and (d), EPMA signals from the area in a patch.

10–200 μm. The EPMA pattern from the area without the patches showed no signals other than silicon as shown in Fig. 2–5b. Examples of EPMA patterns from the patches are shown in Figs. 2–5c and d. In the case of Fig. 2–5c, 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. 2–5d, 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 accord with the XRD results.

Figure 2–6a 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. 2–6a gave the signal patterns shown in Figs. 2–6b and c, 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 pretreatment at 493 K, indicating that a chemical interaction exists between the silicon surface and copper(I) chloride. It is concluded that the size of the alloy formed under mild pretreatment conditions is too small to be detected by an XRD or an EPMA technique.

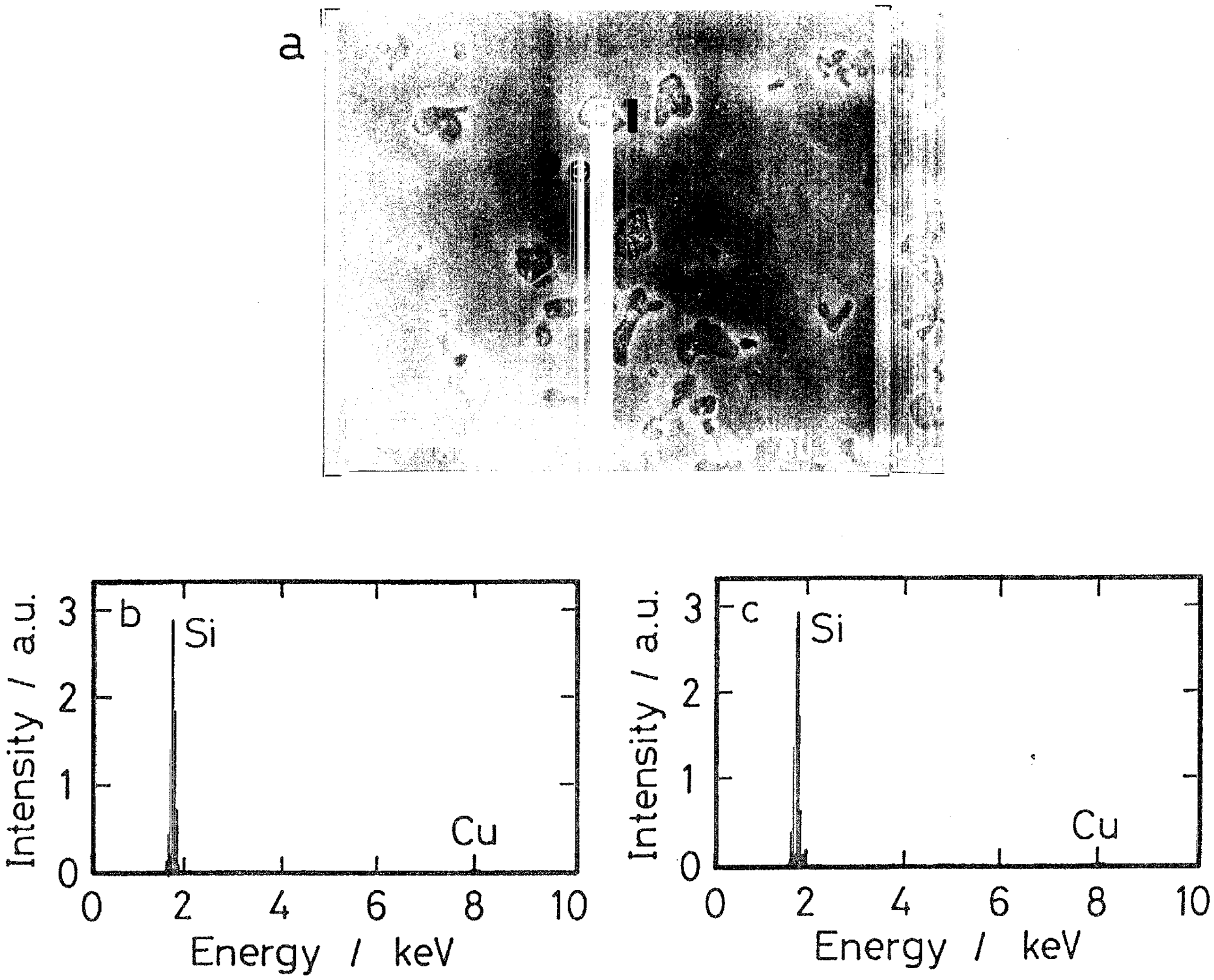


Figure 2-6 Electron probe microanalysis (EPMA) of the silicon wafer pretreated at 493 K.
The silicon was heated with copper(I) chloride at 493 K for 1 h.
(a) electron micrograph at 78 magnifications.
(b) and (c) EPMA signals from the areas designated as 1 and 2 in (a), respectively.

The results described above clearly show that the pretreatment conditions of silicon-copper(I) chloride mixtures, especially pretreatment 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 pretreated mainly at two temperatures (723 and 513 K), which represent the pretreatment under high and low severity conditions, respectively.

2-3-5 Effect of the Pretreatment Temperature on the Formation of Reactive Site by SEM

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 [10]. We observed the formation of the pits in the copper(I) chloride-catalyzed reaction of methanol with silicon with SiO_2-overlayers [4].

As described above, the patches of Cu_3Si phase are formed on 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 technique.

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, pretreated at 723 K 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.

(a) Reaction after the Pretreatment at 723 K

Figure 2-7 shows the SEM photographs of the grains and the wafer, after the 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 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. 2-8. 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 appreciably 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 discrete area on the surface and that the silicon atoms

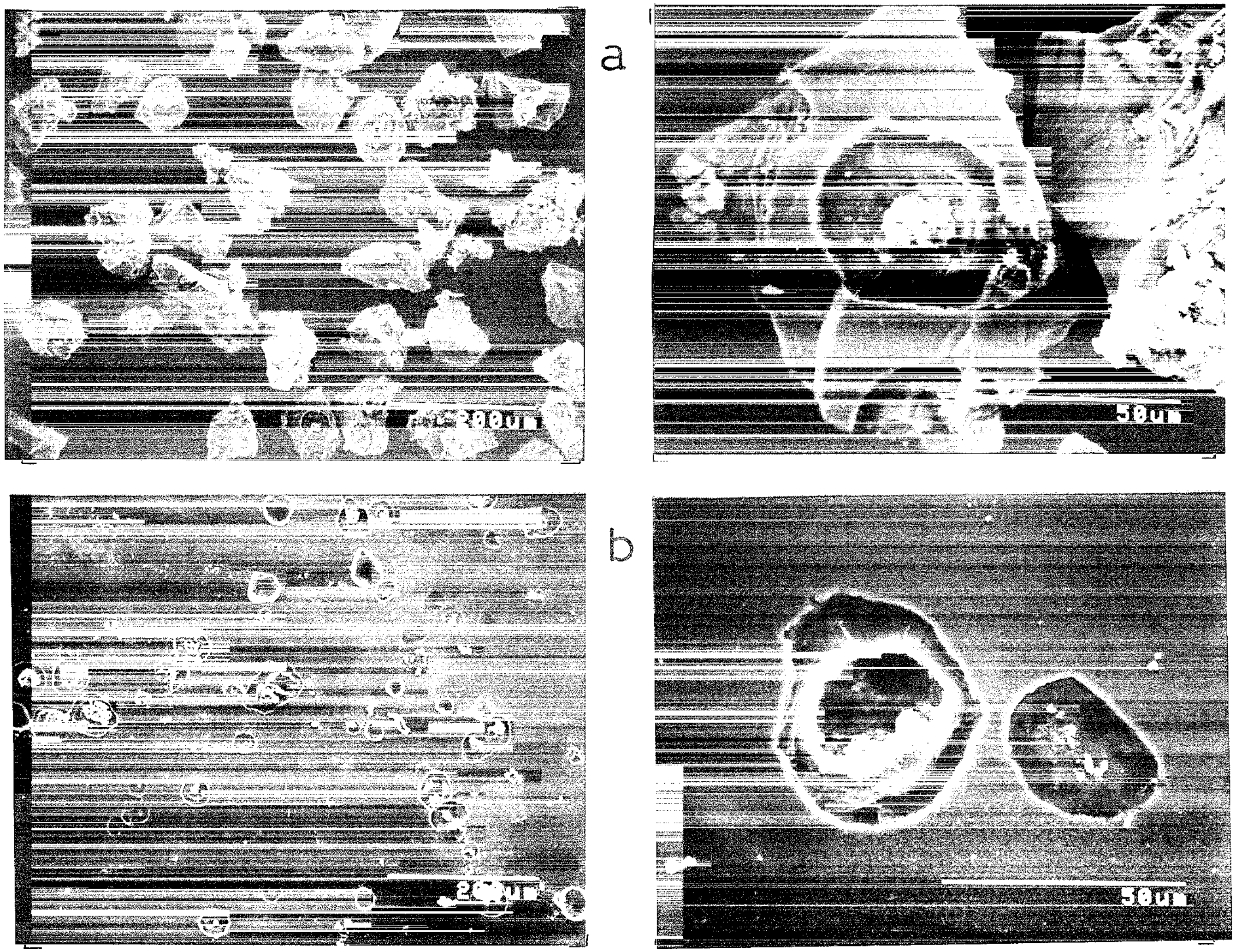


Figure 2-7 Surface morphology of silicon grains (a) and silicon wafer (b) upon reaction with methanol after pretreatment at 723 K.
Reaction temperature= 493 K, CH_3OH= 16 kPa. Si conversion = 30%. The left and the right plates were obtained at 120 and 780 magnifications, respectively.

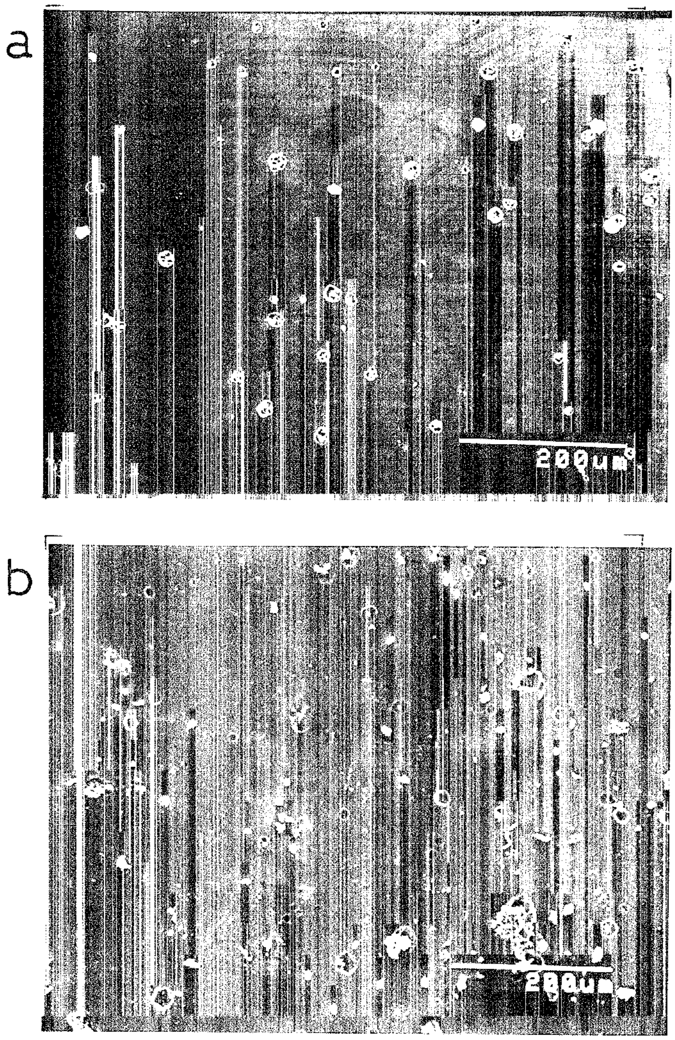


Figure 2-8 Change in the distribution of pits on the surface of silicon wafer with silicon conversion. Reaction conditions are the same as those in Fig. 2-7. Silicon conversion= 1(a), 5(b), 10(c), 30(d), and 45%(e). The plates were obtained at 120 magnifications.

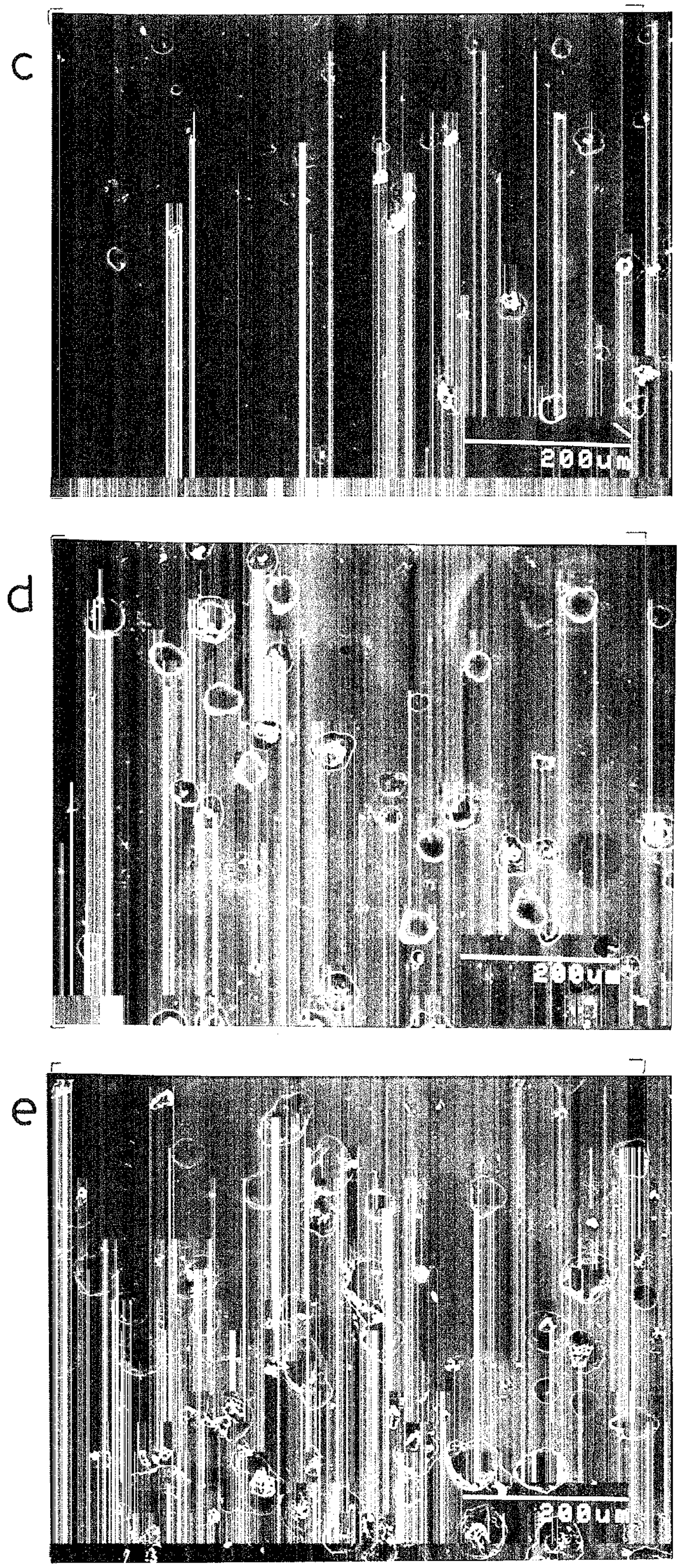


Figure 2-8 Continued.

are consumed around the area.

Distribution of the size of the pits is shown in Fig. 2-9. 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 a 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 the 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 Chapter 4.

As described above, the patches of Cu_3Si phase are formed on the silicon surface during the pretreatment of the silicon-catalyst mixtures. The number of the 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 the pretreatment 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

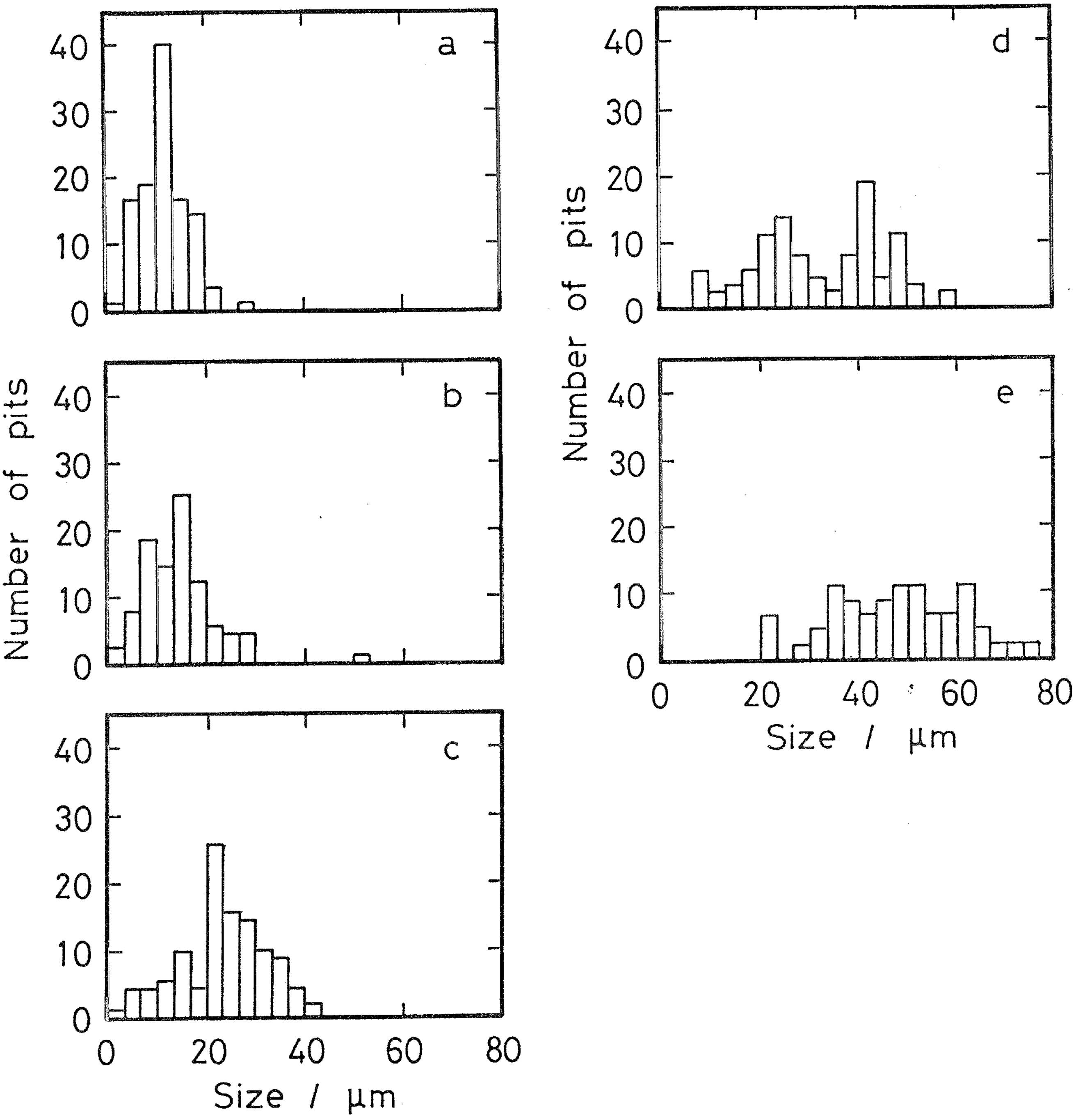


Figure 2-9 Size distribution of pits on the silicon surface during the silicon-methanol reaction.
Experimental conditions and notation (a-e) are the same as those in Fig. 2-8.

intermediate is probably an intermetallic compound of Si and Cu, but that the Cu_3Si phase formed during the pretreatment is merely a source of Cu for the real reactive intermediate. Banholzer and Burrell [11] 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 the pits on the silicon surface. An image of an area where the small pits are located is shown in Fig. 2-10a. The EPMA signals from the center of the pits are shown in Fig. 2-10b and c. 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 Cu_3Si phase has been located.

The formation of the alloy phase by a transport of copper(I) chloride onto silicon surface from the vapor phase has been reported [7,12,15]. To confirm the transfer of copper(I) chloride through 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

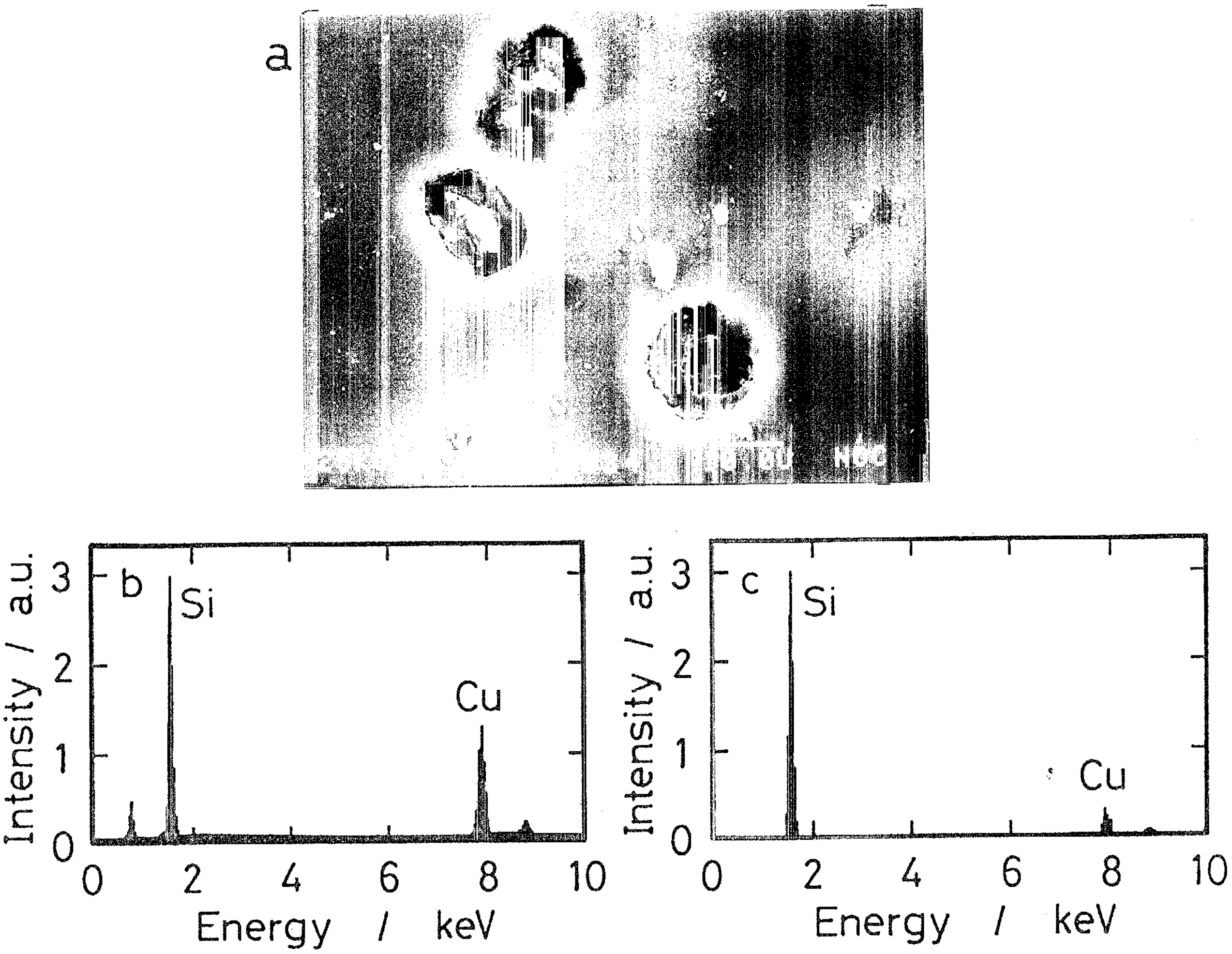


Figure 2-10 Electron probe microanalysis of the silicon wafer pretreated at 723 K and exposed to methanol. Reaction temperature= 493 K, CH_3OH= 18 kPa. Si conversion = 0.3%.
(a) Electron micrograph at 950 magnifications,
(b) and (c) EPMA signal patterns from the center of pits.

those in the reaction where a mixture of silicon and copper(I) chloride was subjected to the reaction.

(b) Reaction after the Pretreatment at 493 K

A mixture of silicon, a silicon wafer, and copper(I) chloride grains was packed in a fixed-bed reactor. The mixture was pretreated at 493 K for 1 h and methanol was fed at the same temperature. The reaction was stopped when the silicon conversion reached a certain value.

Figure 2-11 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. 2-11, pits were observed even at the conversion of 0.01%. Upon increasing the conversion to 0.4%, the number of pits sharply increased (Fig. 2-11b), indicating that the reaction sites were newly formed after feeding methanol. The number 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. 2-11c), 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. 2-11d and e), the number of smaller pits 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

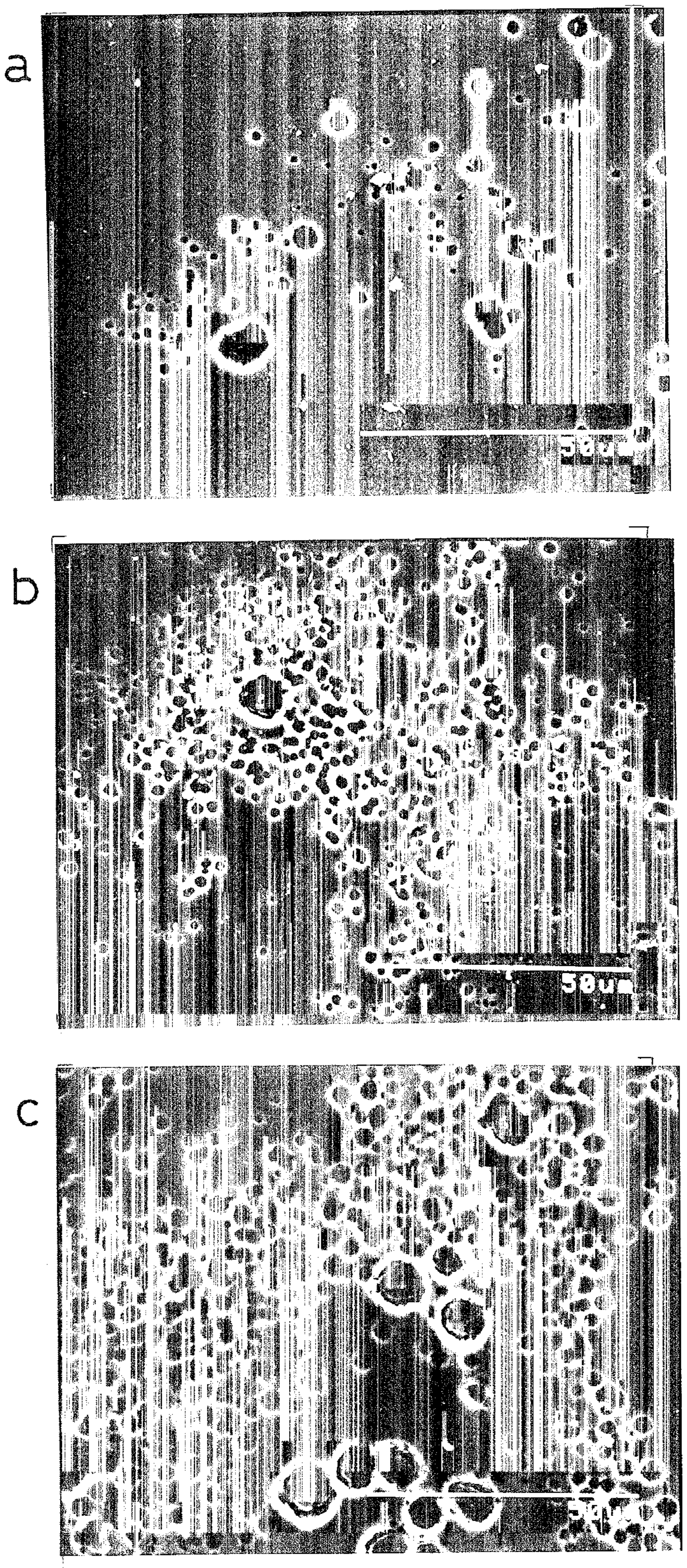


Figure 2-11 Scanning electron micrographs of silicon wafers reacted with methanol up to various silicon conversions after pretreatment at 493 K.
Preheating temperature= 493 K, Cu= 10 wt%.
Reaction temperature= 493 K, CH_3OH= 27 kPa.
Silicon conversion= 0.01(a), 0.4(b), 0.7(c), 4.8(d), 15.1(e), and 43.5%(f).
The plates were obtained at 780 magnifications.

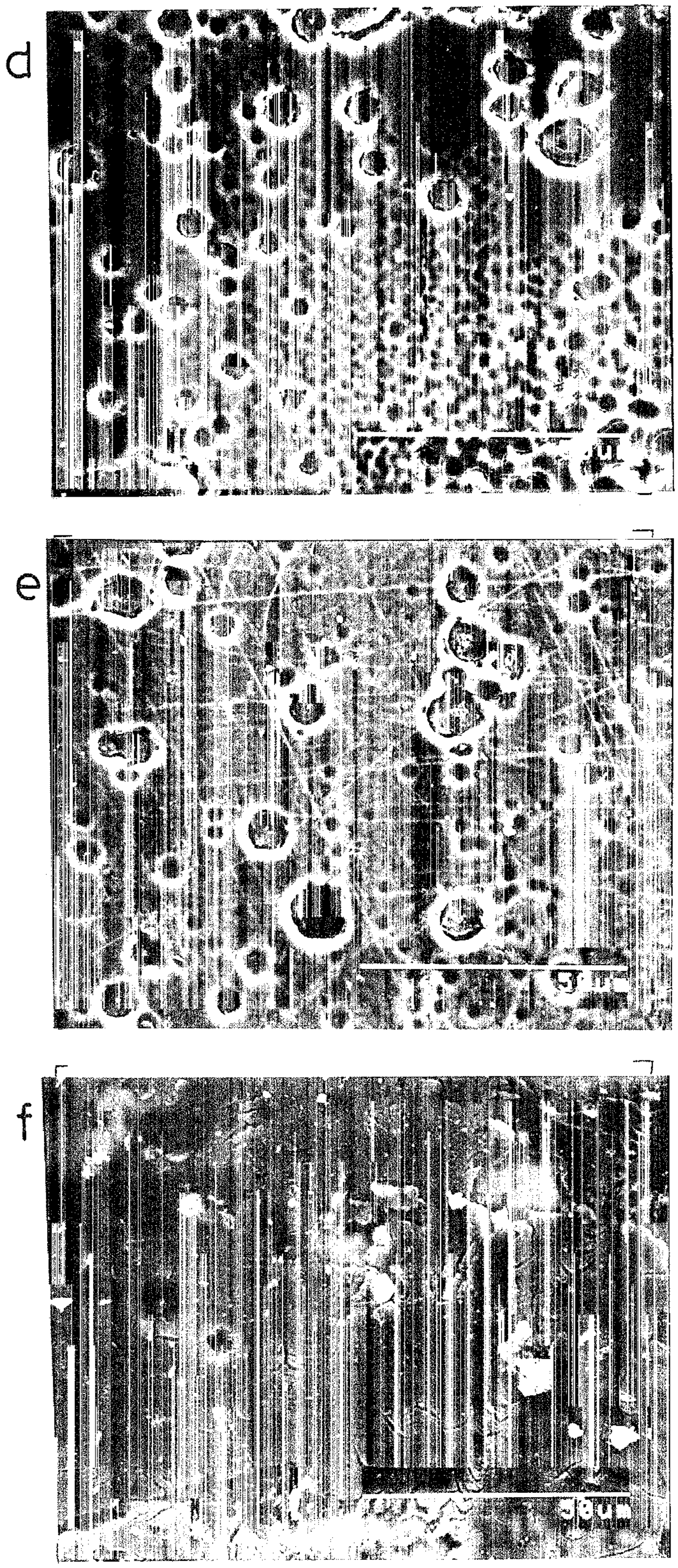


Figure 2-11 Continued.

in Fig. 2-11e). At 43.5% conversion (Fig. 2-11f), 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 during the reaction with methanol indicates that the Si-Cu colonies 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 pits with observable size due to the consumption of silicon atoms around the patches. The micrographs of the silicon grains are shown in Fig. 2-12. 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.

