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Preliminary communication

Direct synthesis of ethylmethoxysilanes by the liquid-phase reaction of silicon, methanol and ethylene

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Abstract

The liquid-phase reactions of silicon, methanol and ethylene in an autoclave gave ethylmethoxysilanes ($HSi(C_2H_5)(OCH_3)_2$ and $Si(C_2H_5)(OCH_3)_3$) besides $HSi(OCH_3)_3$ and $Si(OCH_3)_4$. The reaction conditions for obtaining a high selectivity for the ethylmethoxysilanes were examined. With the use of a high pressure of ethylene and a small amount of methanol in toluene as a solvent at 433 K, ethylmethoxysilanes were obtained in 26% selectivity at silicon conversion of 59%. The direct reaction of silicon with ethanol and ethylene gave $HSi(C_2H_5)(OC_2H_5)_2$ and $Si(C_2H_5)(OC_2H_5)_3$.

Keywords: Silylene; Alkene; Silane; Methanol; Liquid-phase reaction; Silicon

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