At conversion of 0.01%, the formation of small pits are seen (Fig. 2-12a). As seen in Fig. 12b, the number of pits increased when the conversion increased to 0.4%. The size of pit increased with increasing silicon conversion (Figs. 2-12c and d). At conversion of 4.8%, every part of the surface became reacting area (Fig. 2-12d). This tendency is more clearly seen at higher conversion level (Fig. 2-12e). As the result, the number of pit decreases and the surface becomes smooth. When the conversion was increased to 43.5%, most of pits disappeared and the surface became very smooth (Fig. 2-12f). This means that silicon atoms are consumed homogeneously at all areas of the surface at this stage. These change in the surface morphology of the grains with silicon conversion is very similar to that found on the surface of the wafer, except for the stripping of surface skins

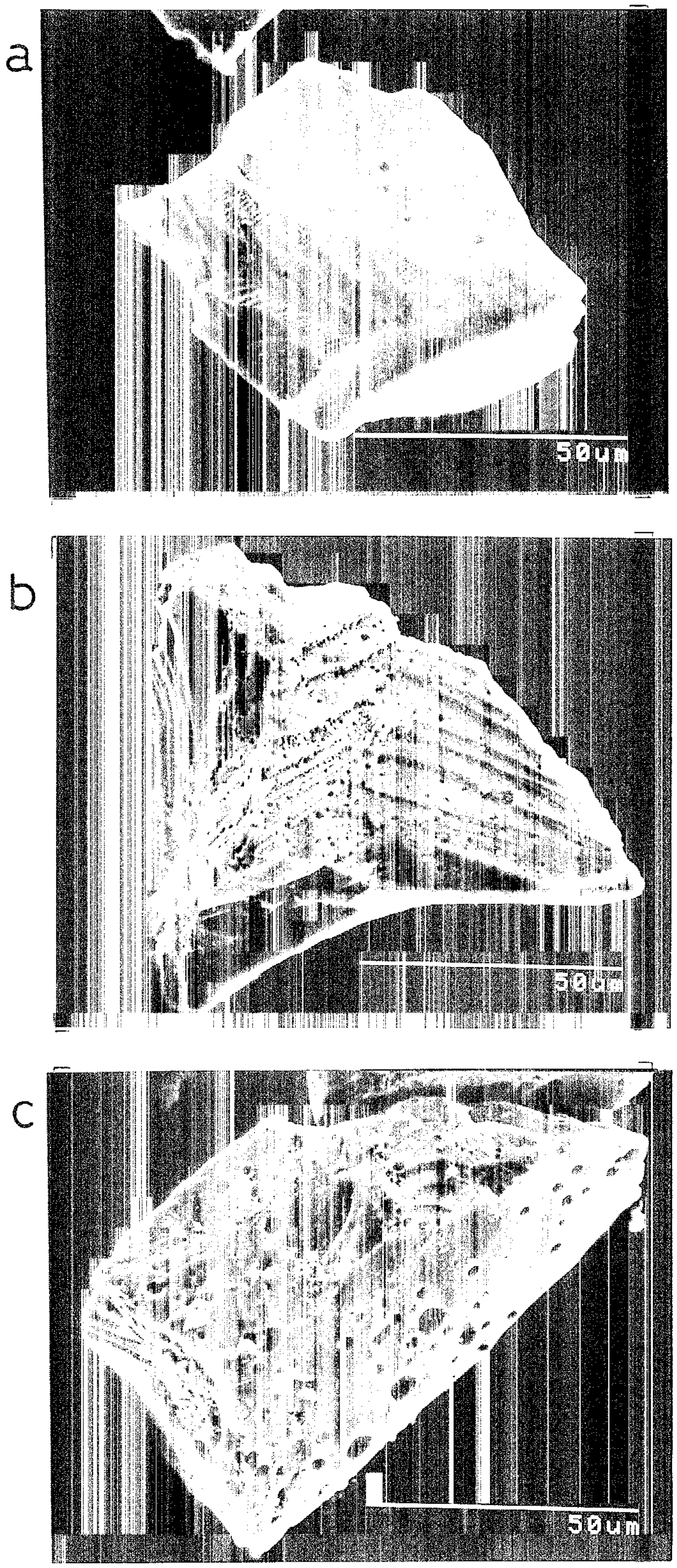


Figure 2-12 Scanning electron micrographs of silicon grains reacted with methanol up to various silicon conversions after pretreatment at 493 K.
Conditions of sample preparation and silicon conversions are same as those in Fig. 2-11. The plates were obtained at 780 magnifications.

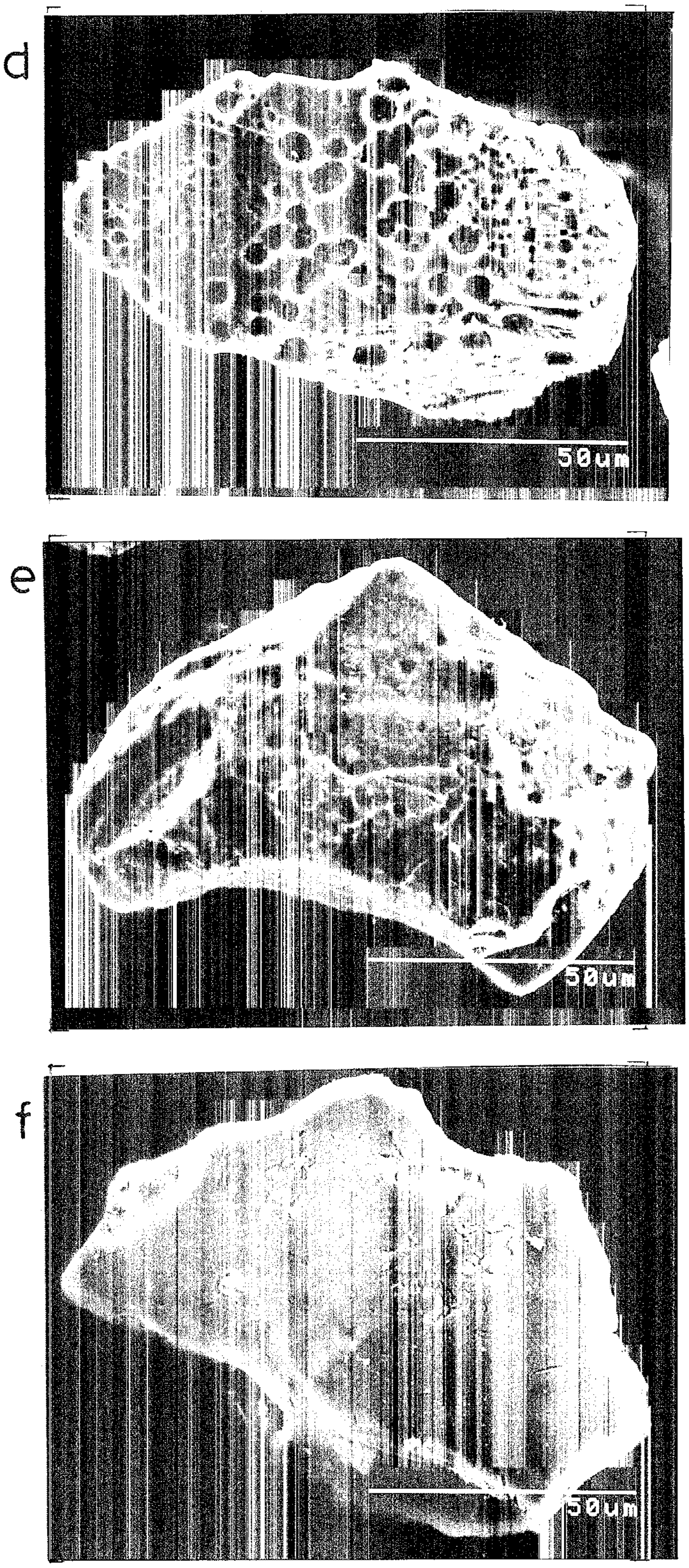


Figure 2-12 Continued.

found only on the wafers.

As described above, it is shown that copper(I) chloride is easily transferred onto silicon surface through 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 of 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 silicon surface does not occur in this temperature range and that silicon grains and copper grains must be present in a close vicinity with 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 is not formed by a direct contact of the grains. The actual mechanism of copper transport from copper(I)-chloride grains to silicon surface is not clear at this moment. Perhaps copper(I) chloride migrates from the contact points of silicon and copper(I) chloride grains over the silicon surface. 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 chemical species containing copper is still too small to be detected.

2-4 Conclusions

The silicon-methanol reaction using copper(I) chloride catalyst proceeds at different reaction environments depending on the conditions of pretreating the silicon-catalyst mixture prior to feeding methanol. Thus, a low-severity pretreatment such as low temperature and short time, results in a highly selective formation of trimethoxysilane, while a high-severity pretreatment results in a lower selectivity. When the pretreatment was carried out at 513 K for 1 h, the silicon conversion reached 88% at 5 h of reaction time, the selectivity for trimethoxysilane being 98%.

The XRD and EPMA revealed that Cu_3Si phase is scattered on the surface of silicon after pretreatment under the high severity conditions. The higher rate of copper(I)-chloride transfer and the easier migration of copper-species on 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 vapor phase onto silicon surface to form patches of 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 has been located, resulting in the formation of pits on the silicon surface.

Upon a low-severity pretreatment, the formation of the Cu_3Si phase was not confirmed, though the rate of the reaction was higher than that upon pretreatment under a high-severity conditions. The formation of pits was, however, 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.

The failure to detect the alloy phase with XRD and EPMA techniques may be attributed to small size of each alloy ensemble. The high initial reaction rate following low-temperature pretreatment is due to the high number of the 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.

References

1) E.G. Rochow, J. Am. Chem. Soc., 70, 2170 (1948).

2) W.E. Newton, and E.G. Rochow, Inorg. Chem., 9, 1071 (1970).

3) Japan Tokkyo Kokai Koho 55-28928 (1980): 55-76891 (1980): 57-108094 (1982): 62-96433 (1987).

4) E. Suzuki, and Y. Ono, J. Catal., 125, 390 (1990).

5) E. Suzuki, and Y. Ono, Chem. Lett., 1990, 47.

6) E. Suzuki, M. Okamoto, and Y. Ono, Solid State Ionics, 47, 97 (1991).

7) D. Viale, G. Weber, and B. Gillot, Oxidation of Metals, 35, 415 (1991).

8) R.J.H. Voorhoeve, and J.C. Vlugter, J. Catal., 4, 123 (1965).

9) R.J.H. Voorhoeve, "Organohalosilanes, Precursor to Silicones", Elsevier, Amsterdam, p. 175, 1967.

10) W.F. Banholzer, N. Lewis, and W. Ward, J. Catal., 101, 405 (1986).

11) W.F. Banholzer, and M.C. Burrell, J. Catal., 114, 259 (1988).

12) G. Weber, N. Gourgouillon, B. Gillot, and P. Barret, React. Solids, 3, 127 (1987).

13) G. Weber, B. Gillot, and P. Barret, Phys. Status Solidi A, 75, 567 (1983).

14) H. Souha, D. Viale, G. Weber, and B. Gillot, J. Mater. Sci., 24, 1767 (1989).

15) C. Lampe-Onnerud, A. Harstra, and U. Jansson, J. Phys. IV, C2, 1, 881 (1991).

Chapter 3 Kinetics of the Formation of Methoxysilanes

3-1 Introduction

As described in Chapter 2, the pretreatment conditions greatly affects the selectivity for trimethoxysilane as well as the rate of methoxysilanes formation. When the silicon-copper(I) chloride mixture was pretreated at 723 K, the selectivity for trimethoxysilane was low (74%). The formation of Cu_3Si phase was confirmed by XRD and SEM. Silicon reacted with methanol only around the Cu_3Si patches formed during the pretreatment. On the other hand, when the pretreatment was done at 493 K, the selectivity was almost 100%. No direct indication of the formation of Cu-Si intermetallic compound was obtained, probably because the size of the alloy was very small. A large number of pits were formed upon consumption of silicon by its reaction with methanol. These facts suggests that surface state of the reacting silicon changes with the pretreatment temperature.

The rate of methoxysilanes formation increases with reaction time in the beginning of the reaction after the pretreatment both at 723 and 493 K, indicating that methanol participates in the formation of the reactive sites. The reaction temperature probably also affects the formation of the reactive sites.

In this chapter, in order to obtain information on the mechanism of the reactive-sites formation, the reactions were carried out at various methanol pressures and reaction temperatures and the kinetics of methoxysilanes formation was examined. The pretreatment was done at high (723 K) or low temperature (493 or 513 K). Furthermore, to examine the effect of the pretreatment temperature on the nature of reactive sites, the reaction order with respect to methanol pressure and the apparent activation energy were measured.

3-2 Experimental

The procedures of the silicon-methanol reactions are the same as those described in Chapter 2.

3-3 Effect of Methanol Pressure on the Rate of Methoxysilanes Formation

As described in Chapter 2, the state of silicon surface sharply depends on the pretreating temperature of the Si-CuCl mixtures. The kinetics of the reactions upon pretreating silicon-copper(I) chloride mixtures at 723 K and 493 K were examined to see if the change in the surface state is reflected on the reaction kinetics.

3-3-1 Reaction after Pretreatment at 723 K

(a) Time Courses of the Rate of Methoxysilanes Formation at Various Methanol Pressures

After pretreating 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 3-1 shows the change in the rate of methoxy-

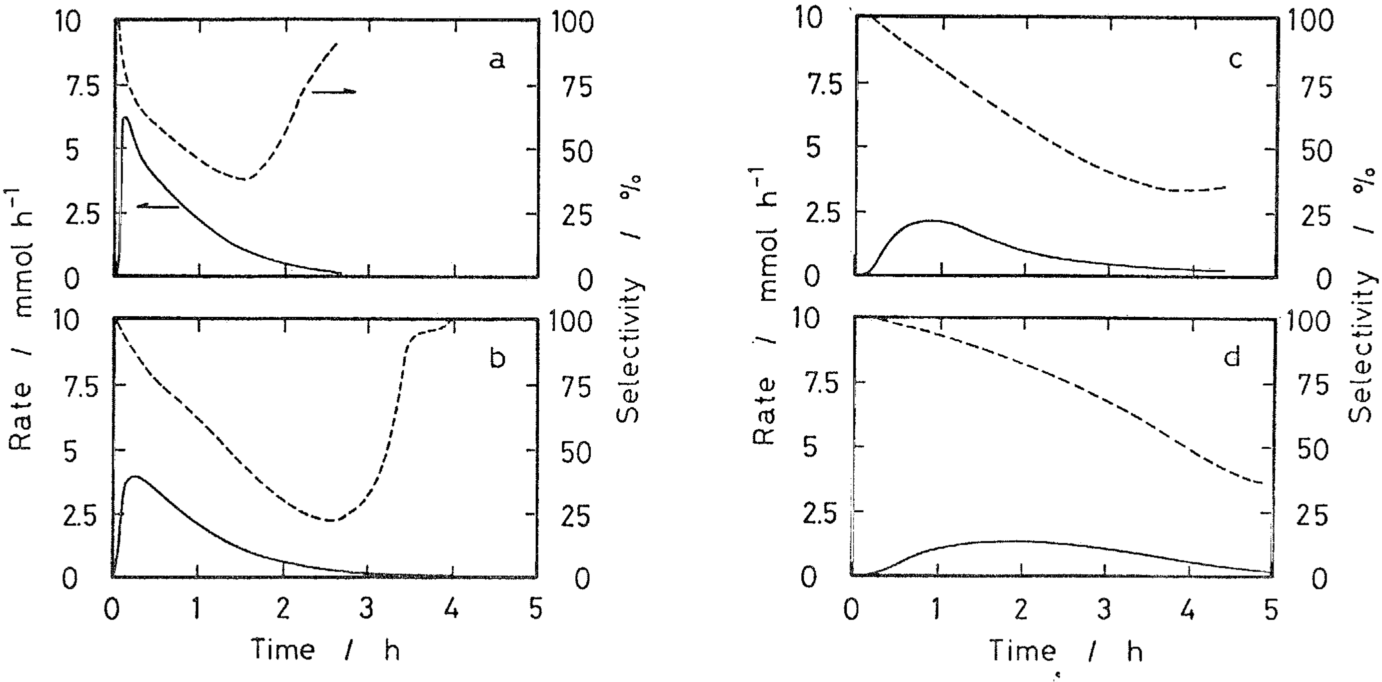


Figure 3-1 Effect of methanol pressure on the change in the rate of methoxysilanes formation with time, when the pretreatment was done at 723 K.
Reaction temperature= 513 K, CH_3OH= 87(a), 59(b), 29(c), and 16 kPa (d).

silanes formation with reaction time for each methanol pressure. At 87 and 59 kPa of methanol pressure, the rate increased immediately after methanol was fed (Figs. 3-1a and b). When methanol pressure was reduced (Figs. 3-1c and d), 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 very final stage of the conversion.

(b) Effect of Methanol Pressure on the Formation of Reactive Sites as Observed by SEM

As described above, methanol takes part in the reactive-sites formation. Here, the reacting silicon surface was examined with SEM. A silicon wafer was embedded in silicon-copper(I) chloride mixture, pretreated at 723 K for 1 h, and then reacted with methanol at 493 K.

Figure 3-2 shows the SEM photographs of the wafer upon the reaction with methanol of 16, 22, 28 kPa for 50 min. Pits were formed on the silicon wafer in every case. The size of pits increased with increase in the pressure since high pressure gives high silicon conversion in the same reaction time. The numbers of pits were almost constant (about 110 per mm^2) irrespective of methanol pressure, indicating that methanol reacts with only

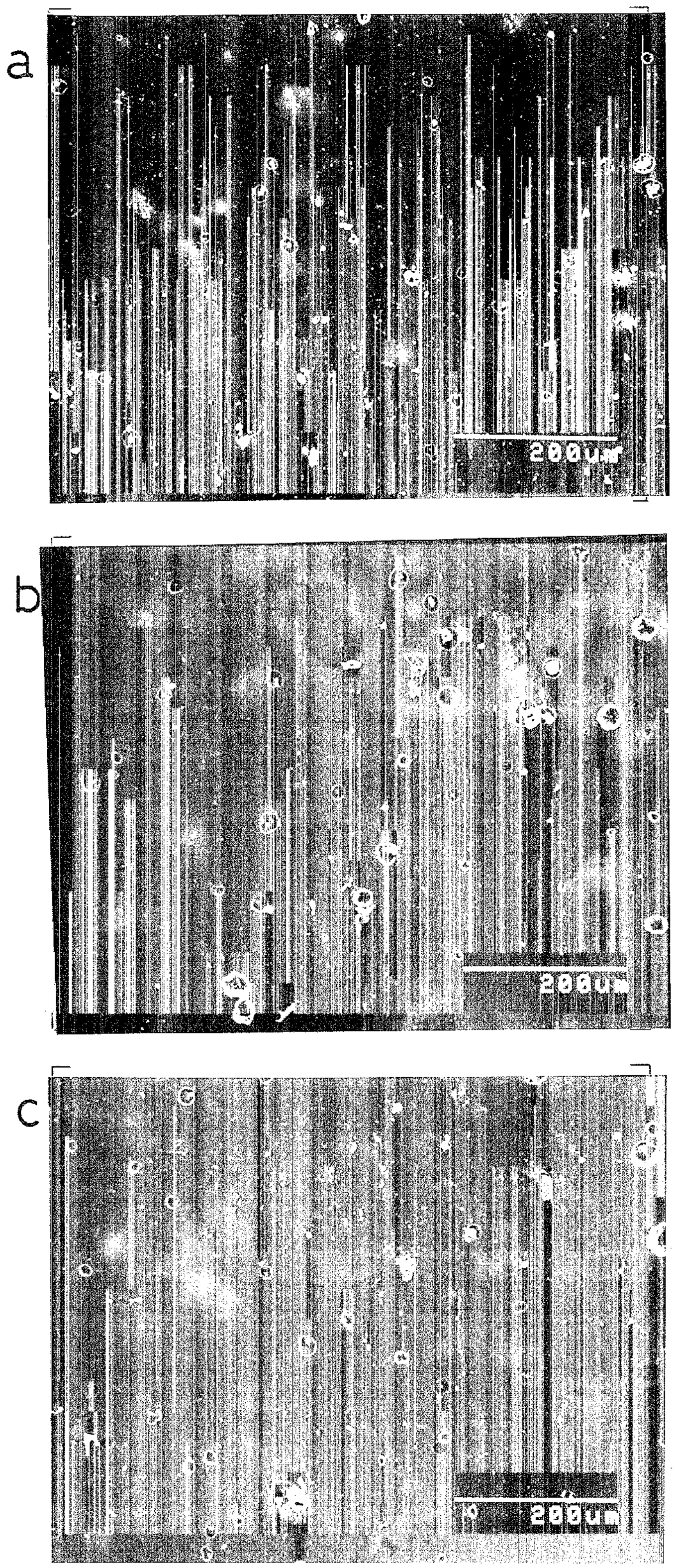


Figure 3-2 Scanning electron micrographs of silicon wafers reacted at various pressure of methanol after the pretreatment at 723 K.
Pretreatment temperature = 723 K.
Reaction temperature = 493 K. Reaction time = 50 min.
Methanol pressure = 16 (a), 22 (b), 28 kPa (c).
Micrographs were taken at 120 magnifications.

vicinity of Cu_3Si patches formed on the silicon surface at the pretreatment stage, as mentioned in section 2-3-5.

3-3-2 Reaction after Pretreatment at 493 K

(a) Time Courses of the Rate of Methoxysilanes Formation at Various Methanol Pressures

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 3-3 shows the change in the rate of methoxysilanes formation with reaction time at various methanol pressures. As in the case of high-temperature pretreatment, methanol pressure affects the induction time, but the effect is more significant at lower pretreatment temperatures. At 98 kPa of methanol pressure, the rate increased immediately after methanol was fed (Fig. 3-3a). With decreasing methanol pressure (Figs. 3-3 b-f), the initial rate increase slowed and eventually a long induction period appeared. The reciprocal of the induction period may be a measure of the the rate of the reactive-site formation on the silicon surface. As shown in Fig. 3-4, the reciprocal of the induction period ($1 / t_{ind}$) depended greatly on methanol pressure. These results show that methanol participates in the formation of reactive sites on the silicon surface.

(b) Effect of Methanol Pressure on the Formation of Reactive Sites as Observed by SEM

As described above, the influence of methanol pressure on the induction period indicates that methanol takes part in the

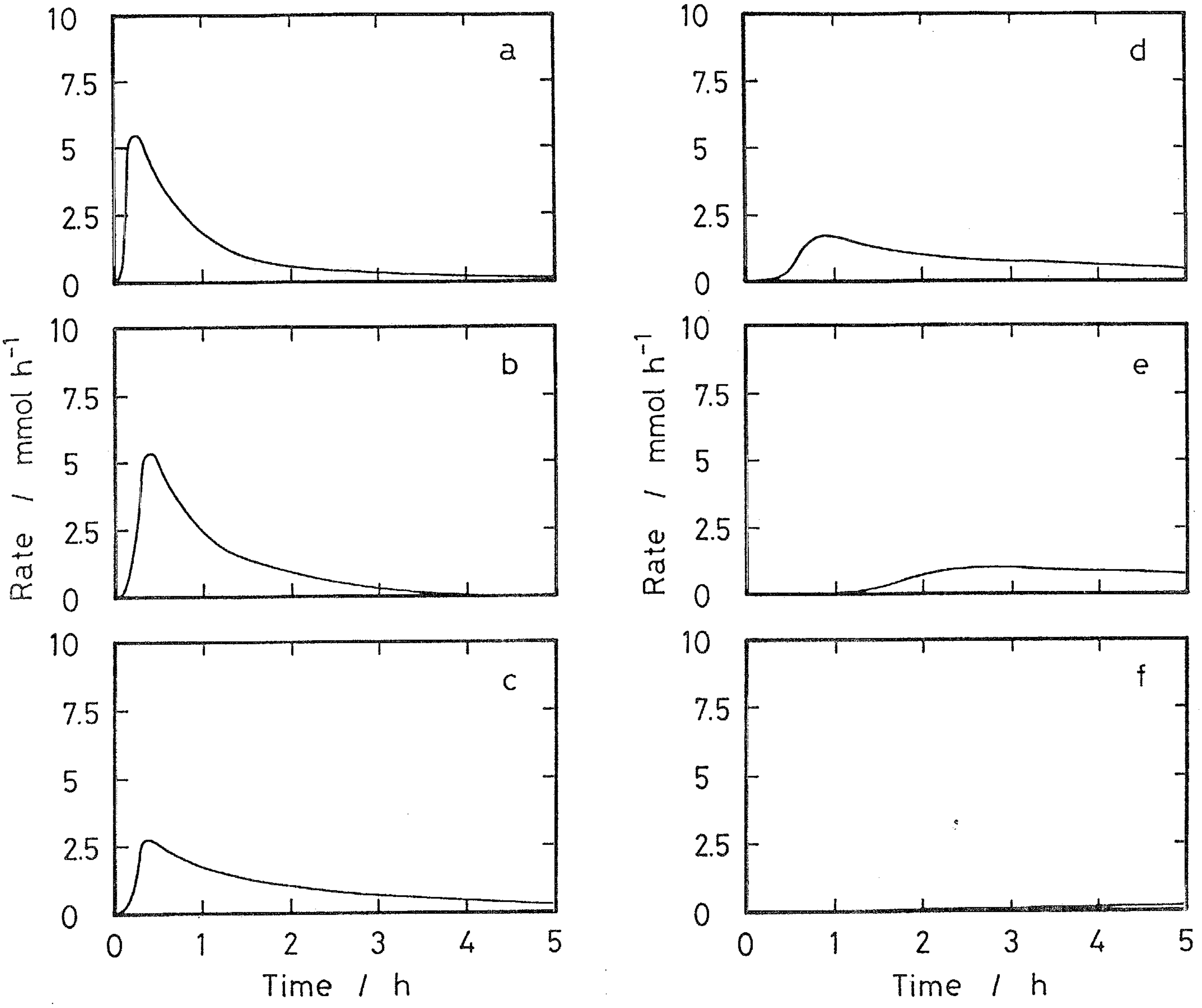


Figure 3-3 Effect of methanol pressure on the change in the rate of methoxysilanes formation with time, when the pretreatment was done at 493 K.
Pretreating temperature= 493 K, Cu= 5 wt.%.
Reaction temperature= 493 K, CH_3OH= 98(a), 86(b), 59(c), 29(d), 18(e), and 12 kPa(f).

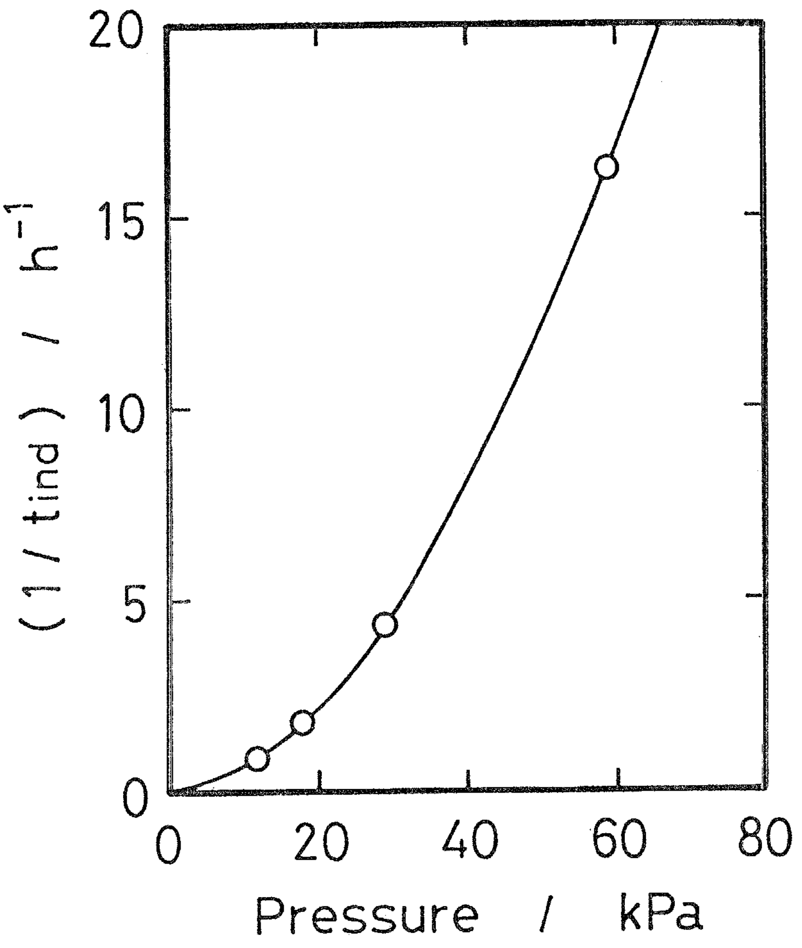


Figure 3-4 Dependence of the reciprocal of induction period on methanol pressure.
Experimental conditions are the same as those in Fig. 3-3.

reactive-site formation. The effect of methanol pressure on the morphology of the reacting silicon surface was examined. The silicon-copper(I) chloride mixture with a silicon wafer was pretreated at 493 K for 1 h and then reacted with methanol for 52.5 min at 493 K.

Figure 3-5 shows the SEM photographs of the wafer reacted with methanol of 19, 24, 27 kPa for 52.5 min. Pits were formed on the silicon wafers. The number of pits increased with increase of the methanol pressure, indicating that the number of reactive site is large at high pressure of methanol.

3-4 Kinetics of the Methoxysilanes Formation

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, the 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 number of reactive site, a pressure- and temperature-jump method was employed.

3-4-1 Dependence of the Rate of Methoxysilanes Formation on Methanol Pressure

(a) Reaction Order with Respect to Methanol Pressure

The partial pressure of methanol was changed during a run. The rate change just before and after the pressure change may be

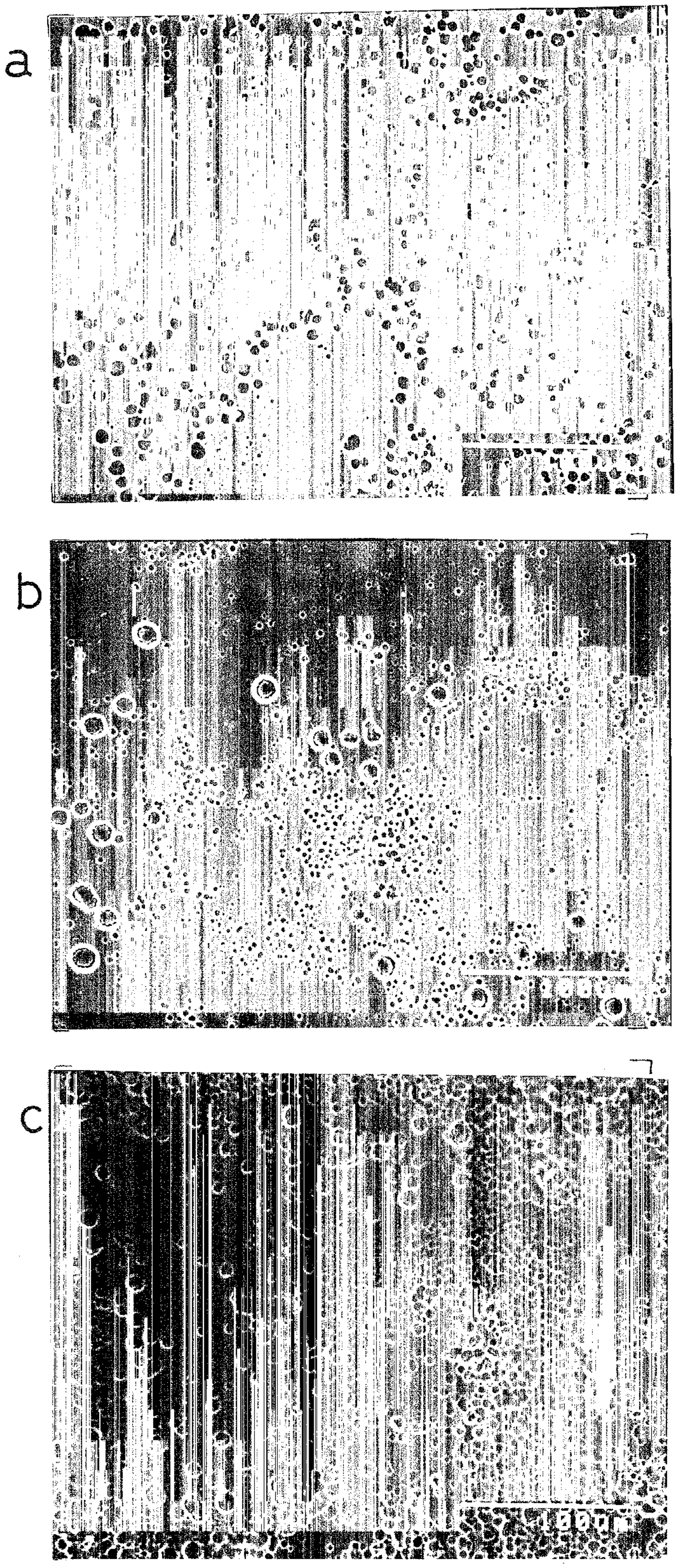


Figure 3-5 Scanning electron micrographs of silicon wafers reacted at various pressure of methanol after the pretreatment at 493 K.
Pretreatment temperature = 493 K.
Reaction temperature = 493 K. Reaction time = 52.5 min.
Methanol pressure = 19 (a), 24 (b), 27 kPa (c).
Micrographs were taken at 240 magnifications.

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 after high-temperature pretreatment (723 K), 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. 3-6, where P_1 is 85 kPa. The rate changed sharply upon the stepwise change of methanol pressure. The pressure of methanol shifted to a new steady state after 3 min. The pressure P_1 was varied and the time, at which the pressure was jumped, was also varied. The logarithmic ratio of the rates before and after the pressure jump (relative rate) was plotted against the logarithm of pressure P_1 (Fig. 3-7). 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.

When the pretreatment at low temperature was carried out or was not done, the pressure-jump method revealed that the rate per reaction site is the first order with respect to methanol pressure as shown in Fig. 3-7. 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.

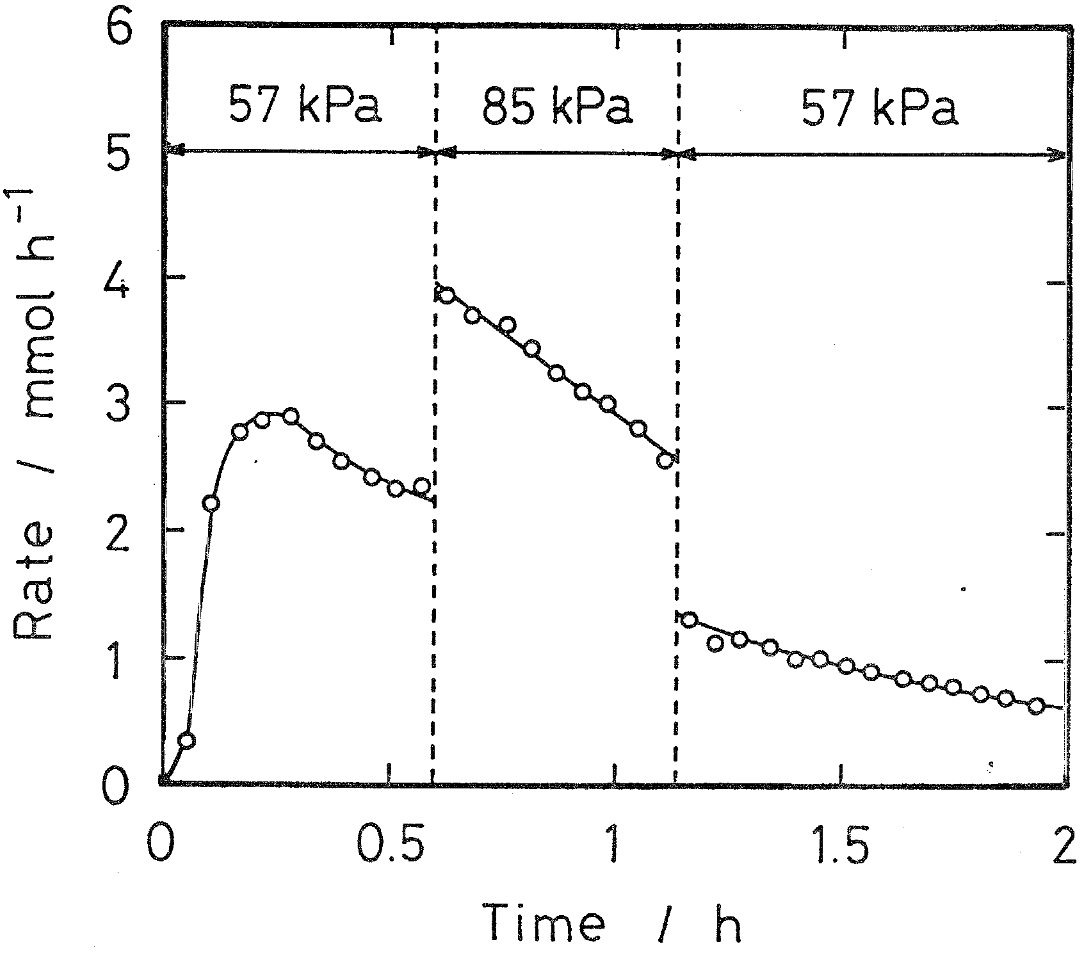


Figure 3-6 Effect of stepwise change in methanol pressure on the reaction rate.
Reaction temperature= 513 K, reaction was started at 57 kPa of methanol pressure and the pressure was changed stepwise to 85 kPa and afterwards back to 57 kPa.

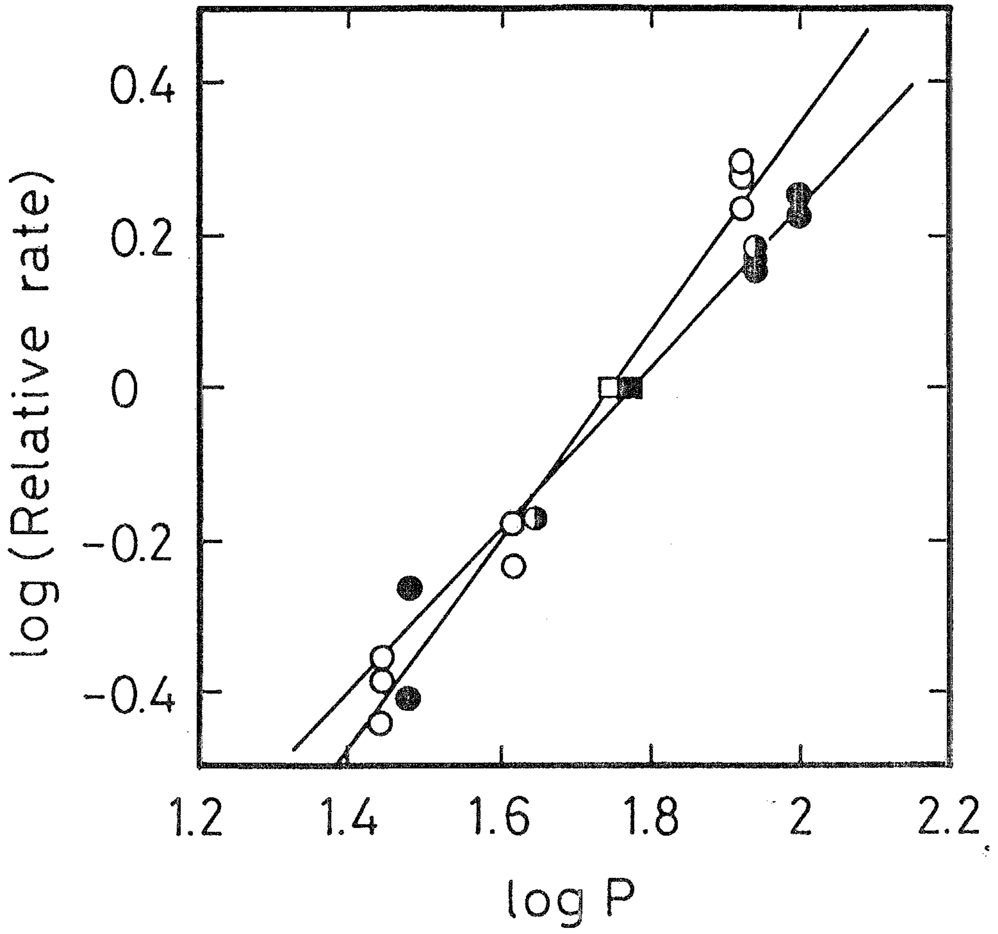


Figure 3-7 Dependence of the relative rate on methanol pressure.
(○) pretreating at 723 K and reaction at 513 K, (●) pretreating at 493 K and reaction at 493 K, (◑) no pretreating and reaction at 463 K.
Rates at 57 kPa (□) are taken as unity for the reaction with 723 K-pretreating, and those at 59 kPa (■) for the reactions with the 493 K-pretreating and without the pretreating.

(b) Dependence of the Formation Rate of Reactive Site on Methanol Pressure

The rate of methoxysilanes formation ($r(t)$) at reaction time t is proportional to both of the number of reactive site ($C(t)$) and the term of methanol pressure (P^n, n: the reaction order).

$$r(t) = kC(t)P^n \qquad \text{(k: rate constant)}$$

Thus,

$$(r(t)/P^n) = kC(t)$$

The term ($r(t)/P^n$) is proportional to the number of reactive site. When the pretreatment is carried out at high and low temperature, the order of methanol pressure is 1.4 and 1.0, respectively, as mentioned above. The reaction rates at various methanol pressures (Fig. 3-1 and 3-3) were divided by P^n ($P^{1.4}$ and $P^{1.0}$) to re-draw the time courses of (r/P^n) at various methanol pressures. These results are shown in Figs. 3-8 and 3-9, respectively. The values of the ordinate (r/P^n) in Figs. 3-8 and 3-9 should be proportional to the number of reactive site $C(t)$.

In the reaction after the high-pretreatment (Fig. 3-8), a high methanol pressure gave a rapid increase of (r/P^n) in the beginning of the reaction, showing that the increase of number of reactive sites was large in the reaction at high pressure. This clearly indicates that the formation rate of reactive sites is high when the methanol pressure is high.

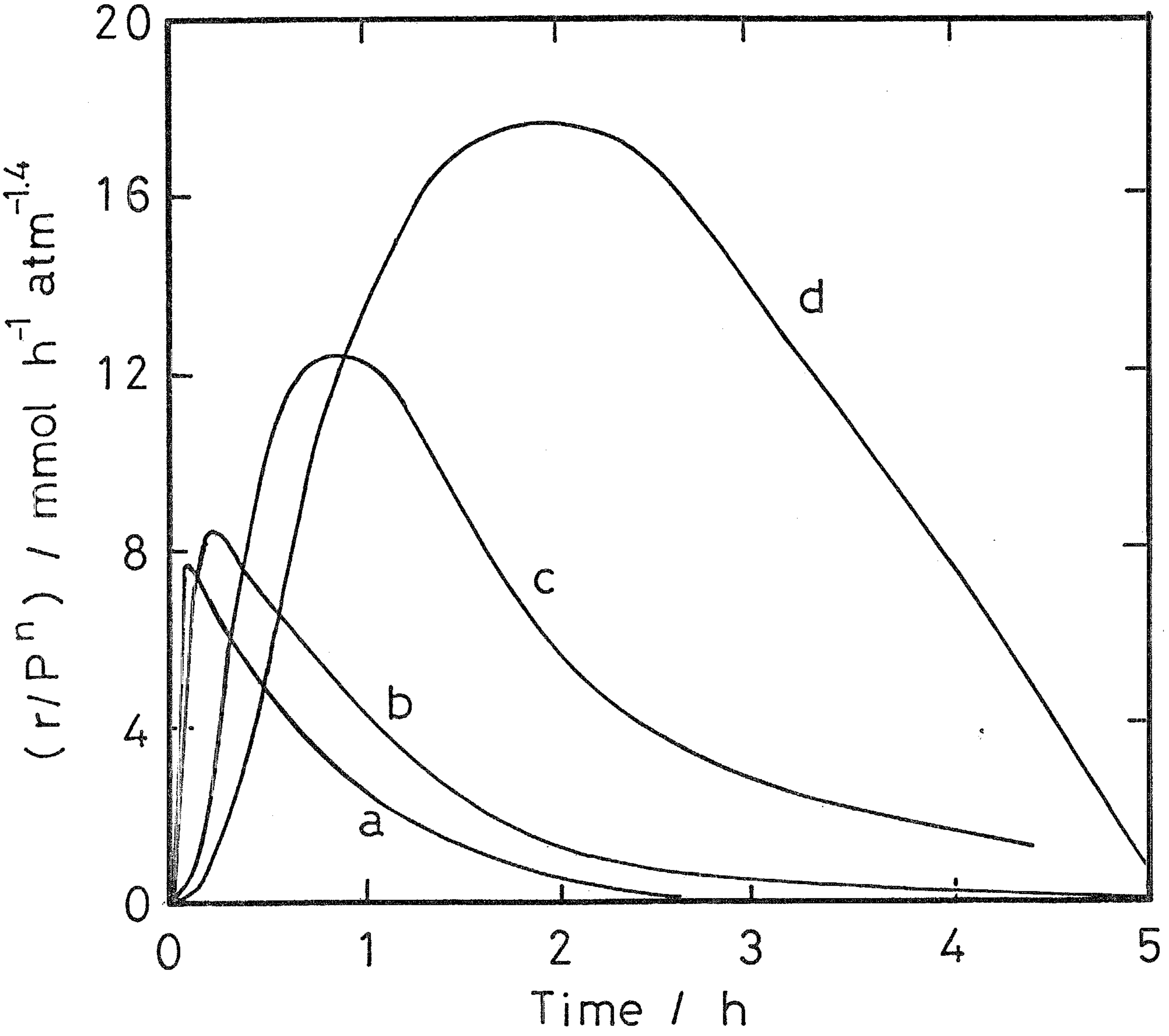


Figure 3-8 Change in (r/P^n) with time at various methanol pressure, when the pretreatment was done at 723 K. Reaction temperature= 513 K, CH_3OH= 87(a), 59(b), 29(c), and 16 kPa (d).

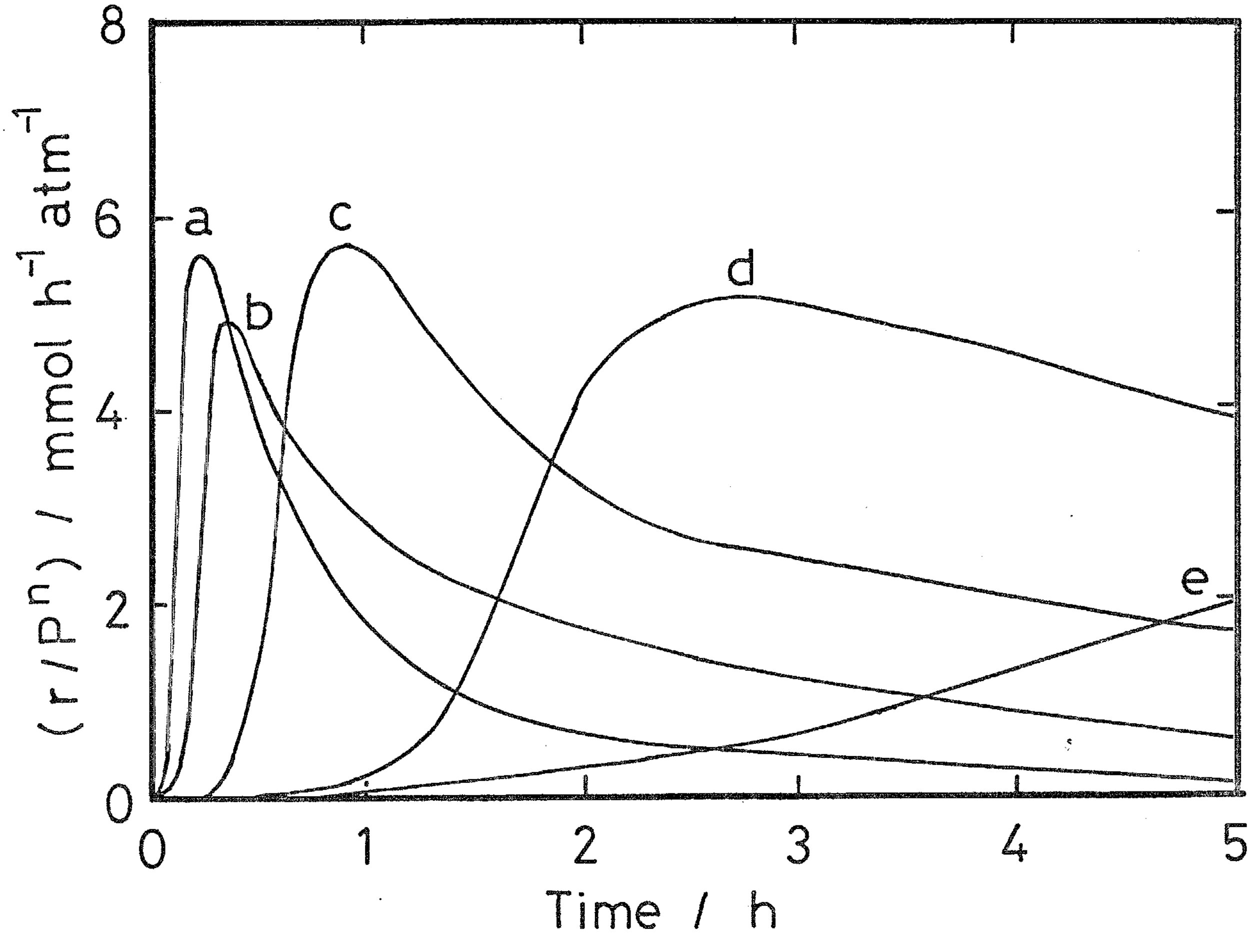


Figure 3-9 Change in (r/P^n) with time at various methanol pressure, when the pretreatment was done at 493 K. Pretreating temperature= 493 K, Cu= 5 wt.%. Reaction temperature= 493 K, CH_3OH= 98(a), 59(b), 29(c), 18(d), and 12 kPa(e).

When the pretreatment was done at 723 K, methanol reacted with silicon only at the vicinity of Cu_3Si patches (Chapter 2). Thus, the number of pits formed upon the silicon-methanol reaction was independent on reaction time, meaning that the number of reactive regions was constant. However, the number of reactive sites depended on reaction time, since (r/P^n) increased with time in the beginning of the reaction in Fig. 3-8. These results shows that the number of reactive sites per reactive region increase with time. This suggests that the wall of pit is reactive and that its area is in proportion to the number of reactive sites.

When the pretreatment was carried out at low-temperature (Fig. 3-9), the increase of (r/P^n) is high at high pressure of methanol. This shows that methanol participates in the formation of reactive site, thus high pressure of methanol gives high formation rate of reactive site. As compared with the result of high-temperature pretreatment, methanol pressure affected the change in (r/P^n) with time more significantly, indicating that high methanol pressure is more effective on the formation rate of reactive site than that in the reaction after pretreating the silicon-catalyst mixture at high temperature.

3-4-2 Dependence of the Rate of Methoxysilanes Formation on Reaction Temperature

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. 3-10. The reaction rate was sharply increased just after

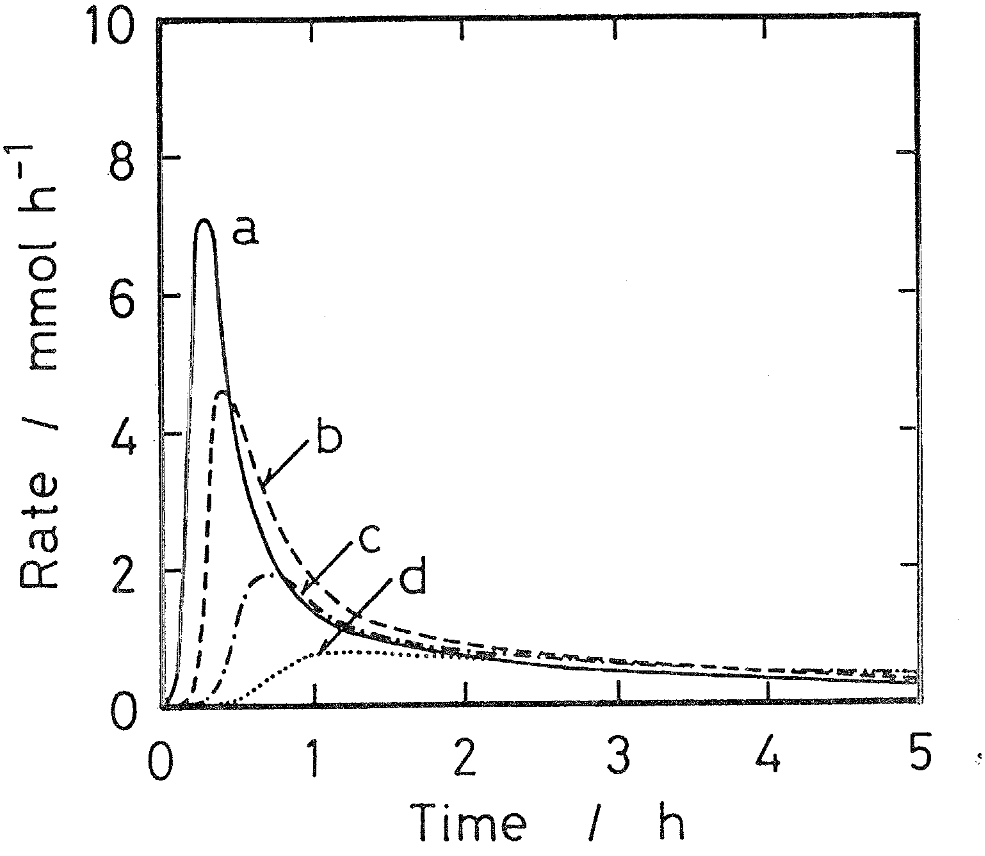


Figure 3-10 Effect of reaction temperature on the change in the rate of methoxysilanes formation with time.
Pretreating temperature= 513 K, Cu= 10 wt.%.
Reaction temperature= 513 (a), 493 (b), 483 (c), and 473 K(d), CH_3OH= 56 kPa.

methanol was fed to the reactor. Almost complete conversion of silicon was attained at 513 K. As the reaction temperature decreases, the induction period appeared and became longer. The selectivity for trimethoxysilane was always close to 100%.

(a) Apparent Activation Energy

The temperature dependence of the reaction rate was also measured by a temperature-jump method. An example is shown in Fig. 3-11. The logarithm of the relative rate was plotted against the reciprocal of the reaction temperature (Fig. 3-12). The activation energy thus determined was 44 kJ mol^{-1}, when the pretreatment was done at 723 K.

The temperature dependence of the reaction rate per reaction site was determined by a temperature-jump method after low-temperature pretreatment. 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. The difference of the activation energy as well as the reaction order indicates that the nature of reactive sites depends on the pretreatment conditions of the silicon-catalyst mixture.

(b) Dependence of the Formation Rate of Reactive Site on Reaction Temperature

The rate of methoxysilanes formation (r(t), t: reaction time) is represented by the following equation:

$$
\begin{aligned}
r(t) &= kC(t)P^n \\
&= k'\exp(-E/RT)C(t)P^n \qquad (k = k'\exp(-E/RT))
\end{aligned}
$$

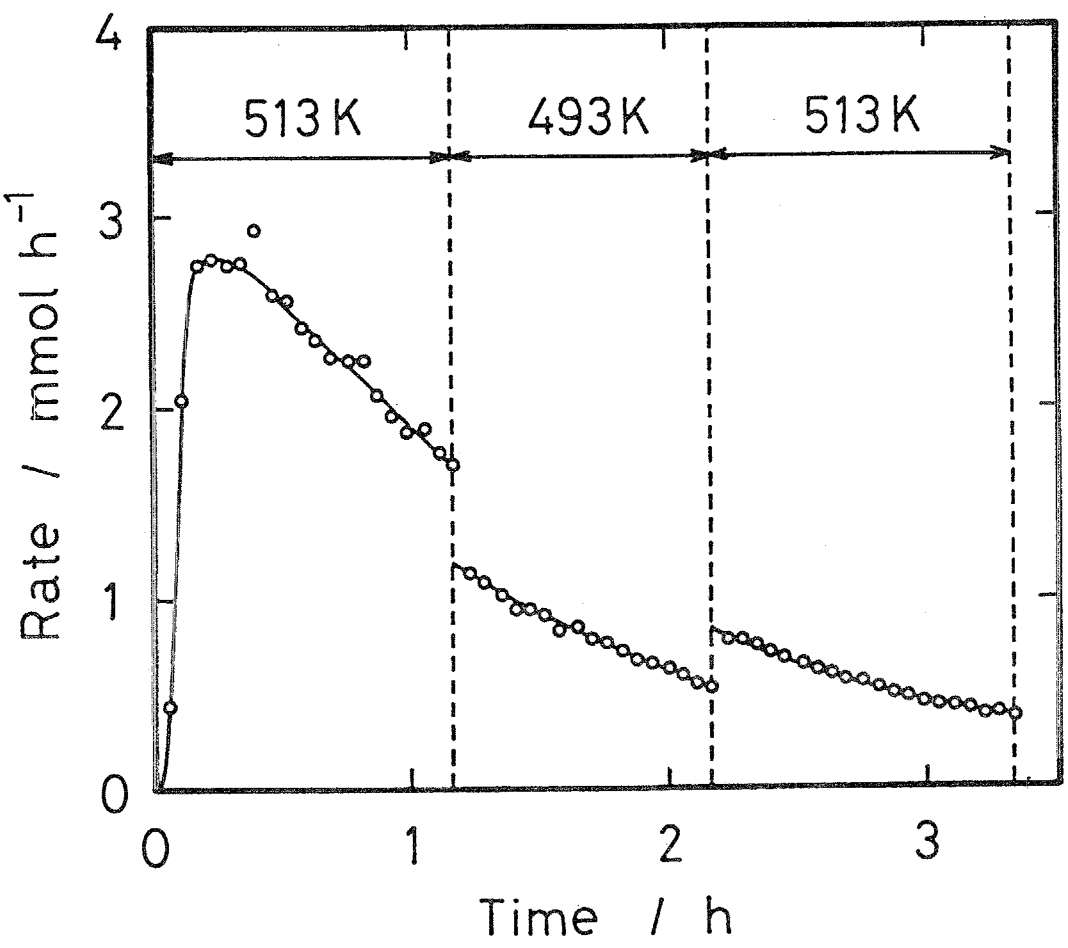


Figure 3-11 Effect of stepwise change in reaction temperature on the time course of reaction rate.
CH_3OH= 57 kPa, reaction was started at 513 K and the reaction temperature was changed stepwise to 493-533 K and afterwards back to 513 K.

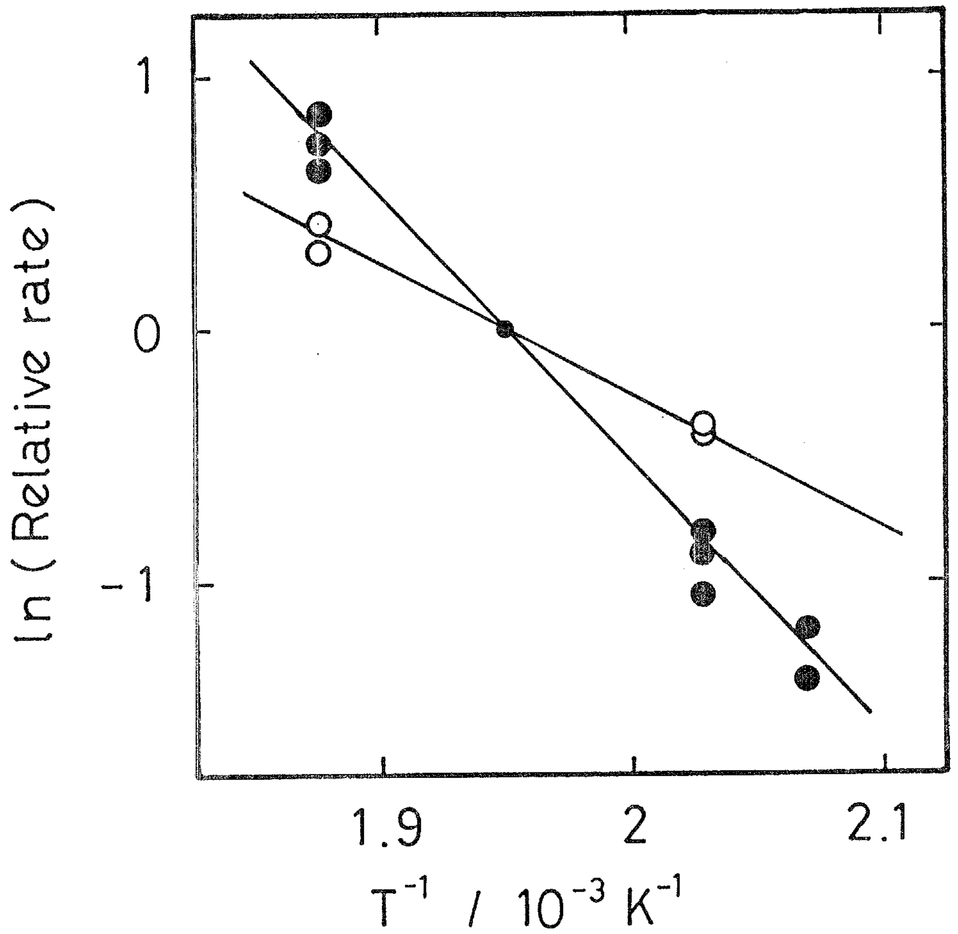


Figure 3-12 Dependence of the relative rate on reaction temperature.
(○) pretreating at 723 K and reaction at 513 K, (●) pretreating at 513 K and reaction at 513 K.
Rates at 513 kPa (●) are taken as unity for the reaction.

The letters, k, C(t), E and T stand for the rate constant, number of reactive site, activation energy and reaction temperature, respectively. Thus,

$$r(t)(\exp(-E/513R)/\exp(-E/RT)) = k'C(t)P^n\exp(-E/513R)$$
$$r(t)(\exp((E/R)(1/T-1/513))) = k'C(t)P^n$$
$$r(t)f(T) = k'C(t)P^n$$
$$(f(T) = \exp((E/R)(1/T-1/513)))$$

r(t)f(T) is proportional to the number of reactive site. r(t)f(T) was calculated from the data in Fig. 3-10. Figure 3-13 shows the time courses of r(t)f(T) at various reaction temperatures. The increase of rf(T) in the beginning of the reaction increased with reaction temperature, indicating that the rate of reactive-site formation at high reaction temperature is high.

3-5 Conclusions

After the mixture of silicon and copper(I) chloride was heated at 723 K, the reactions were carried out at various pressure of methanol. The increase of initial rate was large in the reaction at high pressure of methanol, indicating that methanol participates in the formation of reactive site. On the other hand, when the pretreatment temperature was low, the induction period remarkably depended on the methanol pressure. The number of pits formed on the silicon surface after the reaction increased with increase of methanol pressure. The

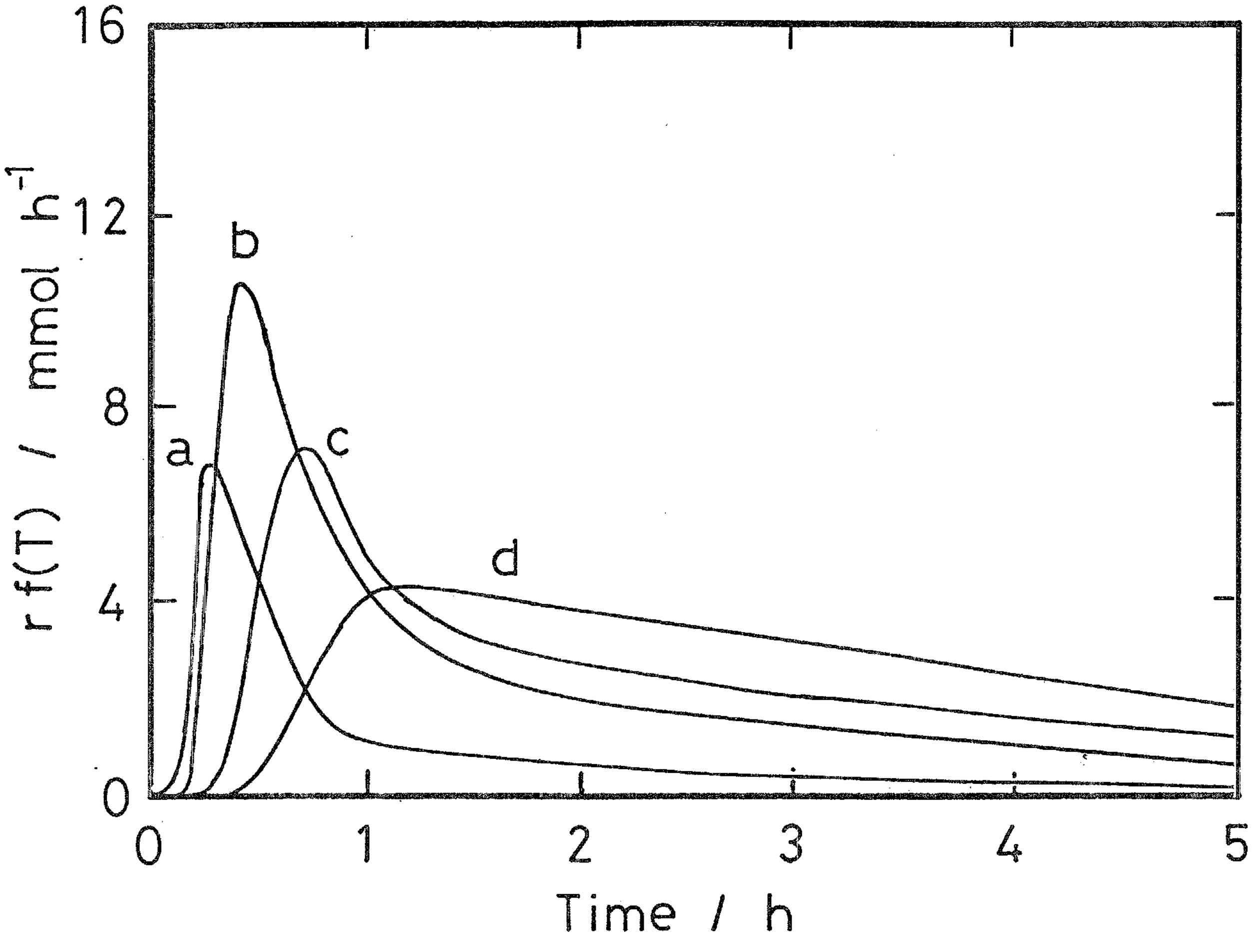


Figure 3-13 Change in rf(T) with time at various methanol pressure, when the pretreatment was done at 513 K. Pretreating temperature= 513 K, Cu= 10 wt.%. Reaction temperature= 513 (a), 493 (b), 483 (c), and 473 K (d), CH_3OH= 56 kPa.

dependence of the methanol pressure on the induction period and the number of pits shows that methanol takes part in the reactive-site formation.

The reaction order with respect to methanol pressure and the activation energy were determined by the pressure- and temperature-jump methods, respectively. The reaction order was 1.4 or 1.0, when the pretreatment was done at high or low temperature, respectively. This shows that the diffusion of silicon atoms to reactive sites is not a rate-determining step in the reaction. The activation energy in the reaction with the pretreatment at high and low temperature were determined to be 44 and 88 kJ mol $^{-1}$, respectively. The differences of the reaction order and the activation energy upon the different pretreatment temperature indicate that the nature of reactive sites depends on the pretreatment temperature.

A high methanol pressure and a high reaction temperature give a large amount of reactive site. Thus, a high yield of trimethoxysilane is obtained by the reaction at a high methanol pressure and at a high reaction temperature after the low-temperature pretreatment.

Chapter 4 Reaction Pathway of Formation of Methoxy-Silanes in the Reaction of Silicon with Methanol Catalyzed by Copper(I) Chloride

4-1 Introduction

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

Trimethoxysilane ($HSi(OCH_3)_3$) is directly synthesized by the reaction of silicon and methanol using copper(I) chloride as a catalyst [1-3]. In this reaction, the selectivity for $HSi(OCH_3)_3$ depends significantly on the pretreatment conditions of silicon - copper(I) chloride mixtures as well as the reaction conditions, tetramethoxysilane ($Si(OCH_3)_4$) being formed as a by-product as described in Chapter 2. In no cases, dimethoxysilane ($H_2Si(OCH_3)_2$) is found in the product.

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

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

It has been reported that metallic copper catalyzes the reaction of $HSi(OCH_3)_3$ with methanol to form $Si(OCH_3)_4$ [4]. This suggests the possibility that the formation of $Si(OCH_3)_4$ during silicon - methanol reaction is caused by the secondary reaction of $HSi(OCH_3)_3$ by the action of metallic copper, which is formed on the silicon surface during the reaction.

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

4-2 Experimental

Pulverized silicon (45 - 63 μm : purity 99.9%) was washed with a 46% HF solution for 1 h to remove SiO_2 overlayers. The silicon grains (0.168 g : 6 mmol) and copper(I) chloride grains (45 - 63 μm : purity 99.9%) were mixed in a small vial with vigorous vibration. The mixture was placed in a quartz tube (i.d. 10 mm) and heated under a helium stream at 553 or 723 K for 1 h. The amount of copper was 0.31 mmol (Cu / (Si + Cu) = 10 wt%, if not otherwise mentioned). Methanol (guaranteed reagent grade) was dehydrated over molecular sieve 3 A. Methanol (39 mmol h^{-1}, 56 kPa) and helium (total flow = 71 mmol h^{-1}) were fed to the reactor at 513 K. The rates of the formation of the products were determined by analyzing the effluent by a gas chromatograph (SE-30 packed column) every 3.5 min.

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

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

4-3 Time Course of the Reaction

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

Figure 4-2 shows the change in the intensity of the diffraction lines due to Cu_3Si and metallic Cu phase in the course of the reaction. The reaction was stopped at different reaction time and the XRD measurements were made on the remaining reaction mixtures. After the pretreatment at 723 K, only the Cu_3Si phase was obtained and the phase of metallic copper was not observed. The formation of Cu_3Si is expressed as

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

The intensity of the Cu_3Si phase decreases with reaction time,

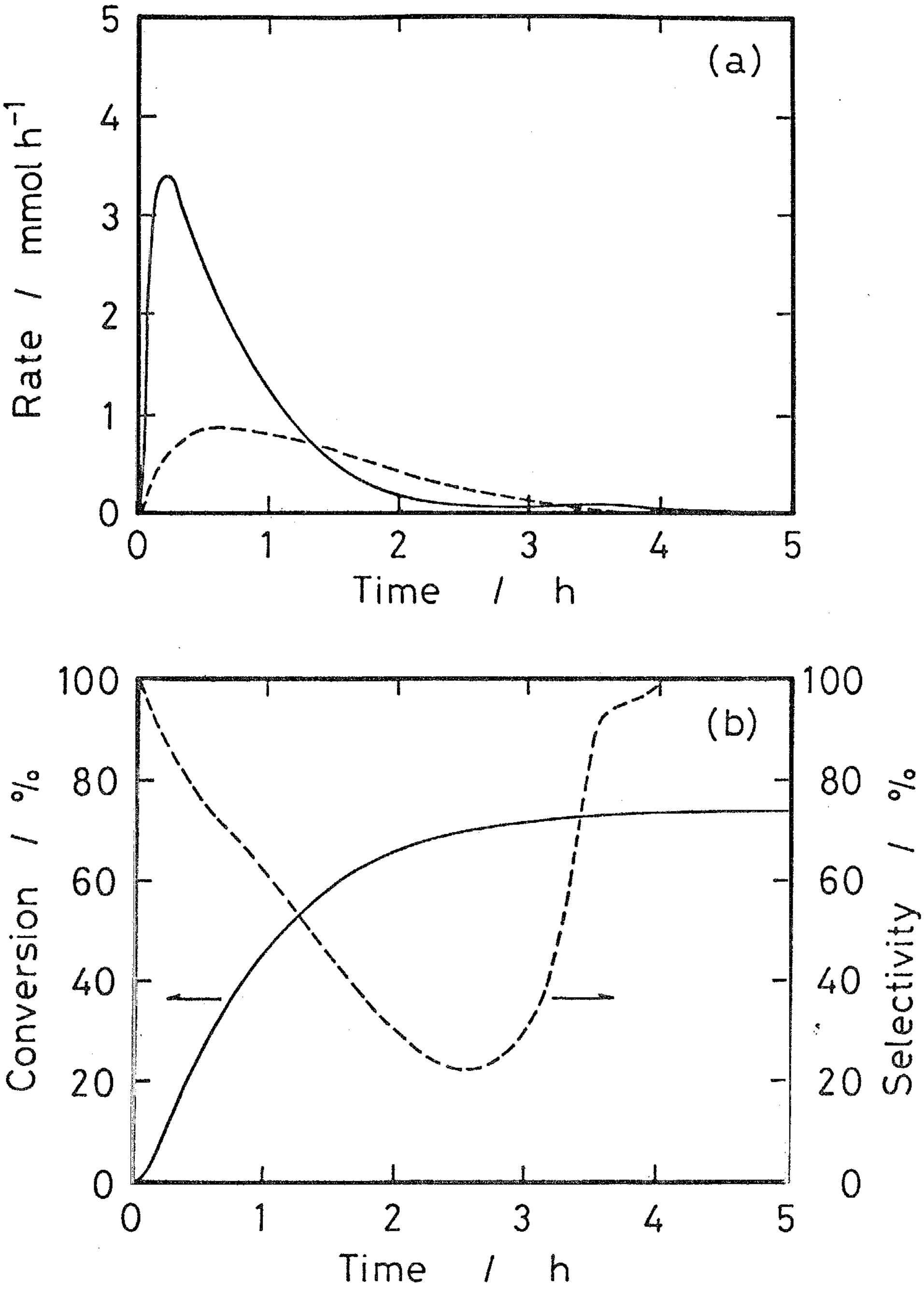


Figure 4-1 Reaction of silicon with methanol at 513 K, when a silicon - copper(I) chloride mixture was preheated at 723 K.

(a): Change in the rate of the formation of $HSi(OCH_3)_3$ (solid line) and $Si(OCH_3)_4$ (dashed line) with time,

(b): Silicon conversion (solid line), selectivity for $HSi(OCH_3)_3$ (dashed line).

Preheating conditions: 723 K, 1 h.

Reaction conditions: 513 K, methanol = 39 mmol h^{-1}(56 kPa).

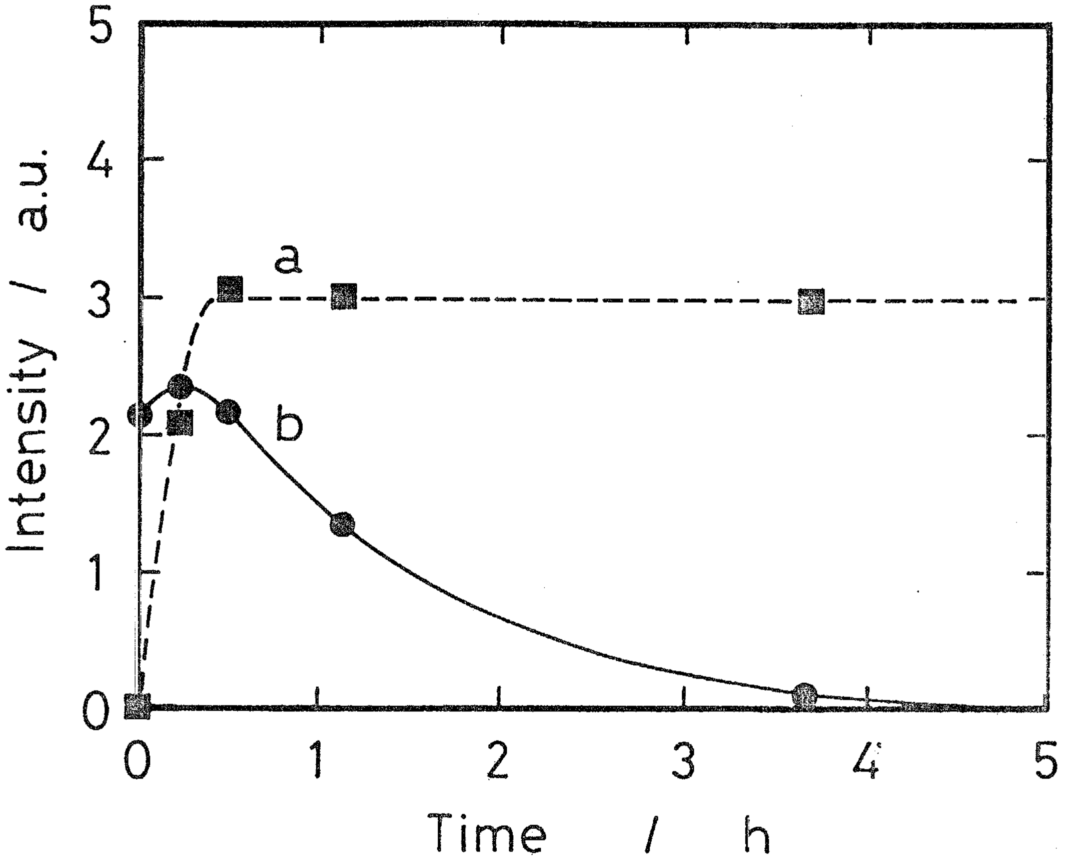


Figure 4-2 Change in the intensity of the diffraction lines due to Cu_3Si and metallic copper phase in the course of the reaction.

a: metallic copper, b: Cu_3Si.

Preheating conditions: 723 K, 1 h.

Reaction conditions: 513 K, methanol = 39 mmol h^{-1}(56 kPa).

while the phase of metallic copper develops in the first 30 min of the reaction. The amount of the Cu_3Si phase monotonously decreases with time. In contrast, the reaction rate increases at the beginning of the reaction (Fig. 4-1a). This shows that Cu_3Si itself is not an reactive intermediate, but the precursor which is composed of silicon and copper. Silicon is removed from the reactive sites and the remaining copper further reacts with underlying silicon to cycle the reaction. The part of copper may coagulate to form metallic copper.

When the temperature of the pretreatment was 513 K, the formation of Si–Cu alloy was not observed by XRD since the size of the alloy is very small (Chapter 2). The silicon conversion after 5 h was 97% (Fig. 4-3) and the average selectivity for $HSi(OCH_3)_3$ was practically 100% under the same reaction conditions. The metallic-copper phase was observed at the end of reaction, but the intensity of the diffraction peak was very small.

4-4 Effect of Addition of Trimethoxysilane to the Feed

In order to examine whether $HSi(OCH_3)_3$ is converted into $Si(OCH_3)_4$ by its reaction with methanol under the reaction conditions, $HSi(OCH_3)_3$ was added to the feed. Figure 4-4 shows the result. The reaction was started under the same conditions as the experiment shown in Fig. 4-1. After 0.7 h of the reaction, $HSi(OCH_3)_3$ (4.0 mmol h^{-1}) was added to the methanol feed. The difference between the rates of effluence of $HSi(OCH_3)_3$ just before and just after the addition was smaller

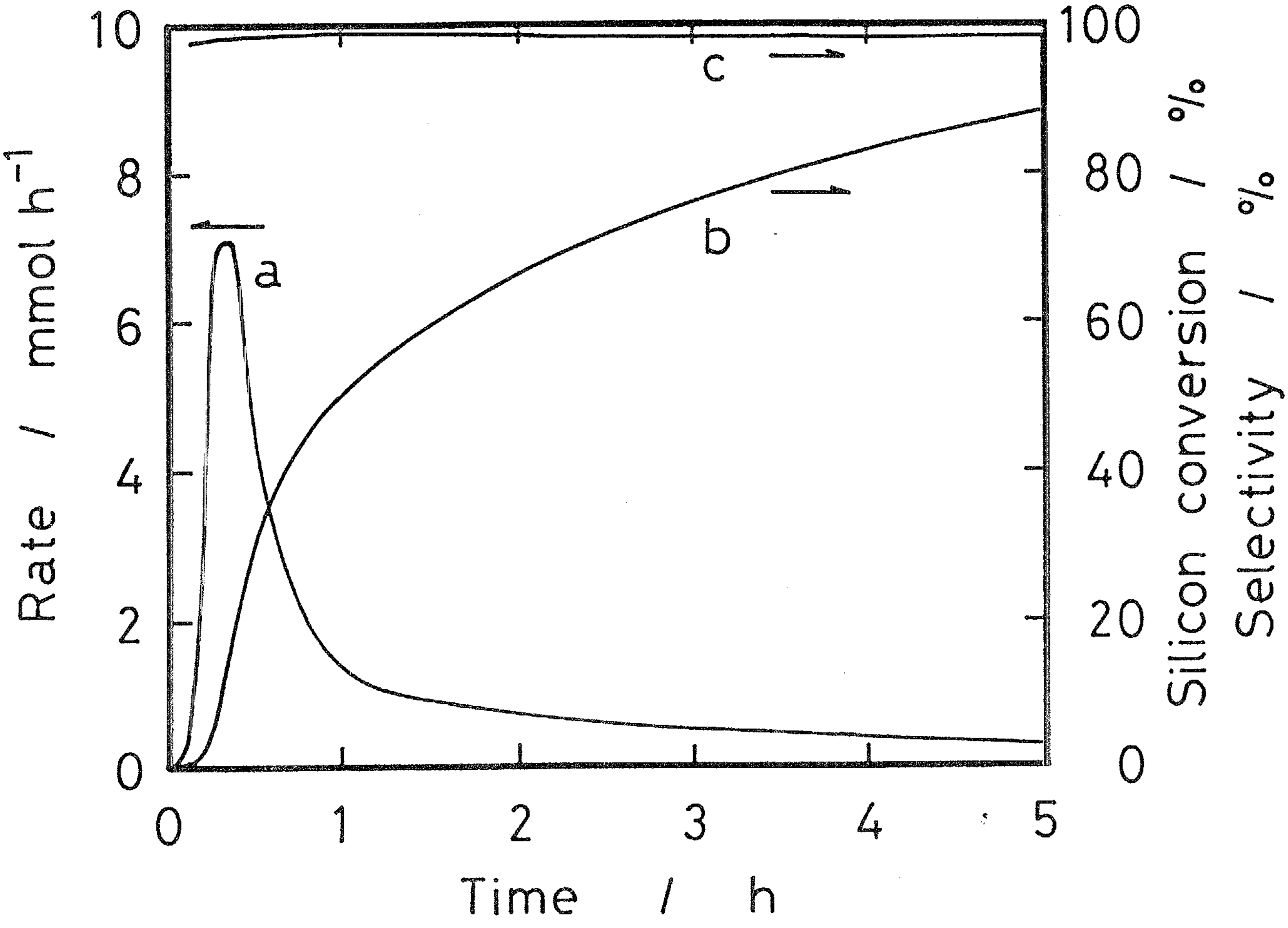


Figure 4-3 The rate of formation of methoxysilanes ($HSi(OCH_3)_3$ + $Si(OCH_3)_4$) (a), the cumulative silicon conversion (b), and the selectivity for $HSi(OCH_3)_3$ (c) in the reaction of silicon with methanol, when a silicon - copper(I) chloride mixture was preheated at 553 K.
Preheating conditions: 553 K, 1 h.
Reaction conditions: 553 K, methanol = 39 mmol h^{-1}(56 kPa).

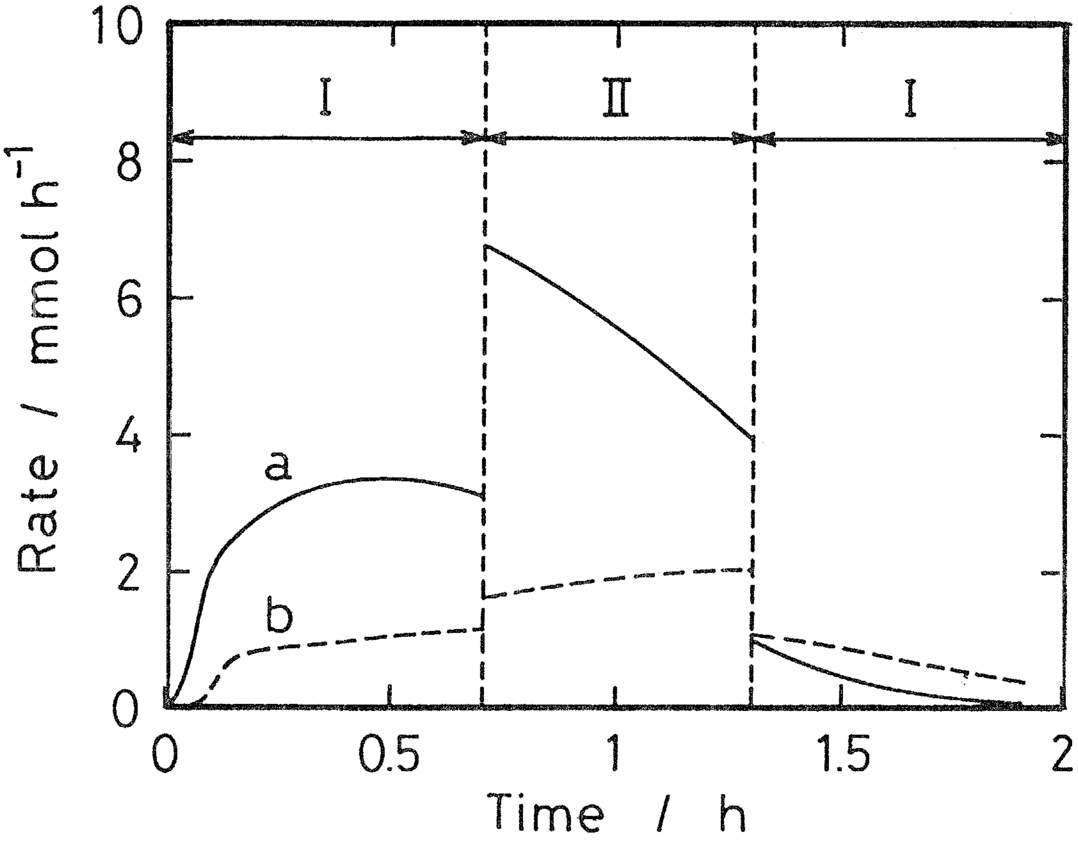


Figure 4-4 Change in the effluent rate of methoxysilanes upon the addition of $HSi(OCH_3)_3$ to the feed.
a: $HSi(OCH_3)_3$, b: $Si(OCH_3)_4$.
Preheating conditions: 723 K, 1 h.
Reaction conditions: 513 K,
(I): methanol = 39 mmol h^{-1}(56 kPa),
(II): methanol = 39 mmol h^{-1}(56 kPa) and
$HSi(OCH_3)_3$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

than the feeding rate of $HSi(OCH_3)_3$. On the other hand, the rate of effluence of $Si(OCH_3)_4$ increased upon addition of $HSi(OCH_3)_3$ to the feed. The rate of the formation of $Si(OCH_3)_4$ decreased when $HSi(OCH_3)_3$ was eliminated from the feed. These results clearly indicate that a part of $HSi(OCH_3)_3$ added was transformed into $Si(OCH_3)_4$ under the reaction conditions. This suggests that, in the silicon - methanol reaction, at least a part of $Si(OCH_3)_4$ is originated from the secondary reaction of $HSi(OCH_3)_3$ with methanol.

4-5 Effect of Addition of Thiophene to the Feed

It has been reported that metallic copper catalyzes the reaction of methanol and $HSi(OCH_3)_3$ to give $Si(OCH_3)_4$ [4]. As described above, metallic copper is formed in the course of the reaction. Thus, it is plausible that metallic copper formed on silicon surface acts as a catalyst to convert $HSi(OCH_3)_3$ into $Si(OCH_3)_4$. It is known that sulfur compounds poison the catalytic activity of copper catalysts. Therefore, thiophene was added to the methanol feed in the silicon - methanol reaction to see if the selectivity for $HSi(OCH_3)_3$ is affected by copper-poisoning.

4-5-1 Effect of Thiophene on the Selectivity for Trimethoxysilane

Figure 4-5 shows how the rate of formation of methoxysilanes and the selectivity for $HSi(OCH_3)_3$ change with addition of thiophene to the feed. In the absence of thiophene, the silicon

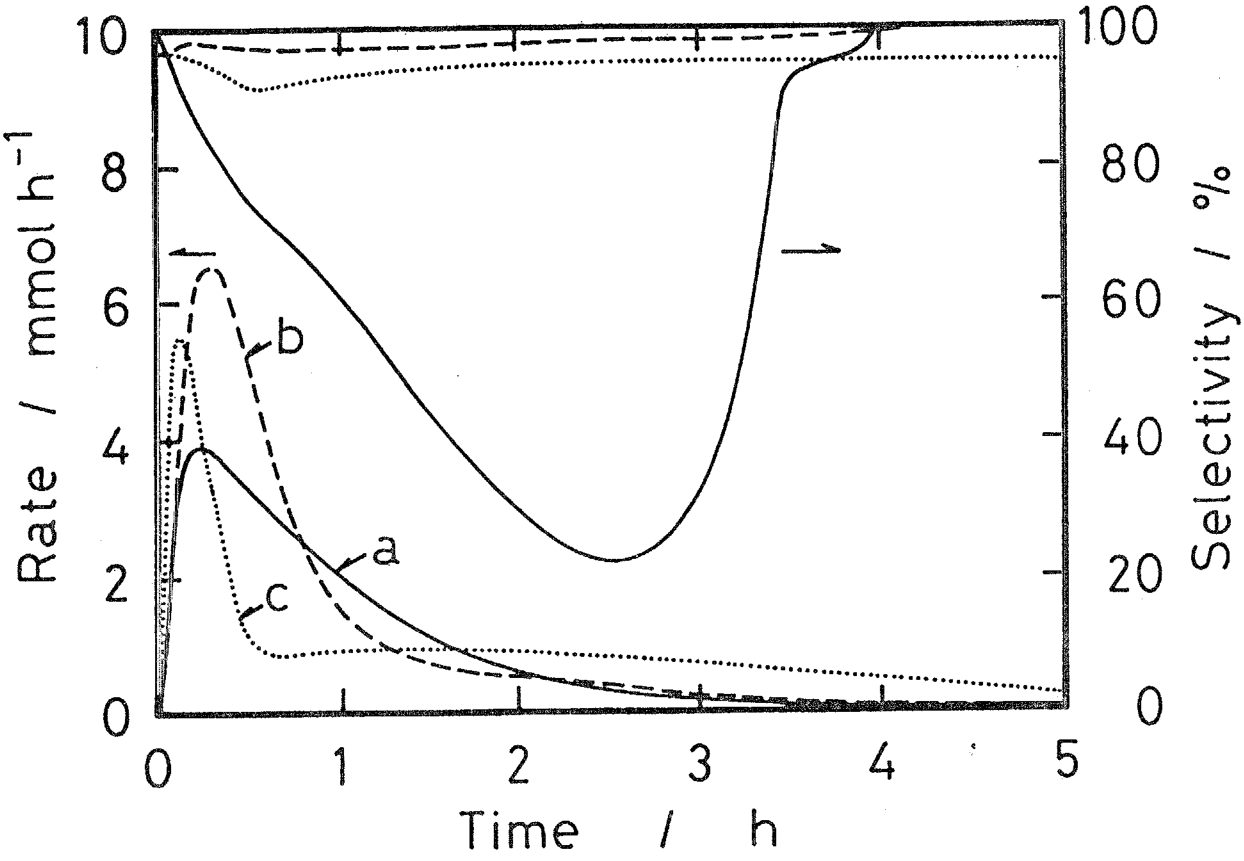


Figure 4-5 Effect of thiophene on the change in the rate of methoxysilanes formation and the selectivity for $HSi(OCH_3)_3$ with reaction time.
Preheating conditions: 723 K, 1 h.
Reaction conditions: 513 K, methanol = 39 mmol h^{-1}(56 kPa), thiophene = 0 (a), 0.39 (b), 1.29 mmol h^{-1} (c).

conversion at the reaction time of 5 h was 73%, and the overall selectivity averaged for 5 h was 64%, as described above. Addition of thiophene affected both the rate and the selectivity. Silicon conversion for 5 h was 84 and 80%, when 0.39 and 1.29 mmol h^{-1} of thiophene was added to the methanol feed, respectively. Thus, the addition of thiophene gave higher silicon conversion.

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

When thiophene was added to the methanol feed, the intensities of the X-ray diffraction peaks due to metallic copper in the mixture at the end of the reaction were 70% of those in the absence of thiophene, showing that thiophene addition inhibits the formation of metallic copper during the silicon - methanol reaction. This suggests that thiophene suppresses the deactivation of the catalytic system by inhibiting the growth of metallic copper. This explains the higher silicon conversion in the presence of thiophene. Thiophene (or sulfur) probably covers the surface of the small copper particles to prevent their coagulation.

In order to further confirm the effect of thiophene on the selectivity, the reaction was started by feeding methanol to the reactor and then thiophene was added to the feed at a later stage. Figure 4-6 shows the change in the rate of the formation of methoxysilanes upon addition of thiophene. At reaction time of 0.7 h, thiophene (0.39 mmol h^{-1}, 1% of methanol) was added to methanol feed. Upon addition of thiophene, the rate of $Si(OCH_3)_4$ decreased and that of $HSi(OCH_3)_3$ increased, while the sum of the rates of the formation of the two methoxysilanes remained constant. This indicates that $Si(OCH_3)_4$ is formed at the expense of $HSi(OCH_3)_3$. It is concluded that $Si(OCH_3)_4$ is formed exclusively by the secondary reaction of $HSi(OCH_3)_3$ with methanol over metallic copper, which is formed during the silicon - methanol reaction. It should be noted that thiophene does not inhibit the silicon - methanol reaction at all.

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

The selective poisoning by thiophene was also observed in the reaction of silicon and ethanol [6]. Thus, $HSi(OC_2H_5)_3$ was almost exclusively formed when thiophene was added to the system.

4-5-2 Poisoning of the Reaction of Trimethoxysilane with Methanol over Metallic Copper by Thiophene

In order to confirm that metallic copper catalyzes the reaction of $HSi(OCH_3)_3$ and methanol to form $Si(OCH_3)_4$, the reaction was carried out using metallic copper as a catalyst at 513 K. Figure 4-7 shows the change in the yield of $Si(OCH_3)_4$ with time. The yield of $Si(OCH_3)_4$ was 100% in the beginning,

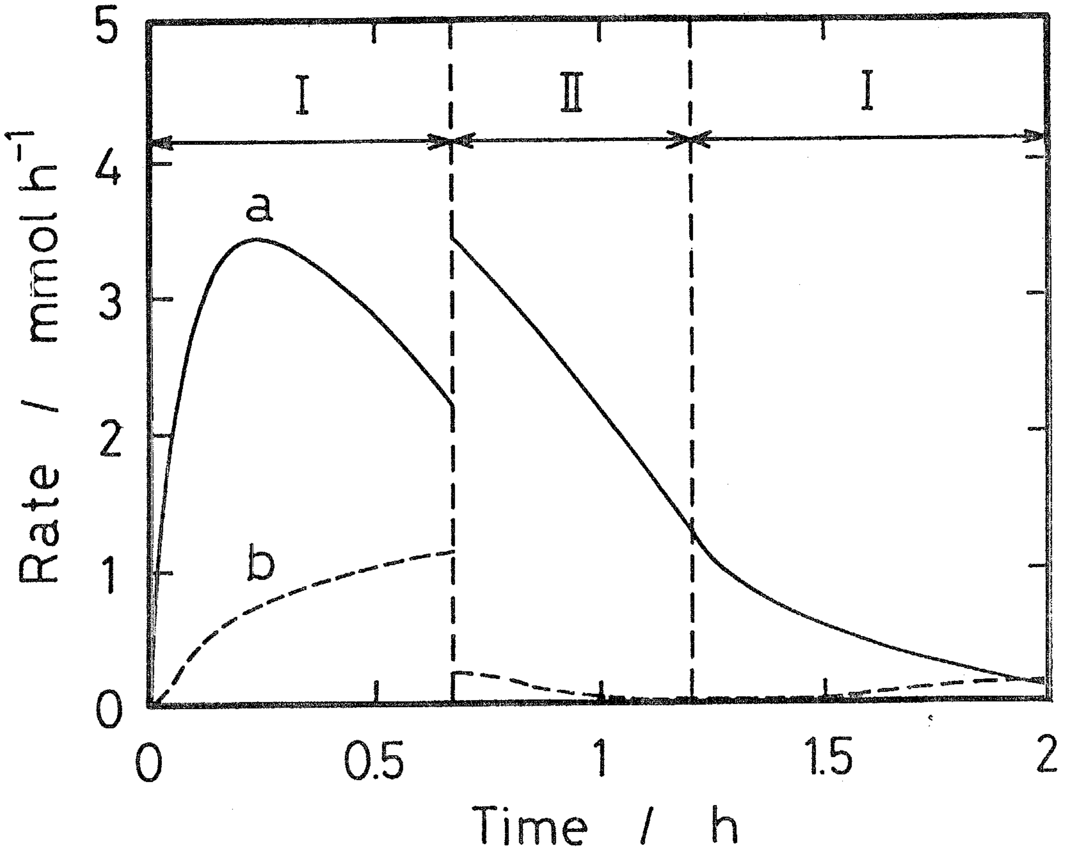


Figure 4-6 Change in the rate of methoxysilanes formation upon addition of thiophene.

a: $HSi(OCH_3)_3$, b: $Si(OCH_3)_4$.

Preheating conditions: 723 K, 1 h.

Reaction conditions: 513 K,

(I): methanol = 39 mmol h^{-1}(56 kPa),

(II): methanol = 39 mmol h^{-1}(56 kPa) and thiophene = 0.39 mmol h^{-1}.

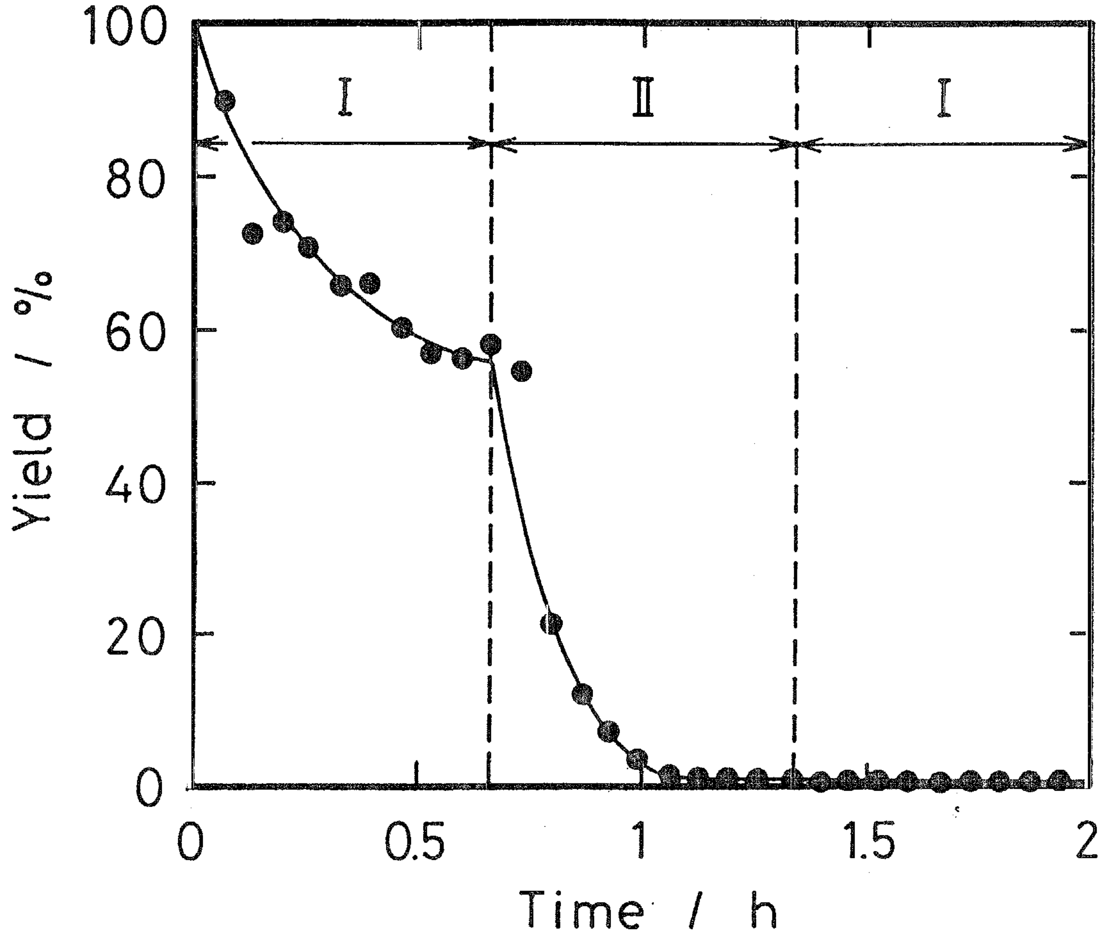


Figure 4-7 Poisoning of the metallic copper catalyst by thiophene in the reaction of $HSi(OCH_3)_3$ with methanol. Reaction temperature = 513 K, metallic copper = 0.33 g.
(I): methanol = 39 mmol h^{-1}(56 kPa),
$HSi(OCH_3)_3$ = 4.0 mmol h^{-1}(5.7 kPa),
(II): methanol = 39 mmol h^{-1}(56 kPa),
$HSi(OCH_3)_3$ = 4.0 mmol h^{-1}(5.7 kPa),
and thiophene = 0.39 mmol h^{-1}(0.56 kPa).

though it decreased with reaction time. Figure 4-7 also shows the effect of addition of thiophene. Upon addition of thiophene at 0.67 h of reaction time, the yield of $Si(OCH_3)_4$ decreased quickly to zero. Even after the feed of thiophene was stopped at 1.33 h, the formation of $Si(OCH_3)_4$ was not observed. These results clearly indicate that the reaction of $HSi(OCH_3)_3$ and methanol is catalyzed by metallic copper and that thiophene irreversibly inhibits the reaction.

A separate experiment showed that metallic copper catalyzes the reaction of $H_2Si(OC_2H_5)_2$ and ethanol into tri- and tetraethoxysilane. This reaction was inhibited, though not completely, by adding thiophene. On the other hand, the formation of $H_2Si(OC_2H_5)_2$ was not observed even in the presence of thiophene during silicon-ethanol reaction, indicating that $H_2Si(OC_2H_5)_2$ is not a primary product of the reaction. In other words, $HSi(OC_2H_5)_3$ is a sole primary product of the silicon-ethanol reaction.

4-6 Effect of Addition of Alkyl Chlorides to the Feed

It has been reported in a patent that addition of alkyl halides enhances the selectivity for $HSi(OCH_3)_3$ [7]. Here, the effect of addition of methyl or propyl chloride as an alkyl halide on the selectivity was examined.

4-6-1 Effect of Methyl Chloride on the Selectivity for Trimethoxysilane

Figure 4-8 shows the effect of methyl chloride. Under the

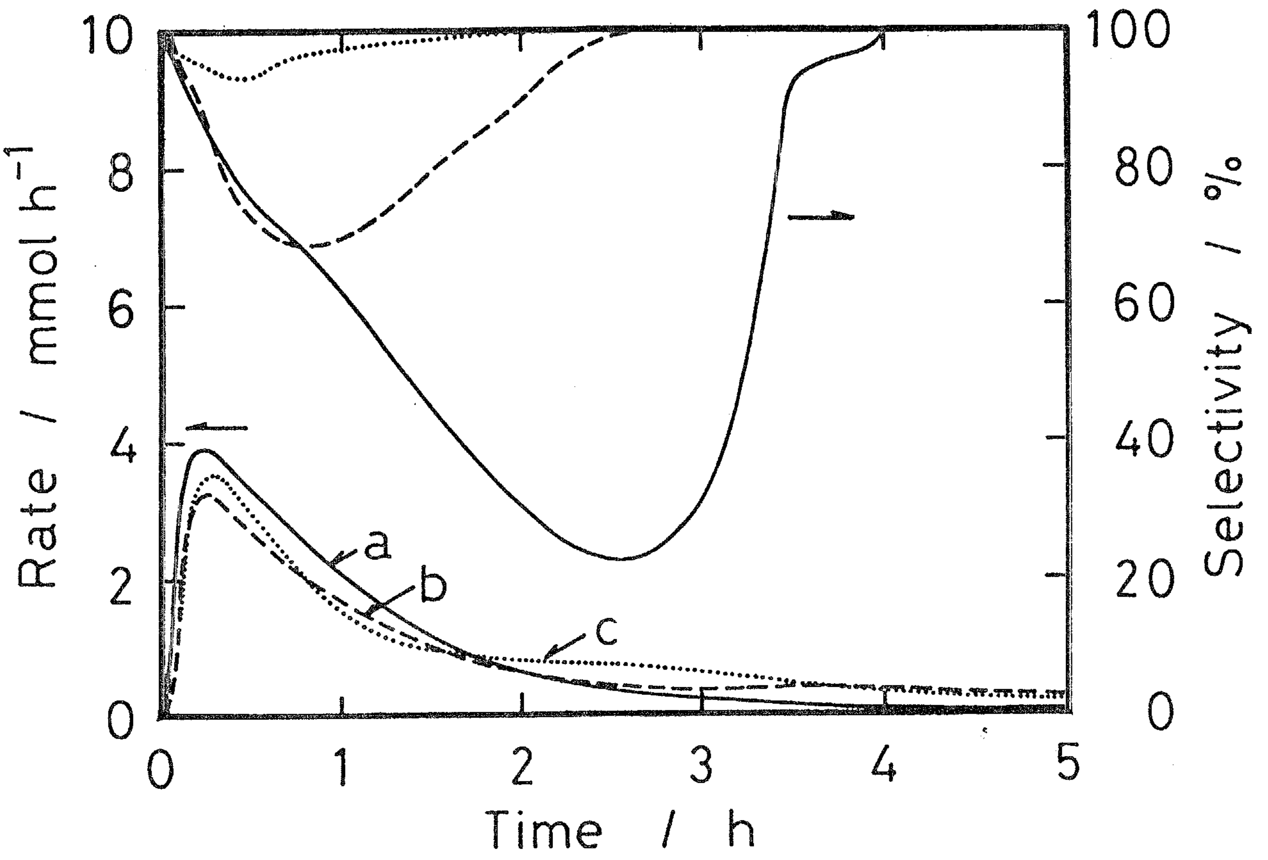


Figure 4-8 Effect of methyl chloride on the change in the rate of methoxysilanes formation and the selectivity for $HSi(OCH_3)_3$ with reaction time.
Preheating temperature = 723 K.
Reaction temperature = 513 K, methanol = 39 mmol h^{-1} (56 kPa),
methyl chloride = 0 (a), 0.39 (b), 1.29 mmol h^{-1} (c).

reaction conditions, no methylchlorosilanes were formed. The overall selectivity for $HSi(OCH_3)_3$ for 5 h increases upon addition of methyl chlorides. Upon adding 0.39 and 1.3 mmol h^{-1} of methyl chloride to the methanol feed, the selectivity for $HSi(OCH_3)_3$ increased to 83% and 97% from 64%, the silicon conversion being 73, 79%, respectively.

4-6-2 Effect of Propyl Chloride on the Selectivity for Trimethoxysilane

Propyl Chloride was added to the methanol feed. The results are shown in Fig. 4-9. When 0.078 and 0.39 mmol h^{-1} of propyl chloride was added, the overall selectivity and silicon conversion for 5 h were 96%, 75% and 98%, 76%, respectively. Propyl chloride is more effective than methyl chloride in enhancing the selectivity.

To further examine the effect of alkyl chloride, 0.39 mmol h^{-1} of propyl chloride was added to the feed at 0.7 h of reaction time. The result is shown in Fig. 4-10. Upon the addition of propyl chloride, the rate of $Si(OCH_3)_4$ decreased and that of $HSi(OCH_3)_3$ increased. The total rate of methoxysilanes formation did not change. This indicates that addition of propyl chloride affects the selectivity, but that propyl chloride does not affect the rate of the silicon-methanol reaction.

4-6-3 Poisoning of the Reaction of Trimethoxysilane and Methanol over Metallic Copper by Propyl Chloride

In order to find if the effect of alkyl chlorides results from poisoning of metallic copper as in the case of thiophene

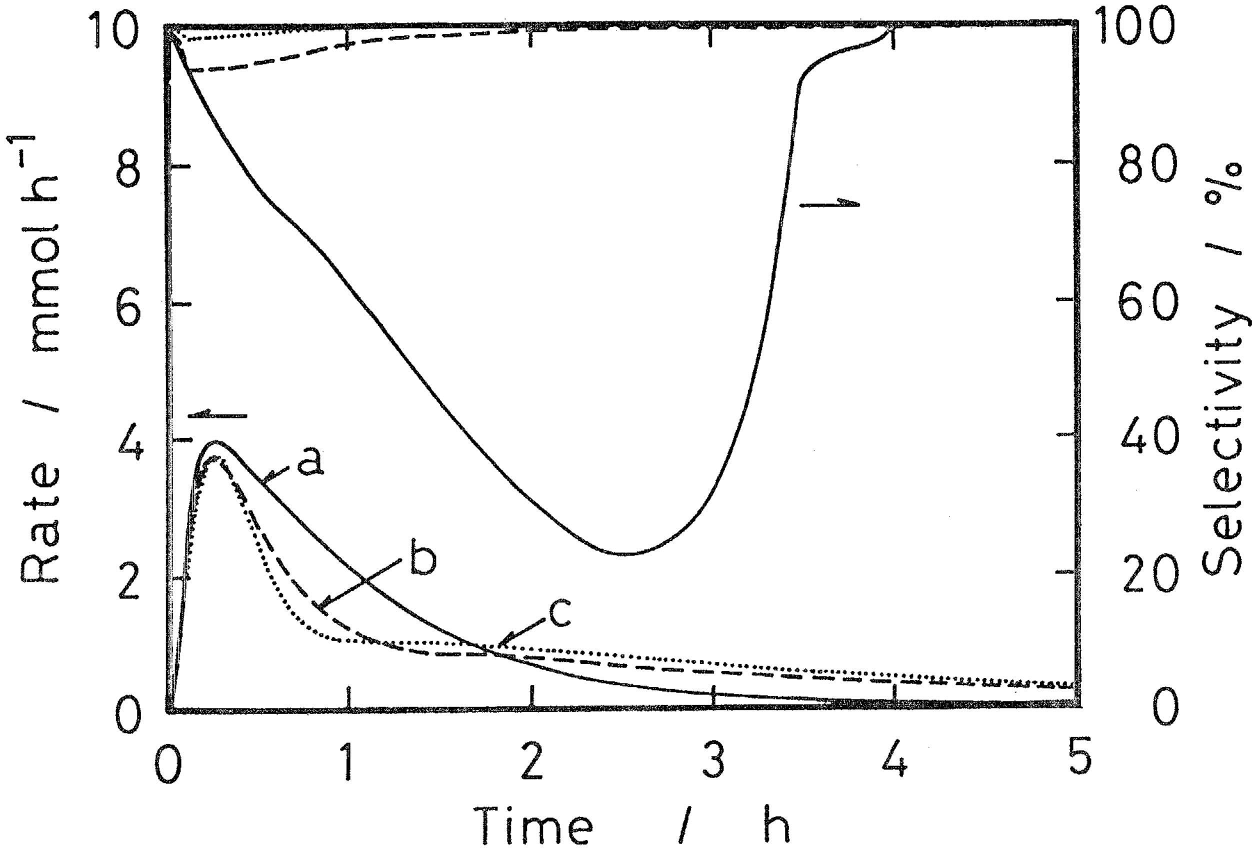


Figure 4-9 Effect of propyl chloride on the change in the rate of methoxysilanes formation and the selectivity for $HSi(OCH_3)_3$ with reaction time.
Preheating temperature = 723 K.
Reaction temperature = 513 K, methanol = 39 mmol h^{-1} (56 kPa),
propyl chloride = 0 (a), 0.078 (b), 0.39 mmol h^{-1} (c).

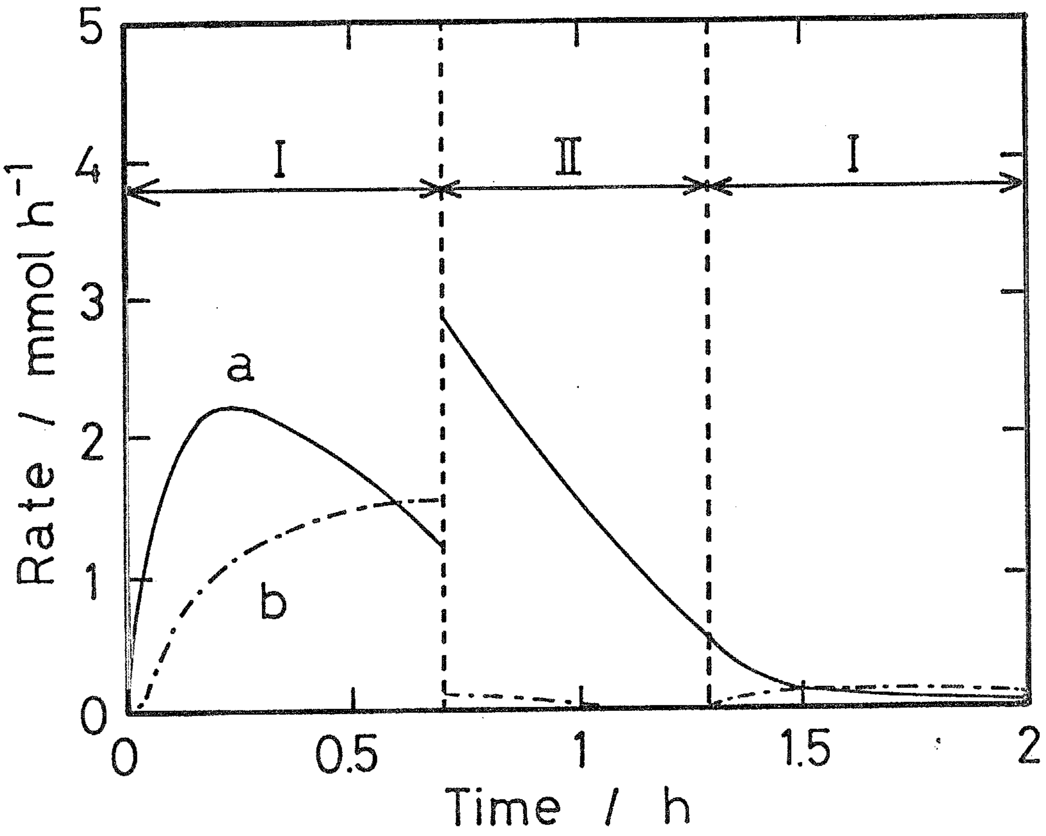


Figure 4–10 Change in the rate of methoxysilanes formation upon addition of propyl chloride.
a: $HSi(OCH_3)_3$, b: $Si(OCH_3)_4$.
Preheating conditions: 723 K, 1 h.
Reaction conditions: 513 K,
(I): methanol = 39 mmol h^{-1}(56 kPa),
(II): methanol = 39 mmol h^{-1}(56 kPa) and
propyl chloride = 0.39 mmol h^{-1}.

addition, propyl chloride was added to the feed in the course of the reaction of $HSi(OCH_3)_3$ and methanol over metallic copper, as shown in Fig. 4-11. The catalytic activity of copper disappeared upon addition of propyl chloride, indicating that propyl chloride poisons metallic copper. When the feed of propyl chloride was stopped, the catalytic activity was completely recovered in 20 min, indicating that the adsorption of propyl chloride on metallic copper is reversible.

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

4-7 Poisoning of Metallic Copper by Copper(I) Chloride in the Silicon - Methanol Reaction

4-7-1 Effect of the Amount of Copper(I) Chloride on the Rate of Methoxysilanes Formation

The selectivity for $HSi(OCH_3)_3$ depends on the amount of copper(I) chloride even when the temperature of the pretreatment is low. Figure 4-12 shows the effect of the amount of copper(I) chloride on the reactivity of silicon and the selectivity for $HSi(OCH_3)_3$ at 553 K. When the amount of Cu is less than 2 wt% of silicon, the selectivity for $HSi(OCH_3)_3$ starts to decrease sometime after starting the reaction. On the other hand, the selectivity is very high throughout the reaction, when the amount of Cu exceeds 2.5%. When the amount of CuCl was 10 wt%, the SEM image showed that the copper(I) chloride grains still remained even after the pretreatment of the silicon - copper(I) chloride

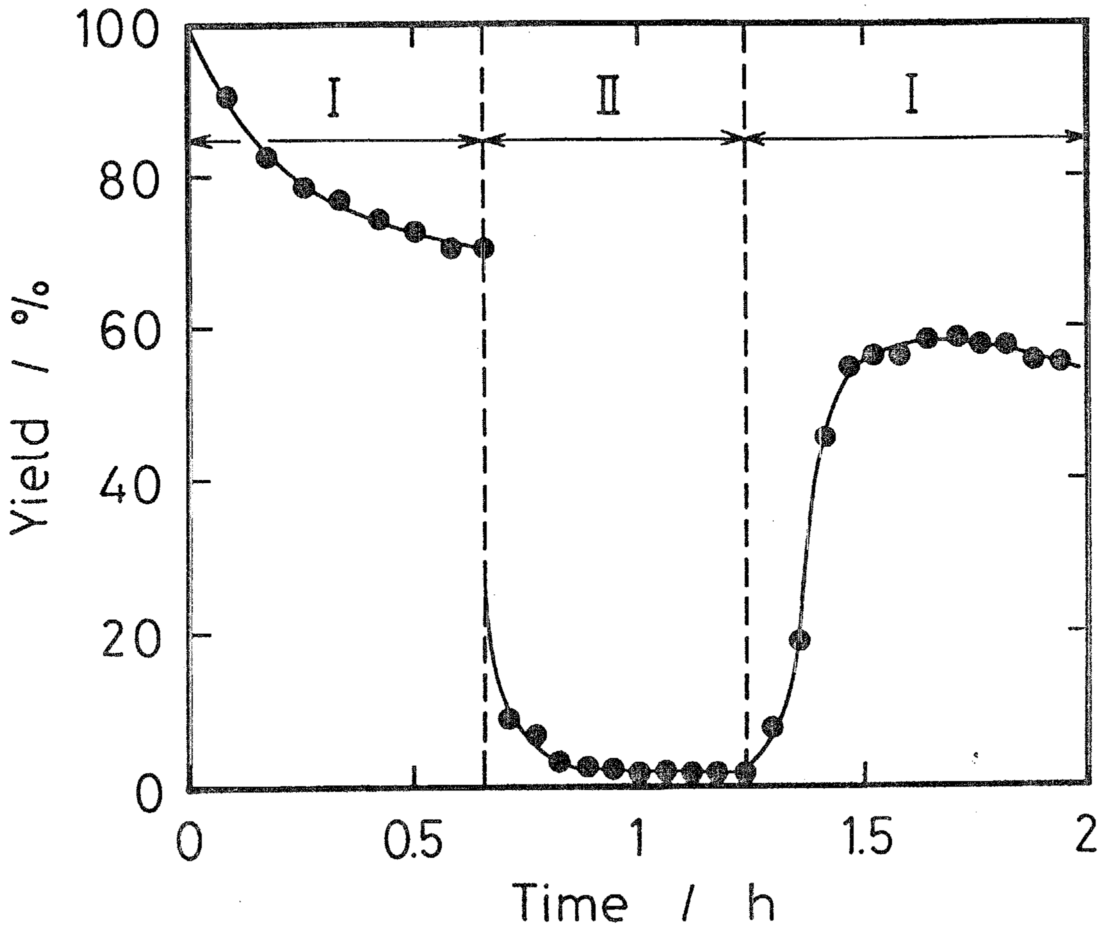


Figure 4-11 Poisoning of the metallic copper catalyst by propyl chloride in the reaction of $HSi(OCH_3)_3$ with methanol. Reaction temperature = 513 K, metallic copper =0.33 g,
(I): methanol = 39 mmol h^{-1}(56 kPa),
$HSi(OCH_3)_3$ = 4.0 mmol h^{-1}(5.7 kPa),
(II): methanol = 39 mmol h^{-1}(56 kPa),
$HSi(OCH_3)_3$ = 4.0 mmol h^{-1}(5.7 kPa),
and propyl chloride = 0.39 mmol h^{-1}(0.56 kPa).

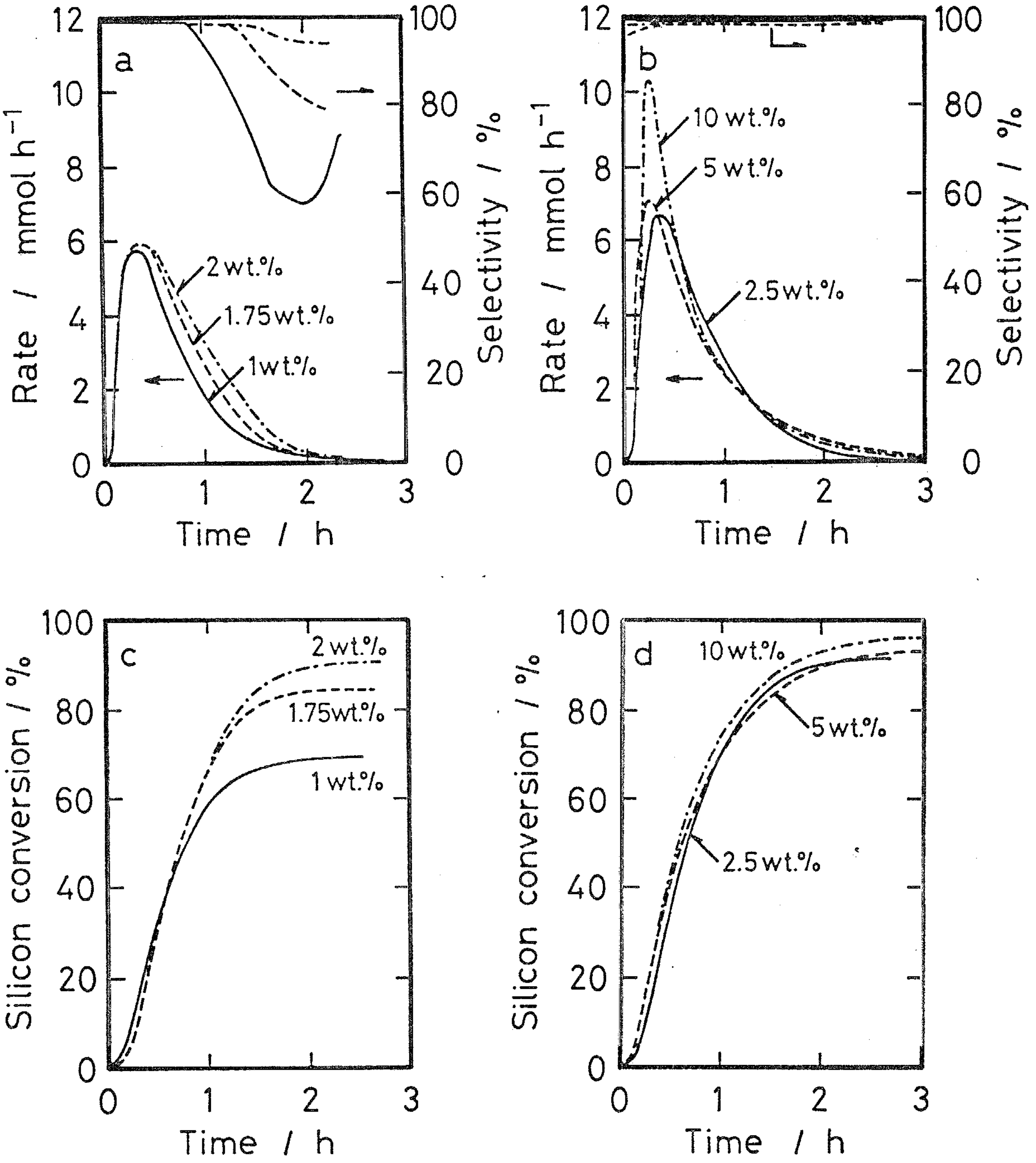


Figure 4-12 Effect of the amount of copper(I) chloride on the rate of methoxysilanes formation and the selectivity for $HSi(OCH_3)_3$.
Amount of copper(I) chloride was indicated in wt.% as Cu.
a, b: Change in the rate of methoxysilanes formation and the selectivity for $HSi(OCH_3)_3$.
c, d: Change in the cumulative conversion of silicon.
Preheating conditions: 553 K, 1 h.
Reaction conditions: 553 K, methanol = 39 mmol h^{-1}(56 KPa).

mixture at 553 K. This indicates that the formation of metallic copper is inhibited or that the metallic copper is poisoned even when it is formed, as long as excess copper(I) chloride exists in the system. As described in a previous section, alkyl halides inhibits the formation of $Si(OCH_3)_4$. The fact that the selectivity for $HSi(OCH_3)_3$ depends on the catalyst amount, indicates that chloride ions from copper(I) chloride are somehow transferred onto the copper surface to inhibit the activity of the metal formed during the silicon - methanol reaction.

The overall conversion of silicon was also a function of the amount of copper(I) chloride. As shown in Fig. 4-12c and d, the conversion of silicon exceeds 90%, when the amount of copper was 2 wt% or more. In contrast, it was only 70% and 80%, when the catalyst amount was 1 wt% and 1.75 wt%, respectively. The increase in silicon conversion with increasing the catalyst amount again suggests that excess copper(I) chloride serves to suppress the deactivation of the silicon - methanol reaction probably by inhibiting the formation of metallic copper. If this is the case, a high selectivity as well as high conversion would be attained by adding proper additives to the system even when the amount of the catalyst is small.

4-7-2 Effect of Propyl Chloride in the Case of a Small Amount of Copper(I) Chloride

Figure 4-13 shows the result of such an experiment. The silicon - methanol reaction was carried out with only 0.1 wt% of Cu, after the silicon - copper(I) chloride mixture was preheated at 553 K for 1 h. Without any additives, the selectivity for

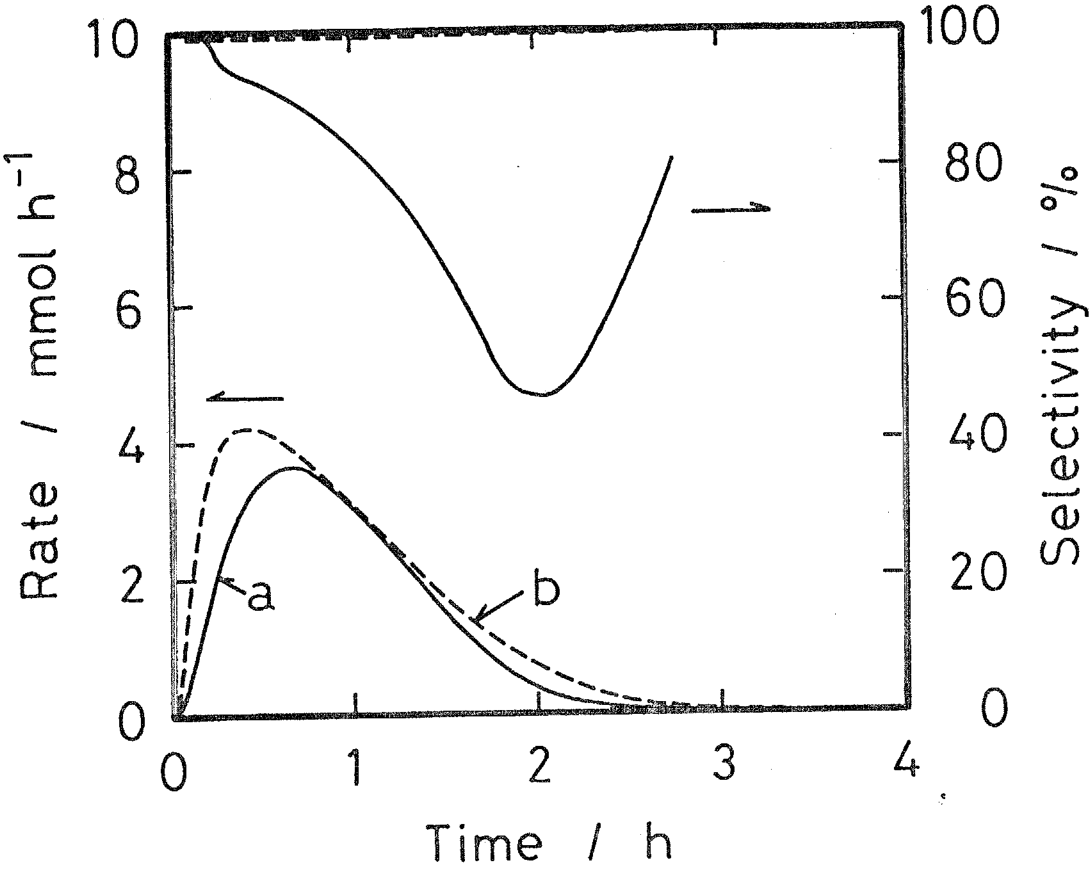


Figure 4-13 Effect of propyl chloride on the selectivity for $HSi(OCH_3)_3$.
Catalyst: copper(I) chloride (0.1 wt.% of Si as Cu).
a: methanol = 39 mmol h^{-1}(56 kPa),
b: methanol = 39 mmol h^{-1}(56 kPa)
+ propyl chloride = 0.39 mmol h^{-1}(0.56 kPa).
Preheating conditions: 553 K, 1 h. Reaction temperature: 553 K.

$HSi(OCH_3)_3$ was sharply dropped just after starting the reaction. When 0.56 kPa of propyl chloride was added to the methanol feed, the selectivity for $HSi(OCH_3)_3$ was 100% throughout the reaction. The overall conversion of silicon also increased from 71% to 89% by adding propyl chloride to the feed.

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

4-8 Addition of Thiophene or Propyl Chloride in the Reaction of Methanol and Silicon with the Oxide Overlayers

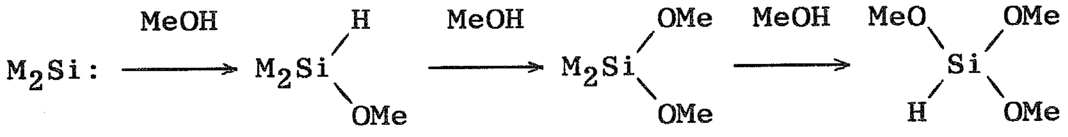
The results described above are all obtained with silicon grains, which had been washed with a HF solution, since silicon grain is usually covered with native oxide overlayers. We have reported that the reactivity of silicon with SiO_2 overlayers is too low to get a high silicon conversion when the pretreatment temperature was low [7]. Therefore, it is essential to pretreat a silicon - copper(I) chloride mixture at a high temperature to obtain a high silicon conversion [3,8]. However, under this preheating condition, the selectivity for $HSi(OCH_3)_3$ is low, as described above. It may not be industrially practical to remove the oxide overlayers from silicon grains before using them for the reaction. The method of poisoning might be useful to improve the selectivity also for the oxide-covered silicon.

The effect of addition of propyl chloride or thiophene on the reaction of silicon with silica overlayers (thickness 1.7 nm) was examined at 513 K, and the results are shown in Fig. 4-14. When the silicon with oxide layer was used for the reaction, the silicon conversion and the overall selectivity for 5 h were 62% and 57%, respectively. When thiophene was added to the feed, the conversion and the overall selectivity for 5 h increased to 69% and 97%, respectively. Addition of propyl chloride also enhanced the conversion and the overall selectivity. They were 76% and 98%, respectively. It is clear that a very high selectivity can be attained without decreasing the silicon conversion, when a proper additive is added to methanol feed.

4-9 Reaction Mechanism

4-9-1 Mechanism of Trimethoxysilane Formation

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



(1)

(I) (II) (III)

Step 1 Step 2 Step 3

(M = Cu)

On the surface of silicon, there may be a copper-rich region as indicated by the formation of a Cu-Si alloy phase. The migration of silicon to this region may give silicon species having a silylene character (I). This species reacts with

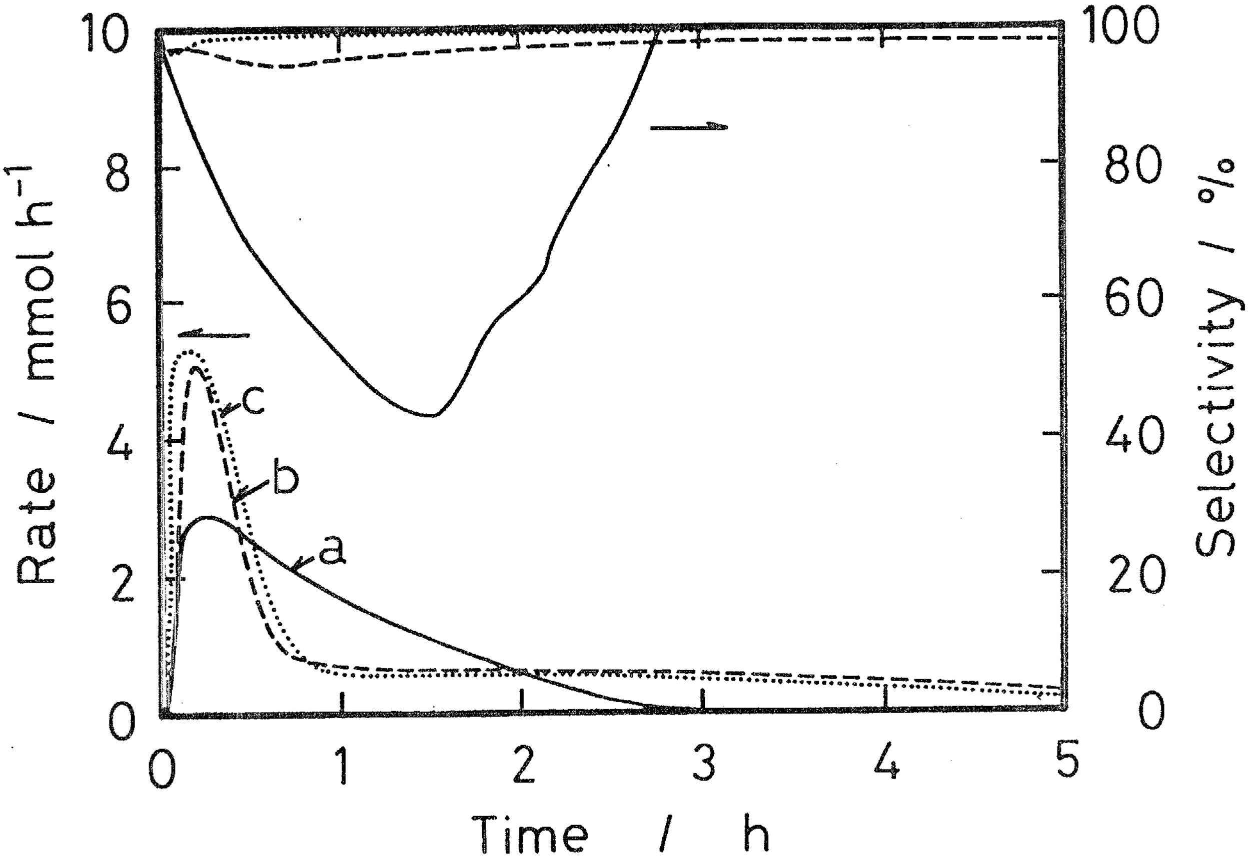


Figure 4-14 Effect of thiophene and propyl chloride on the reaction of methanol with silicon with oxide overlayers.
a: methanol = 39 mmol h^{-1} (56 kPa),
b: methanol = 39 mmol h^{-1}
and thiophene = 0.39 mmol h^{-1} (0.59 kPa),
c: methanol = 39 mmol h^{-1}
and propyl chloride = 0.39 mmol h^{-1} (0.59 kPa).

methanol to form a surface species (II). The reaction of methanol with silylene has been well established [9,10]. The surface Si-H bond undergoes an attack of another methanol molecule to dimethoxysilicon species (III), which undergoes further attack of methanol to form $HSi(OCH_3)_3$. Silicon atoms migrate from the bulk of the metal to the surface to regenerate copper - silicon intermetallic species. A certain fraction of the copper species on the surface combines to form metallic copper, which catalyzes the reaction of $HSi(OCH_3)_3$ with methanol.

4-9-2 Reaction of Methanol with Silicon in the Presence of 2-Propanol

(a) Reaction of 2-Propanol with Silicon

The mechanism of trimethoxysilane formation is supported by the formation of methoxyisopropoxysilanes by the reaction of silicon with 2-propanol in the presence of methanol.

n-alcohols such as methanol, ethanol, 1-propanol and n-butyl alcohol reacted with silicon, while sec-alcohol (2-propanol and 2-butyl alcohol) and tert-alcohol (tert-butyl alcohol) did not [6].

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 (Chapter 2) [6]. 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. 4-15).

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.

(b) Reaction of Methanol with Silicon in the Presence of 2-Propanol

To further elucidate the reactivity of 2-propanol towards silicon, 2-propanol (30 kPa) was fed together with methanol (63 kPa) to a silicon-copper(I) chloride mixture at 513 K. No pretreatment of the Si-CuCl mixture were done. Figure 4-16 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%). Thus, isopropoxy groups are incorporated in the product, though the neat 2-propanol does not react with silicon.

As described above, the mechanism of trimethoxysilane formation is proposed (eq. (1)). There are three steps that alkoxy groups are bonded to a silicon atom; Step 1: The reaction

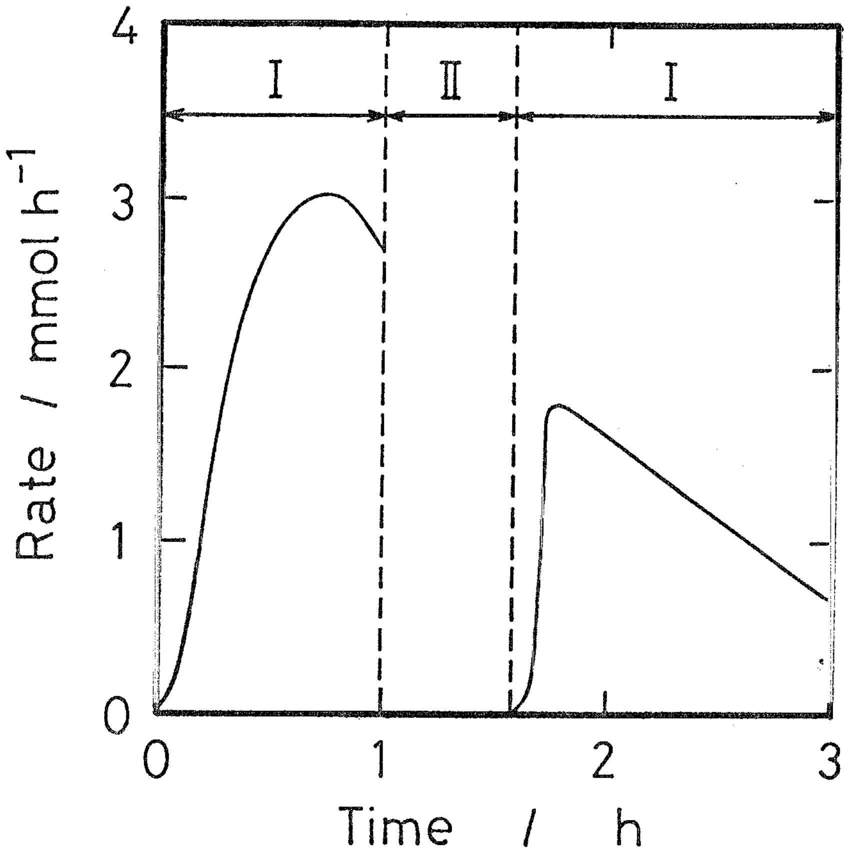


Figure 4-15 Reaction of silicon with 2-propanol after the activation of silicon by 1-propanol.
No pretreating.
Reaction conditions: reaction temperature = 483 K,
(I) 1-propanol = 96 kPa, (II) 2-propanol = 101 kPa.

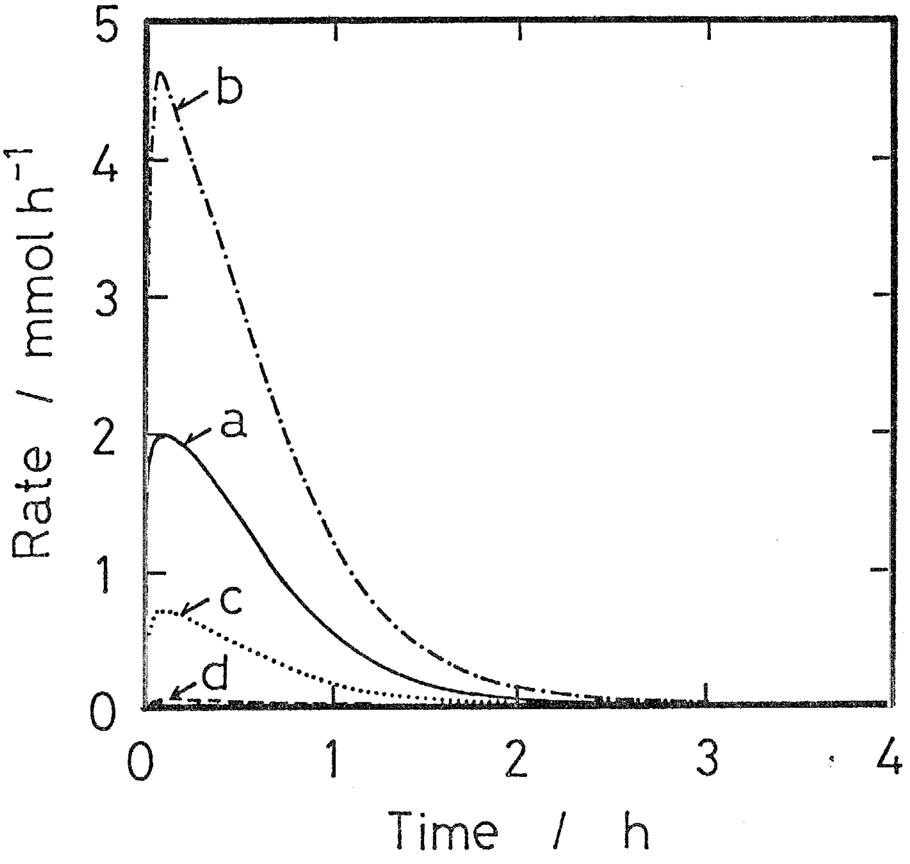


Figure 4-16 Change in the rates of formation of the products with time in the reaction of silicon, 2-propanol and methanol.
a: trimethoxysilane, b: dimethoxyisopropoxysilane,
c: methoxydiisopropoxysilane, d: triisopropoxysilane.
No pretreating.
Reaction conditions: reaction temperature = 513 K, methanol = 63 kPa and 2-propanol = 30 kPa.

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 first two steps out of the three. I 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.

Further evidence for the presence of silylene species was obtained by the reaction of methanol with silicon in the presence of alkenes. This will be discussed in Chapter 6.

4-10 Conclusions

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

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

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

References

1) E.G. Rochow, J. Am. Chem. Soc., 70, 2170 (1948).

2) W.E. Newton, and E.G. Rochow, Inorg. Chem. 9, 1071 (1970).

3) E. Suzuki, and Y. Ono, J. Catal., 125 (1990) 390.

4) J.H. Voorhoeve, "Organohalosilanes: Precursors to Silicones," p. 298, Elsevier, Amsterdam (1967).

5) R.G. Herman, K. Klier, G.W. Simmons, B.P. Finn, and J.B. Bulke, J. Catal., 56 (1979) 407.

6) K. Yamamoto, Master Thesis, Tokyo Institute of Technology, (1993).

7) Eur. Patent 280517 (1988).

8) E. Suzuki, M. Okamoto, and Y. Ono, Solid State Ionics, 47, 97 (1991).

9) D.R. Weyenberg, and W.H. Atwell, Pure Appl. Chem., 19, 343 (1969).

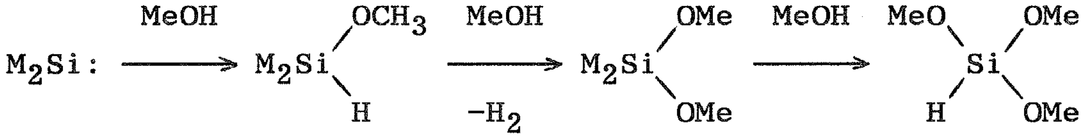
10) U.S. Patent 3,478,078.

Chapter 5 Direct Formation of Organosilicon Compounds from Silicon, Methanol and Alkenes

5-1 Introduction

It is shown in Chapter 2 that $HSi(OCH_3)_3$ is almost exclusively formed upon properly selecting pretreatment temperature of the Si-CuCl mixture as well as the reaction conditions, when the reaction was carried out using a fixed-bed flow reactor. It is also shown in Chapter 5 that, even when $Si(OCH_3)_4$ is appreciably formed, $HSi(OCH_3)_3$ is an exclusive primary product and that $Si(OCH_3)_4$ is formed by the secondary reaction of $HSi(OCH_3)_3$ and methanol by the action of metallic copper formed on the silicon surface during the reaction.

To explain the exclusive formation of $HSi(OCH_3)_3$, I have proposed the following reaction scheme.



(1)

I II III

(M = Cu)

The surface silylenoid, I on the silicon surface reacts with methanol to form methoxysiliconhydride species, II. It is known that silylenes react with methanol to form methoxysilanes [1,2]. The hydride species II rapidly reacts with methanol to form dimethoxysilicon species, III. Finally, two silicon copper bonds of the species III are cleaved by a methanol molecule to form the final product, $HSi(OCH_3)_3$. Silicon atoms diffuse from the bulk to the surface to reform the surface silylenoid. The most important features of the mechanism is the intermediacy of the surface silylenoid and the simultaneous cleavage of the two silicon-copper bonds with a methanol molecule.

This chapter describes the attempts to trap the silylenoid intermediate and to synthesize organosilicon compounds based on this mechanism. Alkenes (butadiene, ethylene and propylene) and allyl compounds were used as trapping agents.

5-2 Experimental

The reaction procedures are the same as those described in Chapter 2. When the reactions of phenol were carried out, phenol dissolved in dipropyl ether was fed by a motor-driven syringe into the reactor.

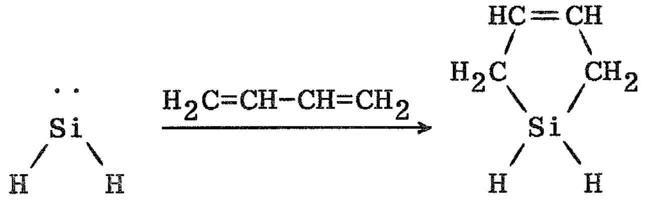
Allyl propyl ether and allyl ethyl ether were synthesized by the following method. Sodium hydride (26.7 g: 1.11 mol) was dissolved in propanol or ethanol (500 cc) to form the sodium alkoxide. Allyl chloride was dropped into the solution at room temperature and the solution was refluxed for 3 h. To remove the precipitated salt and unreacted alcohol, water was added to the solution. Allyl ether was separated from ether phase by distillation. The allyl ethers obtained were 98% in purity (impurity: diethyl ether 2%, allyl chloride <1%).

5-3 Reactions of Surface Silylenoid with Alkenes

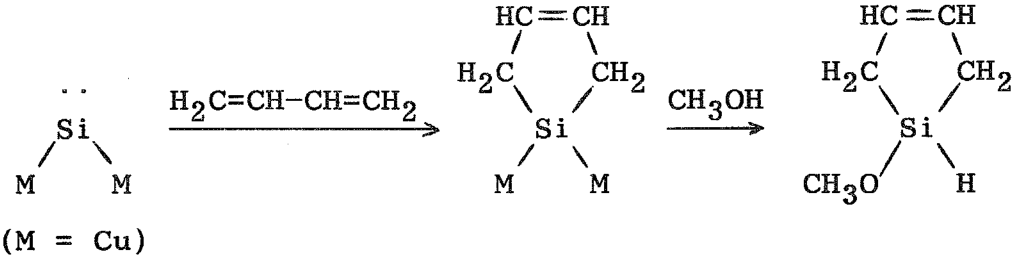
Silylene intermediates are known to react with various alkenes [3,4]. If the surface silylenoid is the intermediate in the reaction of silicon with methanol, alkenes may react with the surface silylenoid. Therefore, the reactions of silicon with methanol were carried out in the presence of alkenes butadiene, ethylene or propylene.

5-3-1 Reaction of Surface Silylenoid with Butadiene

The reactions of silylene intermediates with butadiene are known to form silacyclopent-3-enes [5-7]. This type of butadiene insertion is the inherent nature of silylene intermediate.


(2)

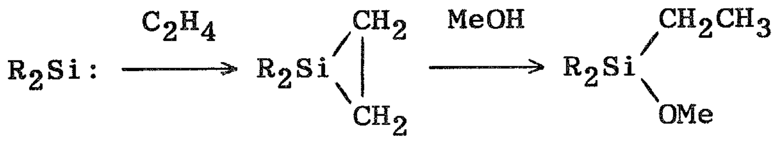
If the surface silylenoid reacts with butadiene and subsequently two Cu-Si bonds are cleaved by attack of methanol molecule, the following reaction would be expected.


(3)

When methanol (56 kPa) and butadiene (40 kPa) were fed to the mixture of silicon and copper(I) chloride at 513 K, 1-methoxysilacyclopent-3-ene was formed in a 3% selectivity, a major product (97%) being trimethoxysilane. This result supports the mechanism of trimethoxysilane formation expressed by reactions (1).

5-3-2 Reaction of Surface Silylenoid with Ethylene or Propylene

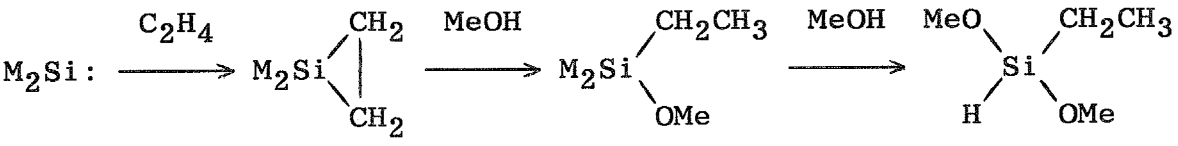
Ethylene reacts with silylene to form vinylsilanes through dimethylsilacyclopropane intermediates [3]. In the reaction of silylene with alkenes in the presence of methanol, alkylmethoxysilanes, the methanolysis products of silacyclopropane intermediates, are obtained [8-10].



(4)

($R = CH_3$)

If this type of the reaction occurs between the surface silylenoid and ethylene and the cleavage of the two Si-Cu bonds are caused by methanol, ethyldimethoxysilane, $HSi(C_2H_5)(OCH_3)_2$, must be found in the products.



(5)

(M = Cu)

Ethylene (63 kPa) and methanol (27 kPa) was fed to the Si-CuCl mixture in a fixed-bed reactor at 513 K. After the reaction for 3 h, 80% of silicon was consumed, the products being composed of 8% of the predicted compound, $HSi(C_2H_5)(OCH_3)_2$ and $HSi(OCH_3)_3$ (92%). The selectivities were calculated by the ratio of the ^1H-NMR peak areas of the products. The change in the formation rates of the two products with time is shown in Fig. 5-1. The rates first increased and decreased. The selectivity for $HSi(C_2H_5)(OCH_3)_2$ was constant during the reaction.

Similarly, the reaction of propylene and methanol with the silicon gave $HSi(C_3H_7)(OCH_3)_2$ together with $HSi(OCH_3)_3$. When propylene (84 kPa) and methanol (16 kPa) reacted with silicon at 513 K for 5 h, $HSi(C_3H_7)(OCH_3)_2$ was formed in a 4% selectivity, the overall silicon conversion being 60%.

The selectivity for alkyldimethoxysilane was high when the pressure of alkene was high. In the atmospheric reaction system, the selectivity for organosilane was below 10%. However, if alkenes was fed at high pressure above 1 atm, the higher selectivity could be obtained and this reaction might offer a new route for the synthesis of organosilanes.

When the vapor-phase reaction of silicon (200 mg: 7.1 mmol), methanol (18 mmol) and ethylene (40 atm at room temperature: about 210 mmol) was carried out in a 120 cc-autoclave at 433 K for 15 h, organosilanes, $HSi(C_2H_5)(OCH_3)_2$ and $Si(C_2H_5)(OCH_3)_3$, were formed, the other products being $HSi(OCH_3)_3$, $Si(OCH_3)_4$ and oligomers containing silicon. The fraction of organosilanes, $HSi(C_2H_5)(OCH_3)_3$ and $Si(C_2H_5)(OCH_3)_3$ among the silane monomers was high (26%), however, the total yield of the four silane monomers was low (19%).

The reaction of ethanol instead of methanol was also carried out. When ethanol (72 mmol), ethylene (20 atm at room temperature: 105 mmol) and silicon (500mg: 18 mmol) were heated

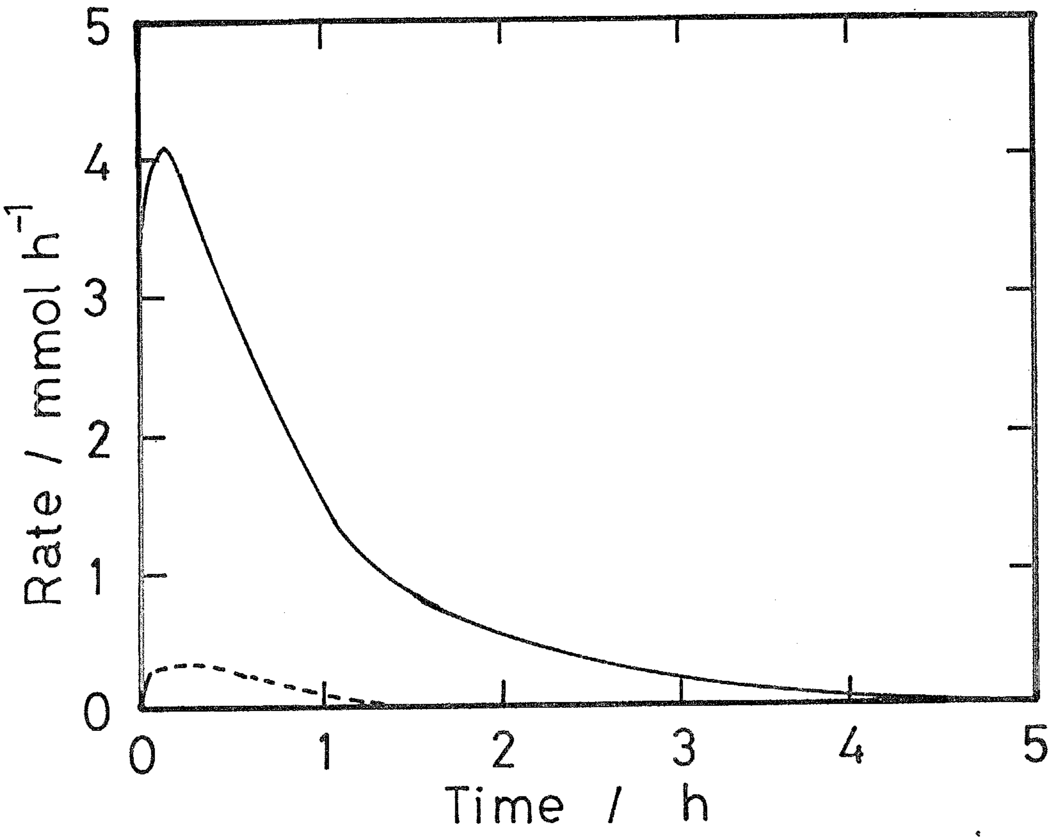


Figure 5-1 Change in the formation rates of the products with time in the reaction of silicon, methanol and ethylene.
Products: $HSi(OCH_3)_3$ (solid line),
$HSi(C_2H_5)(OCH_3)_2$ (dashed line).
No pretreating.
Reaction condition: reaction temperature = 513 K, methanol = 27 kPa, ethylene = 63 kPa.

in the autoclave at 473 K for 3 h, the expected products, $HSi(C_2H_5)(OC_2H_5)_2$ (0.5% yield), $Si(C_2H_5)(OC_2H_5)_3$ (5%), were formed. The yields of $HSi(OC_2H_5)_3$ and $Si(OC_2H_5)_4$ were 1.3% and 17%, respectively.

5-3-3 Reaction of Surface Silylenoid with Ethylene in the Presence of Phenol

(a) Reaction of Silicon with Phenol

It was reported that phenol reacted with silicon fused with metallic copper as a a catalyst to form tetraphenoxysilane [11]. Here, the reaction of silicon with phenol (25 kPa) was carried out in a fixed-bed flow reactor at 513 K without the pretreatment of the silicon-copper(I) chloride mixture. Triphenoxysilane obtained in a 81% yield in 5 h, tetraphenoxysilane being not formed.

(b) Reaction of Surface Silylenoid with Ethylene in the Presence of Phenol

The reaction of surface silylenoid with ethylene in the presence of phenol instead of methanol was carried out without pretreating a silicon-copper(I) chloride mixture. The results are shown in Table 5-1. The expected product, $HSi(C_2H_5)(OPh)_2$, was formed, the formations of $Si(C_2H_5)(OPh)_3$ and tetraphenoxysilane being not observed. When phenol (11 kPa) and ethylene (85 kPa) were fed at 513 K, $HSi(C_2H_5)(OPh)_2$ of a 2.4% yield was obtained, the selectivity being 8.7%. The selectivity for ethyldiphenoxysilane increased with increasing partial

Table 5-1 Product distribution in the reaction of silicon with phenol in the presence of ethylene.

C_6H_5OH / kPa	C_2H_4 / kPa	Reaction temp. / K[a)]	Silicon conv. / %[b)]	Selectivity / %	
				$HSi(C_2H_5)(OPh)_2$	$HSi(OPh)_3$
11	85	513	28 (5 h)[c)]	8.7	91.3
25	66	513	28 (3 h)[c)]	6.4	93.6
25	66	553	37 (3 h)[c)]	5.8	94.2
25	0	513	81 (5 h)[c)]	–	–

a) Reaction temperature.

b) Silicon conversion at the end of the reaction.

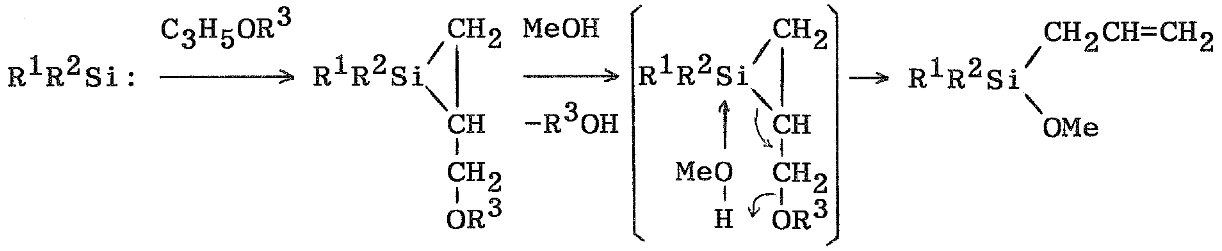
c) Reaction time at the end of the reaction.

pressure of ethylene or decreasing reaction temperature (Table 5-1).

5-4 Reactions of Surface Silylenoid with Allyl Compounds

The formation of organosilanes more effectively proceeds with use of allyl ethers instead of simple alkenes.

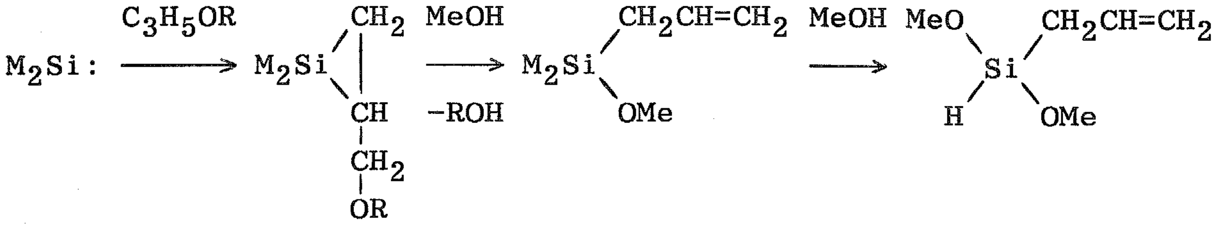
The reaction of allyl alkyl ether with silylene in the presence of methanol was reported to afford allylmethoxysilane [12].



(6)

(R^1 = $SiMe_3$, R^2 = Ph, R^3 = Et)

If the similar type of the reaction occurs on the silicon surface in the presence of allyl alkyl ether and methanol and the Si-Cu bonds are cleaved in the final step, the product allyldimethoxysilane, $HSi(CH_2CH=CH_2)(OCH_3)_2$ must be found in the products.



(7)

(M = Cu, R = C_2H_5, C_3H_7)

The overall reaction can be expressed as

$$Si + CH_2=CHCH_2OR + 2\ CH_3OH \text{ —— } HSi(CH_2CH=CH_2)(OCH_3)_2 + ROH \quad (8)$$

Allyl propyl ether (63 kPa) and methanol (27 kPa) were fed to the Si-CuCl mixture at 513 K. Since commercial allyl propyl ether contained a small amount of allyl alcohol which inhibits the silicon-methanol reaction, I used the ether synthesized by the method without use of allyl alcohol as described in the experimental section. The silicon-containing products were $HSi(CH_2CH=CH_2)(OCH_3)_2$, $HSi(OCH_3)_3$, and $HSi(OCH_3)_2(OC_3H_7)$. $HSi(CH_2CH=CH_2)(OCH_3)_2$ was identified by mass spectrum. The authentic $HSi(CH_2CH=CH_2)(OCH_3)_2$ was prepared by the reaction of $HSi(OCH_3)_3$ with $CH_2=CHCH_2MgCl$. The change in the rates of the formation of the three products is shown in Fig. 5-2. The products were analyzed in every 8 min. The rates of formation of the three products first increased and then decreased. The silicon conversion reached 50%, when the reaction stopped at 3 h. The overall selectivity for $HSi(CH_2CH=CH_2)(OCH_3)_2$ for 3 h was 38%. Thus, the overall yield of $HSi(CH_2CH=CH_2)(OCH_3)_2$ was 19%. The selectivities for other two products, $HSi(OCH_3)_3$ and $HSi(OCH_3)_2(OC_3H_7)$, were 44% and 18%, respectively. The latter product may be formed by the transesterification reaction between $HSi(OCH_3)_3$ and propyl alcohol, a reaction product.

The results of the reactions at various partial pressures of allyl propyl ether and reaction temperatures is shown in Table 5-2. When the pressure of allyl propyl ether increased, the selectivity increased, however, the silicon conversion decreased.

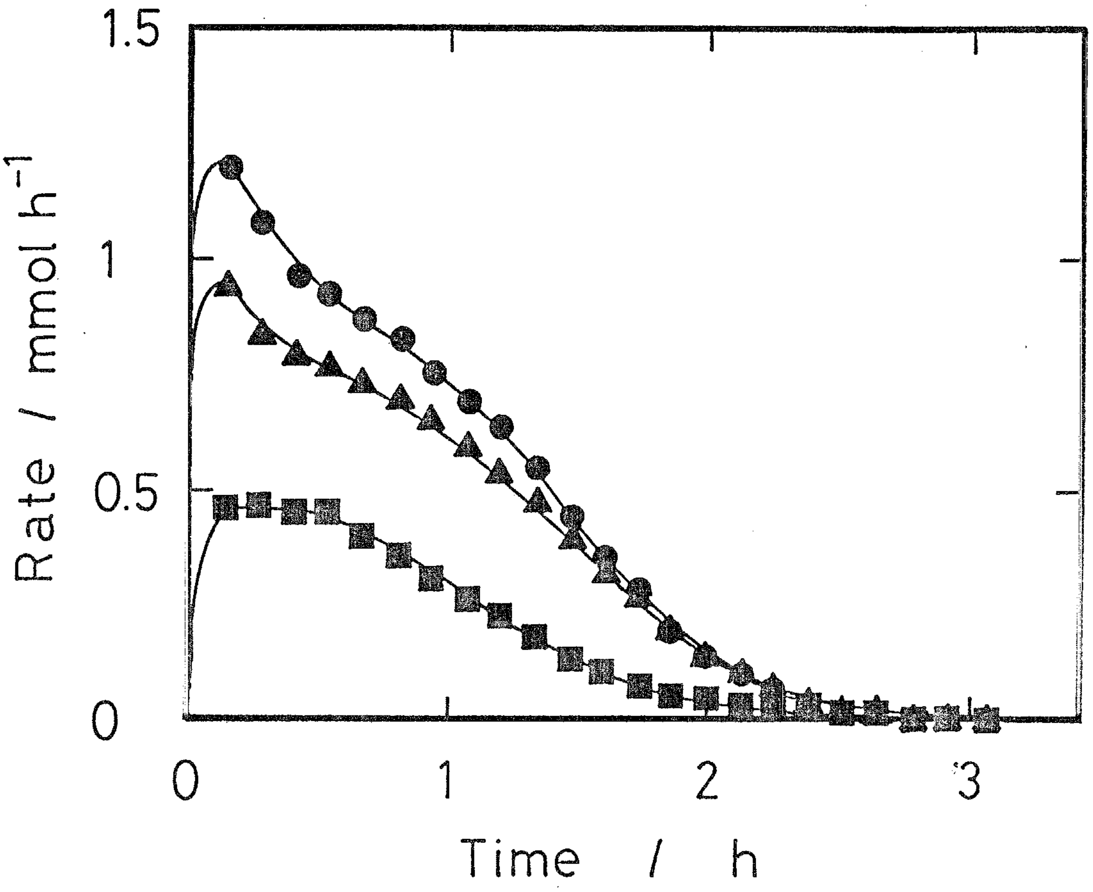


Figure 5-2 Change in the formation rates of the products with time in the reaction of silicon, methanol and allyl propyl ether.
Products: $HSi(CH_2CH{=}CH_2)(OCH_3)_2$ (▲), $HSi(OCH_3)_3$ (●), $HSi(OCH_3)_2(OC_3H_7)$ (■).
No pretreating.
Reaction conditions: reaction temperature = 513 K, methanol = 27 kPa, allyl propyl ether = 63 kPa.

Table 5-2 Product distribution in the reaction of silicon with methanol in the presence of allyl propyl ether.

CH_3OH / kPa	Allyl propyl ether/ kPa	Reaction temp. / K a)	Si conv. / % b)	Selectivity / %		
				ADMS c)	TMS d)	DMPS e)
27	63	513	50 (3 h) f)	38	44	18
27	63	533	57 (3.3 h) f)	30	58	12
55	31	513	80 (2.8 h) f)	26	67	7
55	24	513	81 (5 h) f)	24	70	6

a) Reaction temperature.

b) Silicon conversion at the end of the reaction.

c) $HSi(CH_2CH=CH_2)(OCH_3)_2$.

d) $HSi(OCH_3)_3$.

e) $HSi(OCH_3)_2(OC_3H_7)$.

f) Reaction time at the end of the reaction.

High reaction temperature resulted in a high conversion and a low selectivity.

The use of allyl ethyl ether as an alkene results in the formation of $HSi(CH_2CH=CH_2)(OCH_3)_2$. The selectivity for allylation was 30%, the silicon conversion being 44%. The reaction of diallyl ether was also carried out. The overall selectivity for $HSi(CH_2CH=CH_2)(OCH_3)_2$ was 12%, 58% of silicon being consumed. Allyl alcohol formed as a by-product poisoned the reaction of silicon with methanol. This resulted in a low silicon conversion. Allyl methyl sulfide gave $HSi(CH_2CH=CH_2)(OCH_3)_2$, though the yield was very low because of poisoning of the silicon-methanol reaction by the sulfide. The results and the details of the reaction conditions are summarized in Table 5-3.

These results clearly show the intermediacy of the surface silylenoid in the reaction of metallic silicon with methanol and support the mechanism expressed by eq. (1). Clarke and Davidson attempted to trap silylene intermediates in the reaction of silicon with methyl chloride using butadiene as a trapping agent [13]. The yield of the trapped products, however, was very low and they concluded that silylene was not important in the overall mechanism. In the case of the silicon-methanol reaction, the trapped product $HSi(CH_2CH=CH_2)(OCH_3)_2$ accounts for 38% of the whole product, indicating the importance of the surface silylenoid as an intermediate.

Table 5-3 Product distribution in the reaction of silicon with methanol in the presence of allylic compounds.

CH_3OH / kPa	Allylic compound / kPa	Silicon conversion / %[a]	Products (Selectivity / %)	
27	63	50 (3 h)[b]	$HSi(CH_2CH=CH_2)(OCH_3)_2$	(38)
	$CH_2=CHCH_2OC_3H_7$		$HSi(OCH_3)_3$	(44)
			$HSi(OCH_3)_2(OC_3H_7)$	(18)
27	62	44 (2 h)[b]	$HSi(CH_2CH=CH_2)(OCH_3)_2$	(29)
	$CH_2=CHCH_2OC_2H_5$		$HSi(OCH_3)_3$	(70)
			$HSi(OCH_3)_2(OC_2H_5)$	(1)
56	21	58 (5 h)[b]	$HSi(CH_2CH=CH_2)(OCH_3)_2$	(12)
	$(CH_2=CHCH_2)O$		$HSi(OCH_3)_3$	(88)
56	26	7 (2 h)[b]	$HSi(CH_2CH=CH_2)(OCH_3)_2$	(30)
	$CH_2=CHCH_2SCH_3$		$HSi(OCH_3)_3$	(70)

a) At the end of the reaction.

b) Reaction time at the end of the reaction.

Reaction temperature = 513 K.

5-5 Conclusions

The reaction of metallic silicon with methanol in the presence of alkenes gave alkyldimethoxysilanes. When butadiene was fed to the silicon - copper(I) chloride mixture, 1-methoxysilacyclopent-3-ene was formed, suggesting that surface silylene species is the intermediate in the silicon-methanol reaction. Addition of ethylene or propylene to the methanol feed resulted in the formation of ethyl- or propyldimethoxysilane at 8 or 4% of the selectivity, respectively.

Phenol reacted with silicon to give triphenoxysilane. The reaction of silicon with phenol in the presence of ethylene afforded ethyldiphenoxysilane, the selectivity being about 8%. This indicates that the surface silylenoid as an intermediate is formed in the silicon-phenol reaction.

When allyl ether was used instead of an alkene, allyldimethoxysilane was obtained in higher yield. Especially, the use of allyl propyl ether gave the high selectivity (38%), indicating the intermediacy of surface silylenoid in the silicon-methanol reaction.

High pressure of ethylene (40 atm) gave high selectivity (26%) for ethylmethoxysilanes. Thus, the reactions of silicon, alcohol and alkenes may offer a potential method for synthesis of organosilanes when high-pressure reactor is used.

References

1) D.R. Weyenberg, and W.H. Atwell, Pure Appl. Chem., 19 , 343 (1969).

2) U.S. Patent 3,478,078.

3) P.S. Skell, and E.J. Goldsten, J. Am. Chem. Soc., 86, 1442 (1964).

4) Y.N. Tang, "Reactive Intermediates Vol. 2," Chapter 4, ed. R.A. Abramovitch, Plenum, New York, pp 297-366 (1982).

5) V.J. Tortorelli, M. Jones, Jr., S.-H. Wu, and Z.-H. Li, Organometallics, 2, 759 (1983).

6) W.H. Atwell, and D.R. Weyenberg, J. Am. Chem. Soc., 90, 3438 (1968).

7) P.P. Gaspter, and R.-J. Hwang, J Am. Chem. Soc., 96, 6198 (1974).

8) E.A. Chernyshev, N.G. Komalenkova, S.A. Bashkirova, and V.V. Sokolova, Zh. Obshch. Khim., 48, 830 (1978).

9) M. Ishikawa, and K. Kumada, J. Organomet. Chem., 81, C3 (1974).

10) D. Seyferth, C.K. Haas, and D.C. Annarelli, J. Organomet. Chem., 56, C7 (1973).

11) J. Kius, and H.I. Waterman, Research, 8, S2 (1955).

12) M. Ishikawa, K. Nakagawa, and M. Kumada, J. Organomet. Chem., 214, 277 (1981).

13) M.P. Clarke, and I.M.T. Davidson, J. Organomet. Chem., 408, 149 (1991).

Chapter 6 Effect of Halide ion of Copper(I) Halide Catalyst on the Reaction of Silicon with Methanol

6-1 Introduction

The synthesis of trimethoxysilane from metallic silicon and methanol has been performed by using copper(I) chloride as a catalyst [1,2]. As described in Chapter 2, the rate of methoxysilanes formation and the selectivity for trimethoxysilane greatly depend on the pretreatment conditions of the mixture of silicon and copper(I) chloride as well as the reaction conditions. When the mixture is pretreated at 723 K, the selectivity is low. Copper(I) chloride reacts with silicon to form Cu_3Si phase on the surface during the pretreatment. Silicon is consumed around Cu_3Si patches formed at the pretreatment stage. On the other hand, when the pretreatment is done at low temperature, the selectivity is high. The small size of the Cu-Si intermetallic compounds, whose formation is not observed by XRD, is formed.

In the silicon-methanol reaction, silicon reacts with copper(I) chloride to form Cu-Si alloy at the pretreatment stage. During the pretreatment at 723 K, a liquid- and vapor-phase transport of copper(I) chloride onto the silicon surface occurs and then reacts with silicon. If copper(I) bromide or iodide instead of the chloride is used as catalysts, the difference of halide ion may affect the formation of Cu-Si alloy due to the differences in the reactivity of the copper(I) halide toward silicon and in the physical properties such as vapor pressures.

Therefore, the formation of reactive sites may be influenced by the halide ion. In the reaction with the pretreatment at 513 K, the mechanism of the transport of copper(I) chloride onto the silicon surface has not clarified yet (Chapter 2). It is plausible that the formation rate of reactive sites depends on the kind of the halide ion.

As described in Chapter 3, when the pretreatment temperature was high (723 K) and low (< 573 K), the reaction order with respect to methanol and the activation energy are 1.4, 44 kJ mol^{-1} and 1.0, 88 kJ mol^{-1}, respectively. If the halide ion would affect the nature of the reactive sites, the reaction order with respect to methanol pressure and the activation energy might change with the kind of the halide ion.

In this chapter, in order to examine the role of halide ions in the formation of reactive sites, the reactions of silicon with methanol using copper(I) bromide and iodide as catalysts were carried out. The results are compared with those of the reactions with a copper(I) chloride catalyst and the role of halide ions in the reactive-site formation is discussed.

6-2 Experimental

Copper(I) bromide grains obtained from Wako Pure Chemical Industries, Ltd. were 99.9% in purity. They were sieved into grains of 45-63 μm.

Copper(I) iodide grains (purity: 99.5%) of 1-4 μm were obtained from Wako Pure Chemical Industries, Ltd.

The reaction procedures are the same as those described in

Chapter 2. The silicon and copper(I) halide grains were mixed in the vial vigorously by hands. The mixture, containing 6 mmol of silicon and 0.31 mmol of copper(I) halide, was loaded in a fixed-bed reactor of quartz tube (10 mm i.d.). The mixtures were pretreated under a helium stream (30 cm^3 min^{-1}) at 493, 513 and 723 K for 1 h. Methanol, dehydrated over molecular sieve 3A, was fed into the reactor. The flow rate (CH_3OH + He) was 71 mmol h^{-1}. The methanol pressure was 55 kPa. The products were analyzed automatically every 3.5 min with a gas chlomatograph equipped with a 2 m-long SE-30 column.

6-3 Effect of the Halide Ion on the Rate of Methoxysilanes Formation

When copper(I) chloride catalyst was used, the rate of methoxysilanes formation and the selectivity for trimethoxysilane remarkably changed with the pretreatment temperature as mentioned in Chapter 2. When copper(I) bromide or iodide was used as a catalyst, the pretreatment at high temperature (723 K) or low temperature (513 K) was carried out before methanol was fed into the reactor at 513 K.

6-3-1 Reaction after the Pretreatment at 723 K

Figure 6-1a shows the time course of the rate of methoxysilanes formation when the mixture of silicon and a copper(I) halide were pretreated at 723 K. The rates increased to a maximum and decreased in all cases. The increase of the rate at the beginning of the reactions shows that the reactive

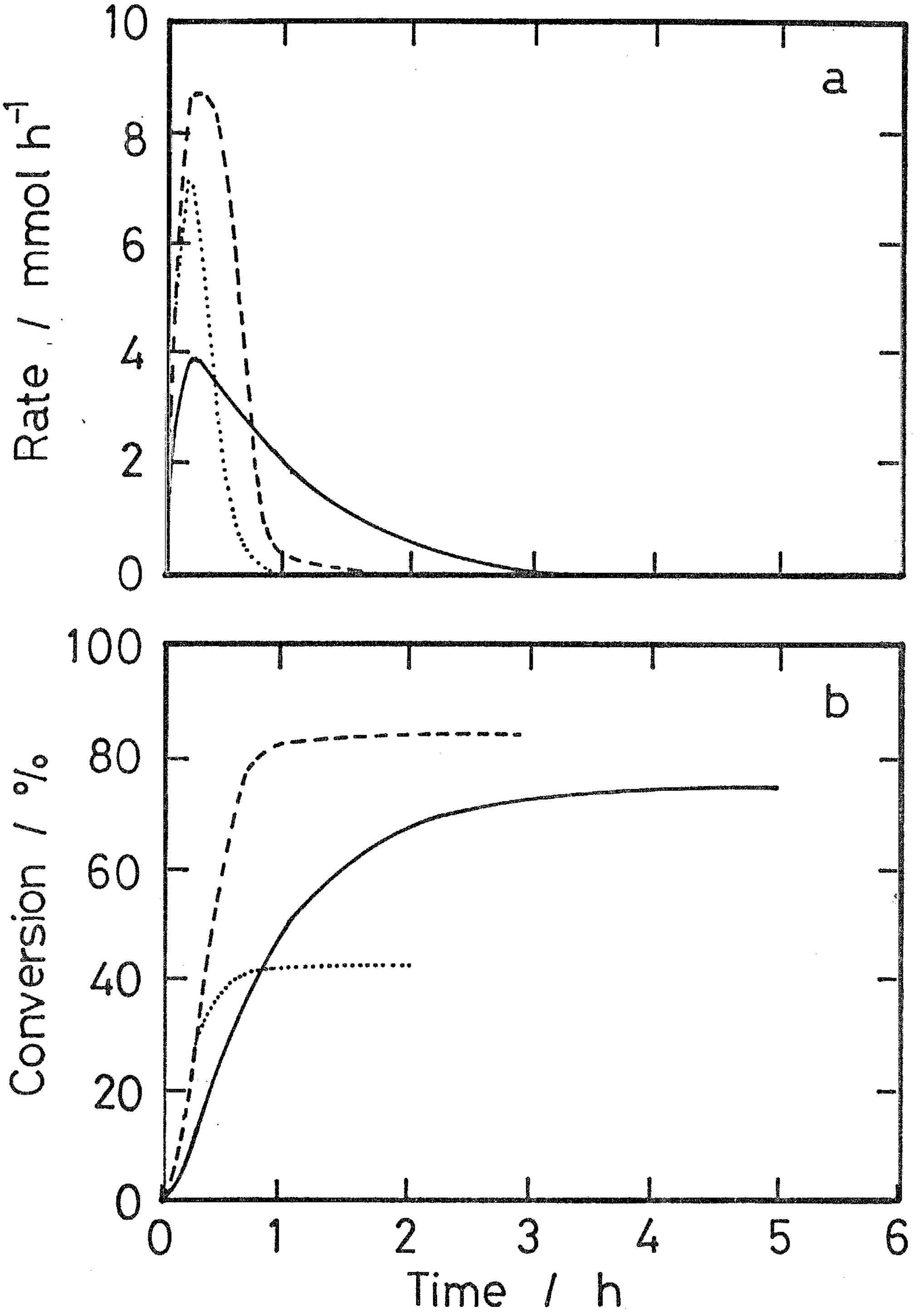


Figure 6-1 Change in the rate of methoxysilanes formation (a) and cumulative silicon conversion (b) with time, when the preatreatment was done at 723 K.
Catalysts are copper(I) chloride (solid lines), bromide (dashed lines) and iodide (dotted lines).
Reaction temperature = 513 K, methanol pressure = 59 kPa.

sites are formed when methanol vapor is in contact with silicon. The maximum rate in the reaction using copper(I) bromide or iodide was larger than that using copper(I) chloride. Figure 6-1b shows the change in the silicon conversion with the reaction time. The silicon conversion were calculated by the integration of the rate of methoxysilanes formation in Fig. 6-1a. When copper(I) bromide or iodide was used, the rate of formation was high at the beginning of the reaction. However, the use of copper(I) iodide resulted in low silicon conversion. The overall silicon conversion till the end of the reaction using copper(I) chloride, bromide, and iodide was 75, 84, and 42%, respectively. The selectivity for trimethoxysilane was decreased from 100% with reaction time in the beginning of the reaction in every case. The overall selectivity was 74, 73, and 94%, when copper(I) chloride, bromide, and iodide was used, respectively.

6-3-2 Reaction after the Pretreatment at 513 K

Figure 6-2a shows the change in the rate with time when the pretreatment was carried out at 513 K. In the case using copper(I) iodide as a catalyst, silicon did not react with methanol. When copper(I) bromide was used, methoxysilanes were formed, the selectivity for trimethoxysilane being almost 100% during the reaction. The rate increased to a maximum and decreased in every time course. This means that the reactive sites are formed when silicon was exposed to methanol. Figure 6-2b shows the change in the silicon conversion with reaction time. The silicon conversion for 5 h was 95% and 68% in the

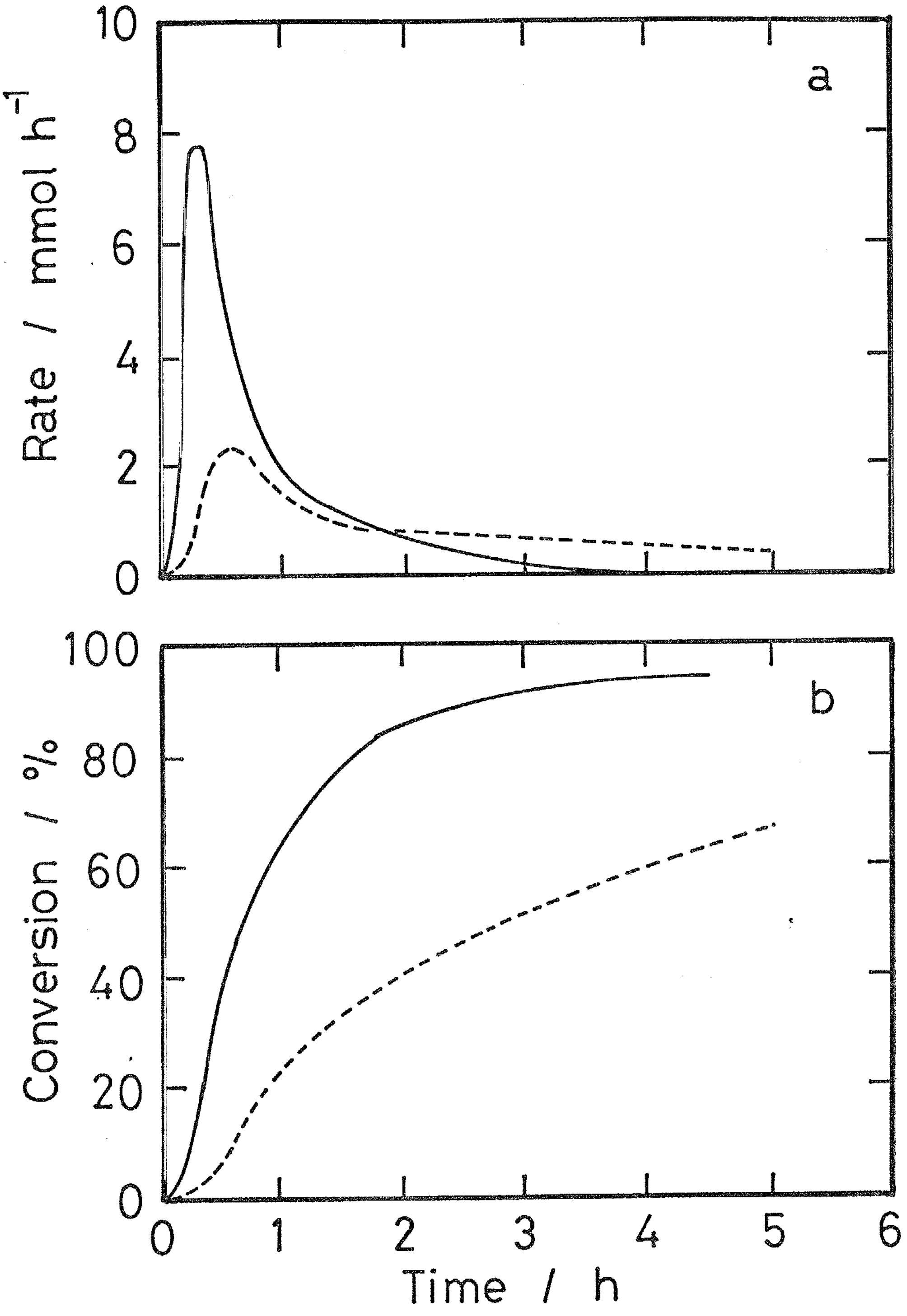


Figure 6-2 Change in the rate of methoxysilanes formation (a) and cumulative silicon conversion (b), when the pretreatment was done at 513 K.

Catalysts are copper(I) chloride (solid lines) and bromide (dashed lines).

Reaction temperature = 513 K, methanol pressure = 59 kPa.

reaction using copper(I) chloride and bromide, respectively. Under this pretreatment conditions, the reaction rate using copper(I) bromide was slower than that using copper(I) chloride. The reaction using copper(I) chloride resulted in a shorter reaction time till the maximum rate of formation than that using copper(I) bromide. This indicates that copper(I) chloride gives a higher rate of formation of the reactive sites than copper(I) bromide.

6-4 XRD Analysis of the Silicon-Catalyst Mixtures after the Pretreatment

In order to examine the effect of the halide ions on the state of silicon-copper(I) halide mixture, the pretreated mixture was analyzed by XRD. When the copper(I) chloride was used as a catalyst, Cu_3Si phase was formed after the pretreatment above 603 K. On the other hand, when the low temperature (< 573 K) pretreatment was carried out, the diffraction peaks of Cu_3Si by XRD were not observed (Chapter 2).

Figure 6-3 shows the XRD patterns of the mixtures after the pretreatment at 723 K. The most intense diffraction peak at $2\theta= 47.3$ is ascribed to silicon. Since this peak was very sharp, the peak diffracted by $CuK\alpha_2$ of X-ray near $CuK\alpha_1$ is observed at $2\theta= 47.5$. When the pretreatment was carried out above 633 K, two diffraction peaks were observed at $2\theta= 44.6$ and 45.1 irrespective of the kind of copper(I) halides. These peaks are attributed to the Cu_3Si phase. As shown in Fig. 6-3, the intensity of the Cu_3Si peak was almost same in every sample.

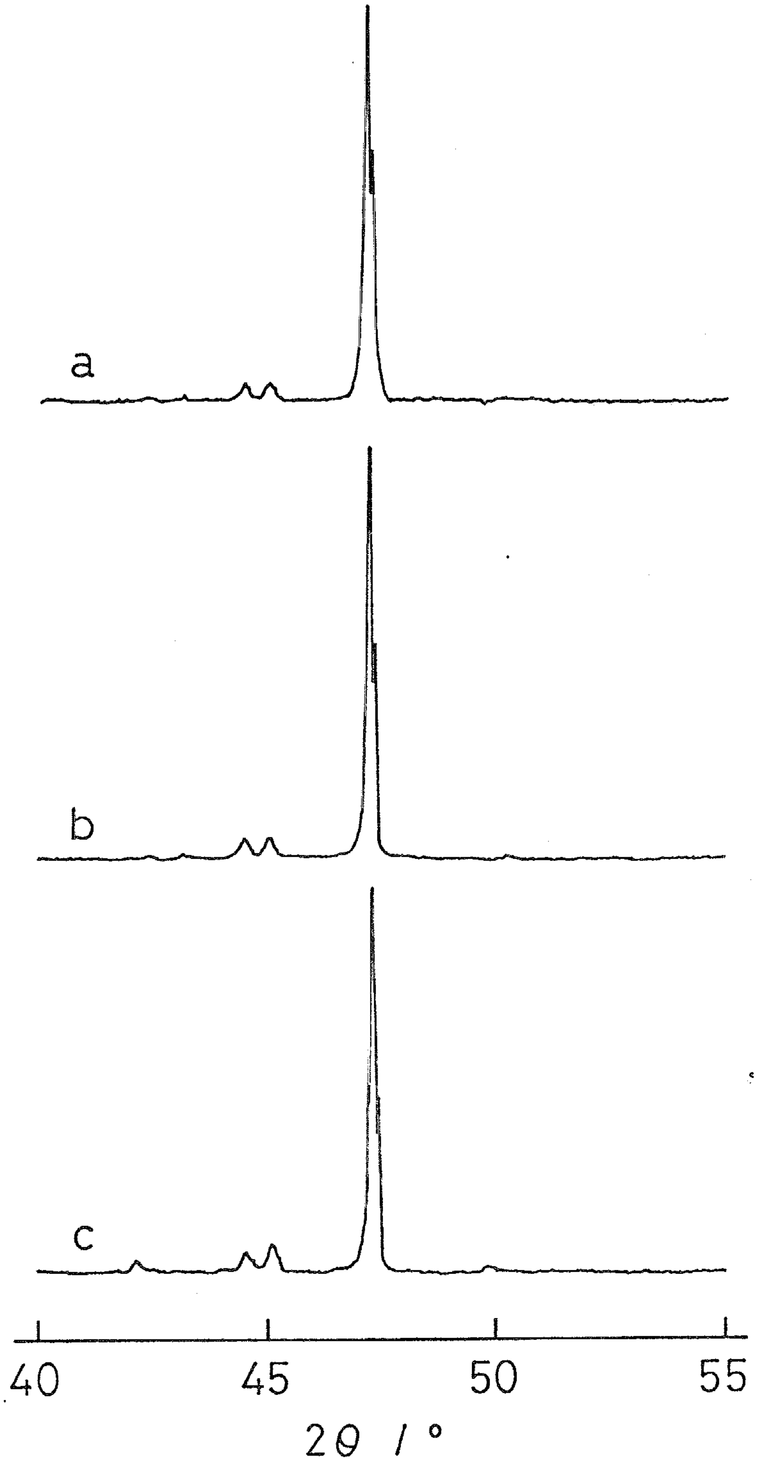


Figure 6-3 X-ray diffraction patterns of the mixtures of silicon and copper halides heated at 723 K for 1 h. Copper(I) halides are chloride (a), bromide (b) and iodide (c).

The fact that no peaks due to copper(I) bromide at 2θ= 45.1 and 53.2 were observed (Fig. 6-3b), indicates that all of copper(I) bromide had reacted. The diffraction peaks due to copper at 2θ= 43.3 and 50.4 appeared only from the sample using copper(I) bromide as the catalyst. The diffraction peaks of copper(I) iodide at 2θ= 41.6 and 49.3 were observed as shown in Fig. 6-3c. Since the diffraction peak of copper(I) chloride appeared at the same diffraction angle as that of silicon, the amount of copper(I) chloride in the system can not be known.

Weber et al. reported that copper(I) chloride reacts with silicon to form Cu_3Si and $SiCl_4$ and subsequently reacts with Cu_3Si to form Cu and $SiCl_4$ [3].

$$Si + CuCl \longrightarrow Cu_3Si + SiCl_4$$

$$Cu_3Si + CuCl \longrightarrow \longrightarrow Cu + SiCl_4$$

The fact that copper(I) iodide remained after the pretreatment at 723 K and the formation of metallic copper only after pretreating the silicon-copper(I) bromide mixture at 723 K suggest that the extent of copper(I) halide deposition on the silicon surface may change in the order CuCl > CuBr > CuI since the vapor pressure of copper(I) halide is in this order at 723 K [3], and that the extent of formation of Cu_3Si upon the reaction of silicon and copper(I) halide may be in the order CuI > CuBr > CuCl. These explain why copper(I) bromide reacted with silicon most easily among copper(I) halides.

In no case, there was any indication of formation of Si-Cu intermetallic compounds upon the pretreatment of the silicon-copper(I) halides mixtures at low temperature (< 603 K).

6-5 Observation of Silicon Surface after the Reaction

In order to examine the surface state of silicon during the reaction with methanol, the silicon surface was examined by SEM.

6-5-1 Reaction after the Pretreatment at 723 K

The morphology of the silicon-copper(I) halide mixtures partially reacted with methanol after the mixtures pretreated at 723 K was examined. Figure 6-4 shows the SEM images of the mixtures of 10% silicon conversion after the reaction at 513 K and the magnified SEM images of silicon grains. In the cases of copper(I) bromide and iodide, silicon reacted with methanol at the large area covered with the small particles as shown in Figs. 6-4(b-2) and (c-2). The morphology of the reacting silicon grain using copper(I) bromide and iodide was very different from that using copper(I) chloride. Upon the reaction of silicon and methanol catalyzed by copper(I) chloride, a few pits were observed on the surface of the silicon grain as shown in Fig. 4-4(a-2). The reacting area was larger than that using copper(I) chloride and was in the order CuBr > CuI > CuCl as shown in Figs. 6-4(a,b,c-1). This order was the same as that of the rate of formation of methoxysilanes, showing that a large reacting area gives a high reaction rate. As shown in Chapter 2, silicon reacts with methanol around the area where Cu_3Si patches are located. Therefore, the large area of Cu_3Si patches formed upon the reaction of silicon and copper(I) bromide or iodide compared

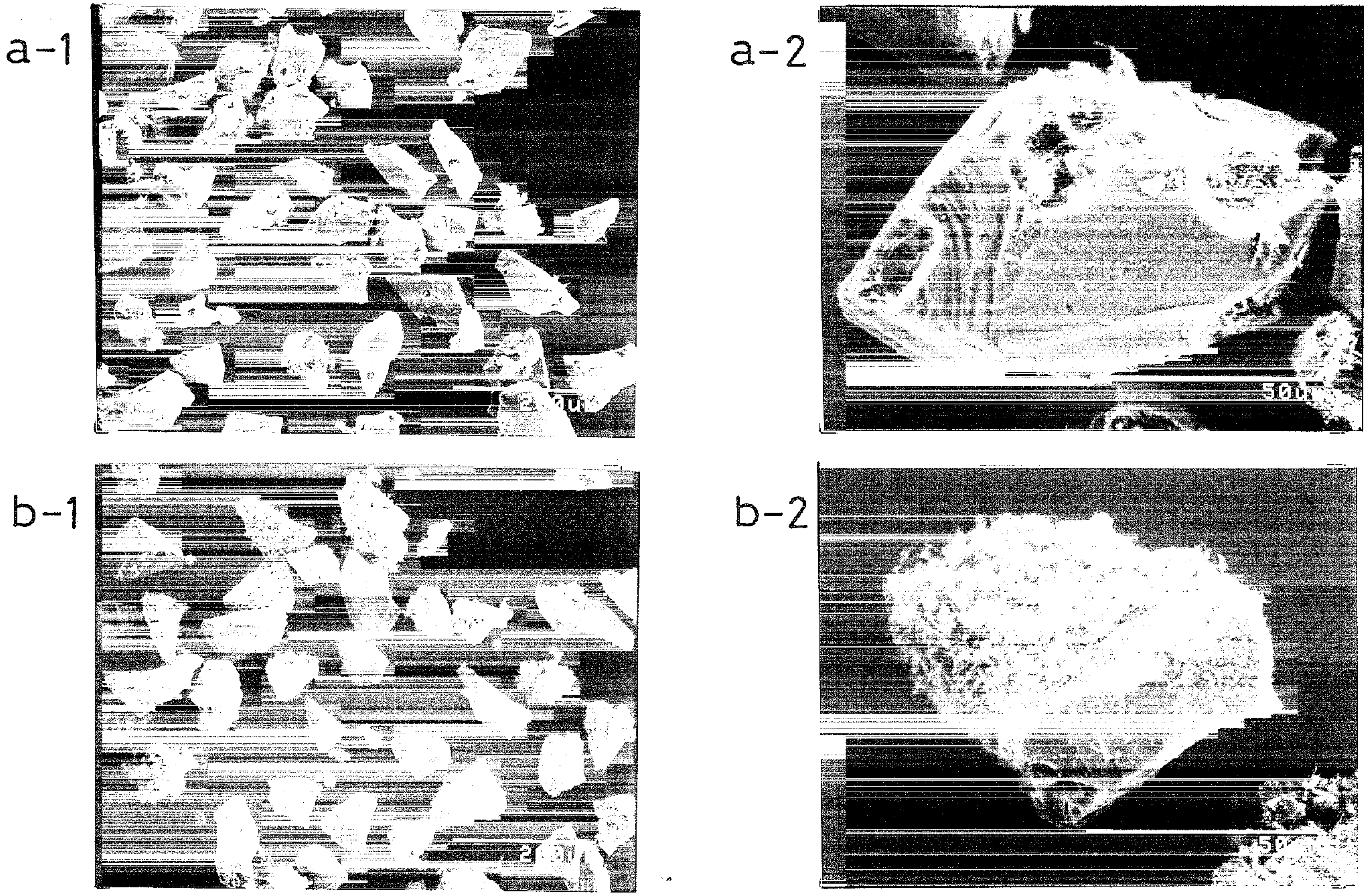


Figure 6-4 Morphology of the reacted mixtures of 10% of silicon conversion after the pretreatment at 723 K.
Methanol pressure = 56 kPa.
Catalyst were copper(I) chloride (a), bromide (b), and iodide (c).
Micrographs (a,b,c-1) and (a,b,c-2) were taken at 120 and 780 magnifications, respectively.

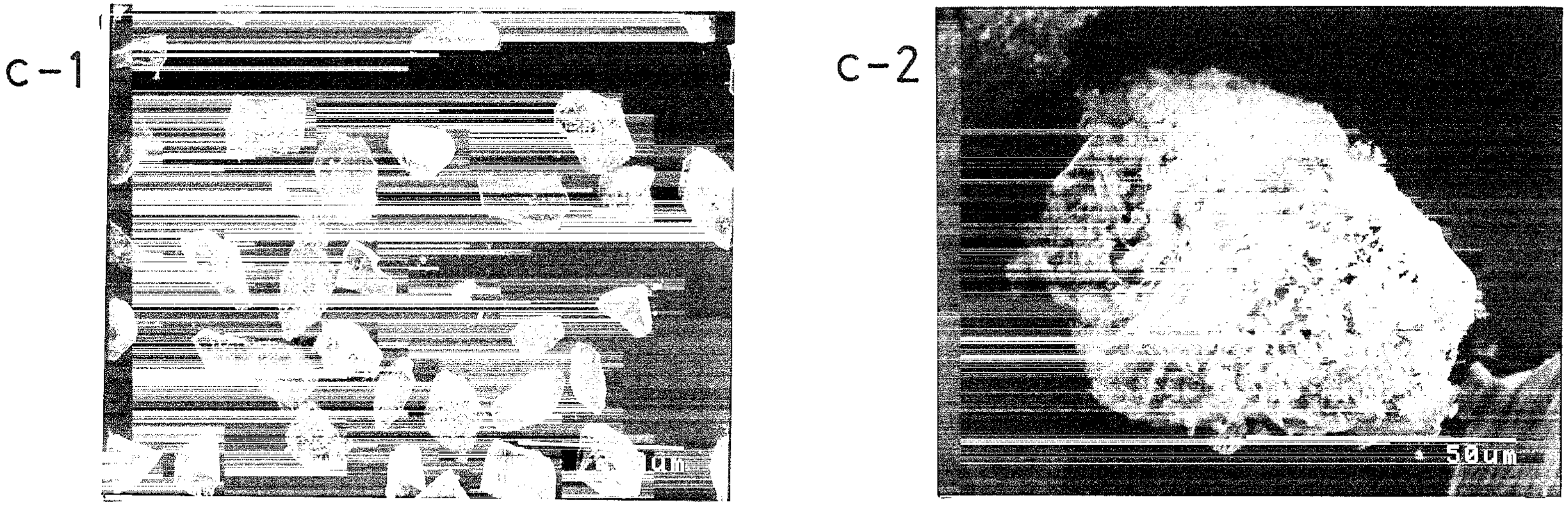


Figure 6-4 Continued.

with the case of copper(I) chloride may be the reason for the higher reaction rate.

6-5-2 Reaction after the Pretreatment at 493 K

The change in morphology of reacting silicon after the pretreatment at 493 K with the kind of the halide ion was examined. No apparent change was observed by heating silicon grains with copper(I) chloride and bromide at 493 K. This result was different from that in the case of the 723 K-pretreatment. Figure 6-5 shows the SEM images of the samples at 2% of silicon conversion, when the catalysts were copper(I) chloride and bromide. Figures 6-5(a-2) and (b-2) are the magnified images of the silicon grains in Figs. 6-5(a-1) and (b-1), respectively. There were many pits (< 1 μm), whose size was much smaller than those found on the surface after the reaction following pretreatment of the silicon - copper(I) bromide mixture at 723 K as shown in Figs. 6-5(b-2). The morphology of the reacting silicon using copper(I) bromide was similar to that using copper(I) chloride. In the case of copper(I) chloride, pits were observed on all the silicon grains (Fig. 6-5(a-1)). However, when copper(I) bromide was used, a few silicon grains did not have pits on the silicon surface (Fig. 6-5(b-1)). The number of pits of the surface using copper(I) chloride was larger than that using the bromide. This result indicates that copper(I) chloride gives a larger number of the reactive sites than the bromide.

The formation of Cu-Si intermetallic compounds in the mixtures of silicon and copper(I) bromide as well as the chloride

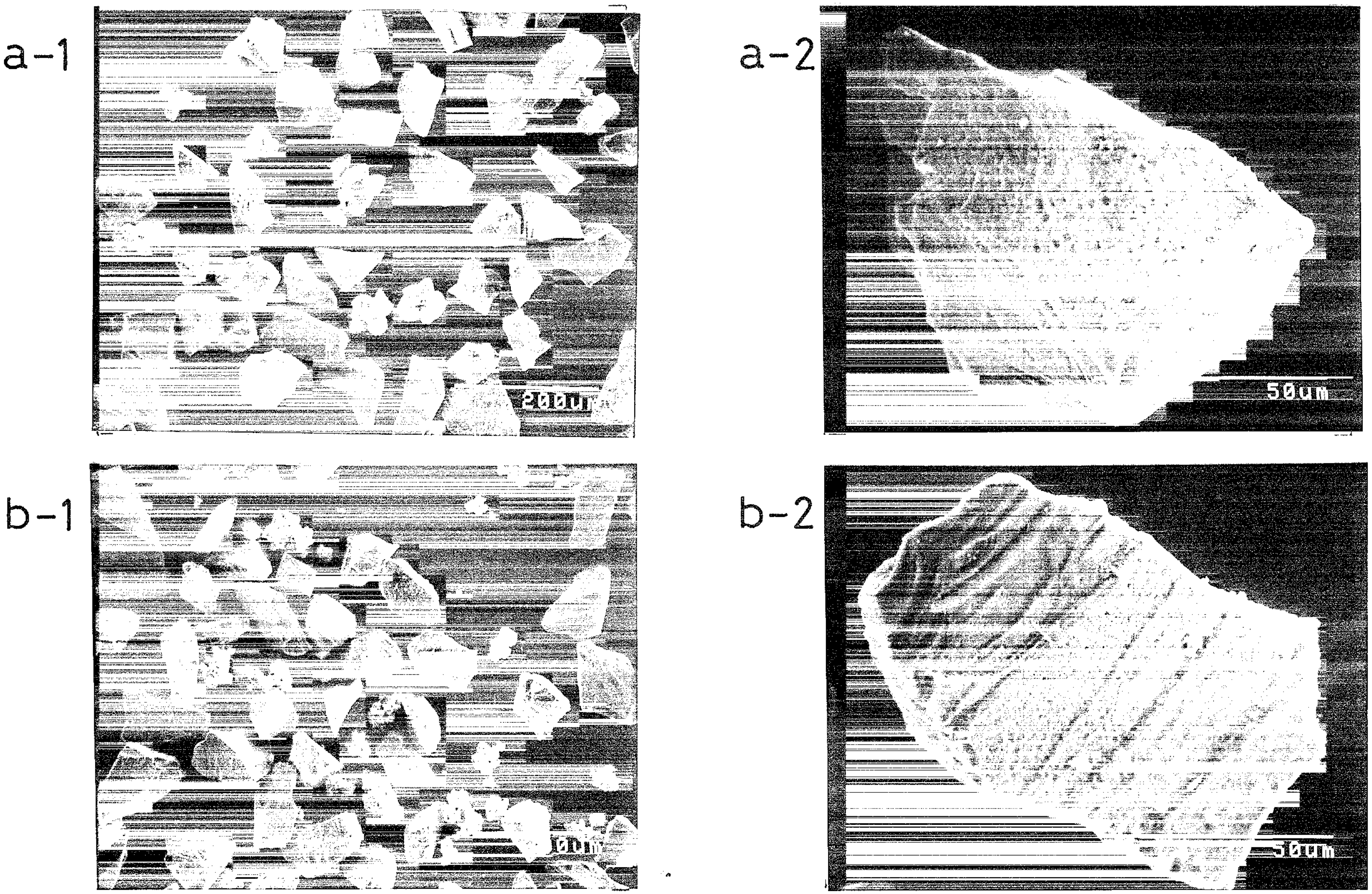


Figure 6-5 Morphology of the reacted mixtures of 2% of silicon conversion after the pretreatment at 498 K.
Methnol pressure = 24 kPa.
Catalyst were copper(I) chloride (a) and bromide (b).
Micrographs (a,b,c-1) and (a,b,c-2) were taken at 120 and 780 magnifications, respectively.

was not confirmed by XRD. However, pits were observed on the surface as shown in Fig. 6-5b. This indicates that the Si-Cu intermetallic compound was formed at the pretreatment stage and that the size of the alloy is very small.

Copper(I) chloride transferred onto the silicon surface only by its vapor does not catalyze the silicon-methanol reaction as described in Chapter 2. The use of copper(I) bromide resulted in smaller number of pits on the silicon surface as compared with the use of the chloride. These suggest that copper(I) halide migrates from the contact points of silicon and catalyst grains over the silicon surface and that the amount of the migrating copper(I) halide at 513 K is in the order CuCl > CuBr > CuI. No formation of pits using copper(I) iodide is probably caused by little amount of migration of copper(I) iodide on the silicon surface.

6-6 Kinetics of Methoxysilanes Formation

A kinetic study of silicon-methanol reaction was made to discuss the reactivity of silicon with methanol per reactive site on the silicon surface when the three copper(I) halides were used. Since the number of reactive sites changes with reaction time, a pressure-jump method is used to determine the reaction order with respect to methanol as described in Chapter 3. The activation energy was determined by jumping the reaction temperature during the reaction. Table 6-1 shows the reaction order and the apparent activation energy after high- (723 K) and low-temperature (493 K) pretreatment when copper(I) halides were

Table 6-1 The reaction order with respect to methanol and the activation energy with pretreating at various temperatures.

Pretreatment temperature	723 K		513 K	
	reaction order[a)]	E_a[b)]	reaction order[a)]	E_a[b)]
CuCl	1.4±0.1	24±2	1.0±0.2	88±8
CuBr	1.4±0.1	24±2	1.3±0.1	76±8
CuI	1.4±0.1	24±2	–	–

a) At 16 kPa of methanol pressure.

b) Activation energy (kJ mol^{-1}).

used as catalysts.

6-6-1 Reaction Order with Respect to Methanol Pressure

The estimated reaction order are 1.0 ± 0.2 and 1.3 ± 0.1 after the pretreatment at low temperature in the reaction using copper(I) chloride and bromide, respectively, and 1.4 ± 0.2 after the pretreatment at high temperature in the reaction using each of three catalysts. No change of the reaction order with the halide ion indicates that the nature of the reactive site does not change with the kind of the halide ion.

6-6-2 Apparent Activation Energy

The apparent activation energy was determined to be 44 and 88 kJ mol^{-1} in the reaction at 59 kPa of methanol pressure after the pretreatment of the mixture of silicon and copper(I) chloride at 723 and 493 K, respectively (Chapter 3). Since the rate of the reaction using copper(I) bromide or iodide rapidly increased and decreased at 59 kPa of methanol pressure (Fig. 6-1), it was difficult to determine the activation energy under these reaction conditions. Therefore, the activation energy was determined at 16 kPa of methanol pressure when the rate change was moderate.

The apparent activation energy at 24 kPa of methanol pressure was different from that at 59 kPa, when the pretreatment of the silicon - copper(I) chloride mixture was done at 723 K. Thus, the activation energy was 24 kJ mol^{-1} at 16 kPa of methanol pressure against 44 kJ mol^{-1} at 59 kPa. The reason of the dependence of methanol pressure on the activation energy is not clear yet.

In the reaction using each of the three catalysts after the pretreatment at 723 K, the activation energy was 24 kJ mol^{-1} at 16 kPa of the methanol pressure. When the pretreatment temperature was 513 K, the activation energy using copper(I) bromide was similar to that using copper(I) chloride. The activation energy did not depend on the catalyst after the pretreatment at the same temperature. This result indicates that the nature of reactive sites does not change with the kind of the halide ion and suggests that the reactive sites do not contain the halide ions.

6-7 Conclusions

The reactions of silicon with methanol were carried out using copper(I) bromide and iodide as catalysts to be compared with the reaction catalyzed by copper(I) chloride.

When the pretreatment was done at high (> 603 K) temperature, the formation rate of methoxysilanes depended on the halide ion, the order of the rate being CuBr > CuI > CuCl. Methanol reacted with silicon only the vicinity of Cu_3Si patches on the silicon surface which was formed during the pretreatment. Thus, since silicon grains pretreated with copper(I) bromide and iodide were widely covered with Cu_3Si patches, the formation rate was high in the beginning of the reaction. The selectivity for trimethoxysilane was low (40-90%).

On the other hand, when the pretreatment was carried out at low temperature (513 K), the reaction using copper(I) bromide occurred to give high selectivity for trimethoxysilane of about

100%. Methanol did not react with silicon upon using copper(I) iodide. The reaction rate using copper(I) bromide was slower than that using the chloride. The number of pits formed on the silicon surface upon the reaction with methanol using copper(I) chloride was larger than that using copper(I) bromide. This indicates that copper(I) chloride gives a larger number of reactive sites than the bromide. Copper(I) chloride and bromide may be transported onto the silicon surface by their migration from the contact points of silicon and catalyst grains. A large amount of the reactive sites in the reaction catalyzed by copper(I) chloride is due to easier migration of copper(I) chloride over the silicon surface. Since no copper(I) iodide may migrate on the silicon surface, the reaction did not occur.

When the pretreatment was done at the same temperature, the reaction order with respect to methanol pressure and the activation energy did not change with the kind of the halide ion. This shows that the nature of reactive sites does not change with the halide ion, though it depends on the pretreatment temperature.

References

1) Japan Tokkyo Kokai Koho, 55-58928 (1980); 55-76891 (1980); 57-18094 (1982); 62-96433 (1987).

2) E. Suzuki and Y. Ono, J. Catal., 125 (1990) 390.

3) G. Weber, D. Viale, H. Souha, and B. Gillot, C.R. Acad. Sci. Paris, Serie II, 1155 (1988).

Chapter 7 General Conclusions

In this work, the reaction of metallic silicon with methanol to form tri- and tetramethoxysilane using copper(I) chloride catalyst in a fixed-bed flow reactor was studied. The mixture of silicon grains and copper(I) chloride grains was heated under a helium stream and then the methanol vapor was fed to the reactor.

In Chapter 2, the effects of the pretreatment conditions on the rate of formation of methoxysilanes and the selectivity for trimethoxysilane were examined. The rate and the selectivity greatly depended on the pretreatment temperature.

When the pretreatment temperature was above 623 K, the selectivity was 60-90%. The XRD and EPMA studies revealed that Cu_3Si phase was formed at the pretreatment stage by the reaction of silicon and copper(I) chloride and are scattered on the silicon surface. Pits are formed upon the reaction of methanol on the surface of the reacting silicon. The number of pits did not change with reaction time and was close to that of Cu_3Si patches formed during the pretreating period, indicating that silicon was consumed only at the vicinity of Cu_3Si patches.

On the other hand, when the pretreatment was done below 603 K, the selectivity was almost 100%. When the reaction was carried out at 56 kPa of methanol pressure at 513 K after the mixture was pretreated at 513 K for 1 h, the silicon conversion reached to 88% in 5 h, the selectivity for trimethoxysilane being 98%. The rate of silicon consumption was higher than that in the case of high-temperature pretreatment. The number of pits increased with increasing reaction time and was much larger than that in the reaction after the higher-temperature pretreatment. The formation of Cu-Si intermetallic compounds was confirmed by XRD. The small pits were observed on the surface of the reacting silicon, indicating that the small size of the Cu-Si intermetallic compound is formed. High silicon conversion (about 90%) with high selectivity (almost 100%) for trimethoxysilane was obtained in the reaction after low-temperature pretreatment.

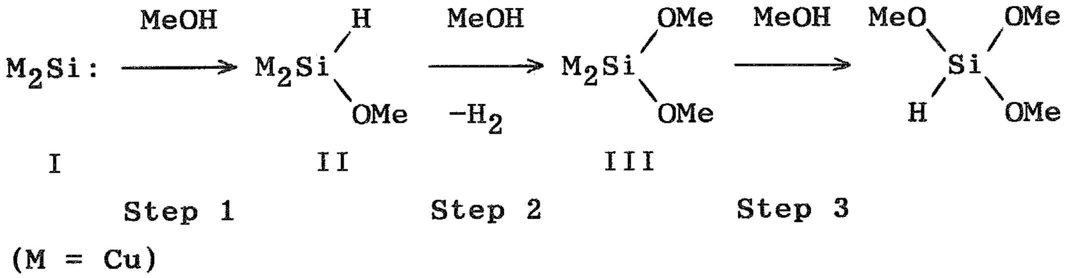
In Chapter 3, the kinetics of the reaction was examined. The kinetics depended on the pretreatment temperature. When the mixture of silicon and copper(I) chloride was pretreated at 723 K, the reaction rate decreased with decreasing the methanol pressure and a short induction period was observed at very low pressure of methanol. When the pretreatment temperature was 513 K, the reaction rate was low and a long induction period was observed at low pressure of methanol. The induction period greatly changed with the pressure. In both cases of the high- and low-temperature pretreatment, the dependence of the methanol pressure on the induction period indicate that methanol participates in the formation of reactive site.

When the pretreatment temperature was 513 K, the number of pits formed upon the reaction of silicon with methanol increased with increasing methanol pressure. The dependence of methanol pressure on the number of pits means that higher methanol pressure gives larger number of reactive site. In the reaction after the pretreatment at 723 K, the number of pits did not change with methanol pressure. This is in conformity with the conclusion that pits were formed only around the Cu_3Si patches. The number of reactive site is probably proportional to the area of the wall of pits. The area of the pit wall was large at a high methanol pressure. This indicates that the large reactive area is formed at the high pressure of methanol.

The reaction order with respect to methanol pressure and the apparent activation energy were determined by the pressure- and temperature-jump method, respectively. The reaction order was 1.4 and 1.0, when the pretreatment temperature was 723 K and 493 K, respectively. The dependence of the methanol pressure on the reaction rate shows that the diffusion of silicon atoms to reactive sites is not a rate-determining step. The activation energy was estimated to be 44 and 88 kJ mol^{-1} in the case of the pretreatment at 723 K and 498 K, respectively. The dependence of the reaction order and the activation energy on the pretreatment temperature indicates that the nature of reactive sites changes with the pretreatment temperature.

In Chapter 4, the reaction pathway in the silicon-methanol reaction was determined. When the mixture of silicon and copper(I) chloride was pretreated at 723 K, addition of a small amount of thiophene to the methanol feed enhanced the selectivity for trimethoxysilane. The formation of metallic copper was observed formed upon the reaction of silicon with methanol. It was confirmed that metallic copper catalyzes the reaction of trimethoxysilane with methanol to give tetramethoxysilane, the tetramethoxysilane formation being completely poisoned by thiophene. These facts indicate that trimethoxysilane is an exclusive primary product and that the formation of tetramethoxysilane is caused by the reaction of trimethoxysilane with methanol by the action of metallic copper formed during the reaction. Alkyl chloride was also an effective additive for improving the selectivity for trimethoxysilane. Alkyl chloride was a poison for the catalytic action of metallic copper.

On the basis of the exclusive formation of trimethoxysilane, the intermediacy of surface silylenoid ($M_2Si:$) was proposed.



The surface silylenoid (I) formed during the silicon-methanol reaction reacts with methanol to give monomethoxysilicon species (II). Dimethoxysilicon species (III) was formed by the reaction of methanol with the species (II) and undergoes an attack from another methanol molecule with the simultaneous cleavage of two Si-Cu bonds to form trimethoxysilane. Silicon atoms migrate from the bulk to the surface to reform the silylenoid (I).

In Chapter 5, on the basis of the speculated mechanism for trimethoxysilane formation, the reaction of silicon with methanol was carried out in the presence of alkenes to trap the silylenoid intermediate (I). When methanol were fed with butadiene, ethylene and propylene to the silicon-copper(I) chloride mixture, 1-methoxysilacyclopent-3-ene, ethyldimethoxysilane and propyldimethoxysilane were formed, respectively, trimethoxysilane being a major product. This suggests that the surface silylenoid is the intermediate in the silicon-methanol reaction. In the case of the reaction of silicon with phenol instead of methanol, the same type of reaction occurred. Silicon reacted with phenol and ethylene to give ethyldiphenoxysilane besides triphenoxysilane. This suggests the intermediacy of silylene species in the silicon-phenol reaction. The use of allyl compounds instead of simple alkenes gave higher selectivity for organosilanes. The feeding of allyl propyl ether with methanol resulted in a 38% selectivity for allyldimethoxysilane. Diallyl ether and allyl methyl sulfide also gave allyldimethoxysilanes.

In Chapter 6, in order to examine the role of chloride ion of copper(I) chloride catalyst in the formation of reactive site, the reactions of silicon with methanol using copper(I) bromide and iodide as catalysts were carried out. When the silicon-catalyst mixture was pretreated at 723 K, the selectivity for trimethoxysilane was low in every case. Copper(I) chloride and bromide gave about 80% of silicon conversion, however, using copper(I) iodide resulted in 42% of silicon conversion. The rate increase in the initial stage using copper(I) bromide or iodide was higher than that using copper(I) chloride. Copper(I) halide may be transferred onto silicon surface and then react with silicon to form Cu-Si alloy during the pretreatment. Copper(I) bromide and iodide reacted with silicon to form the large areas of the alloy on the silicon surface during the pretreatment, suggesting that higher reaction rate at the beginning of the reaction with the two catalysts may be due to the larger area of Cu_3Si on the silicon surface.

When the pretreatment temperature was 513 K, the reaction using copper(I) chloride or bromide occurred, the selectivity being 99%. However, no reaction occurred, when copper(I) iodide was used. The use of copper(I) bromide resulted in low reaction rate and low silicon conversion as compared with the reaction using copper(I) chloride, indicating that the formation rate of reactive sites is lower than that using copper(I) chloride. At 513 K of pretreatment temperature, copper(I) chloride transported onto the silicon surface only by its vapor did not catalyze the silicon-methanol reaction. This suggests that copper(I) chloride is spread from the contact points of silicon and copper(I) chloride grains over the silicon surface. The low reaction rate using copper(I) bromide and no formation of methoxysilanes using copper(I) iodide is probably caused by the difficulty of the spread of copper(I) bromide and iodide over the silicon surface. In both cases of high- and low-temperature pretreatment, the reaction order with respect to methanol pressure and the apparent activation energy did not depend on the halide ion, showing that the nature of reactive sites does not change with the kind of the halide ion after the same pretreatment conditions.

The following problems remains. 1) The reactive sites was formed after the methanol vapor was fed to the silicon-catalyst mixture. This indicates that methanol participates in the formation of reactive sites. However, it is not clear how methanol is involved in the formation of reactive sites. 2) When the silicon-copper(I) chloride mixture was pretreated at 513 K, a large number of pits were formed on the silicon surface upon the silicon-methanol reaction. When copper(I) chloride was placed at upstream of silicon grains, the reaction did not occur, indicating that a long-range vapor-phase transport of copper(I) chloride onto the silicon surface does not occur at 513 K. In the case of the use of copper(I) chloride grains mixed with silicon grains, the reactive sites were formed. The mechanism of the transport of copper(I) chloride onto the silicon surface at lower temperatures is not clear yet. 3) When the reactions of silicon with methanol in the presence of alkenes were carried out, alkyldimethoxysilanes were formed. Allyl compounds instead of alkenes resulted in the high selectivity for allyldimethoxysilane. The reason why organosilane was obtained with a high selectivity only in the case of the reactions of allyl compounds has not been clarified yet. It will be examined what kind of alkene give high selectivity for organosilane.

There are some future possibilities in the direct synthesis. 1) The reactions of silicon, methanol and alkenes were carried out using atmospheric fixed-bed flow reactor. This reaction is expected as a new method of organosilane synthesis. The higher selectivity for organosilane would be obtained if the reaction is carried out at higher pressure of alkenes. A high selectivity for organosilane would be expected if a high-pressure reactor or a batch reactor was used. 2) Methyl chloride reacts with silicon to afford methylchlorosilanes. If methyl chloride and alkenes were fed, the products trapped by alkenes would be formed. There is a possibility that the reaction of silicon, methyl chloride and alkene is a new method of organosilane synthesis. Clarke et al. reported that addition of butadiene to methyl chloride gave the formation of the products trapped by butadiene in a batch flow reactor. The partial pressures of the reactants were very low (< 3 kPa), the yields of trapped products being low. It is expected that high yields of the trapped products are obtained when the reaction of silicon, methyl chloride and alkenes is carried out in the atmospheric reactor used in the silicon-methanol reaction or a high-pressure reactor.

Acknowledgment

I would like to express sincere thanks to Professor Yoshio Ono and Associate Professor Eiichi Suzuki for helpful comments, advice and discussions.

I greatly thank Dr. Toshihide Baba for suggestions and encouragement.

I wish to thank Mr. Hitoshi Hirano and Mr. Touru Ehara of Toshiba Ceramics Co., Ltd. for supplying silicon wafers.

I sincerely thank Mr. Hisahiro Sawabe and Mr. Katsuyuki Sato of Central Technical Research Laboratory of Nippon Oil Co., Ltd. for the EPMA measurements and fruitful discussions.

I sincerely thank Department of Bioengineering, Tokyo Institute of Technology for the use of SEM.

I would like to thank Morikawa and Otsuka Laboratory for the XRD measurements.

Finally, I am grateful to the members of Ono and Suzuki Laboratory for kind helps in the experiments.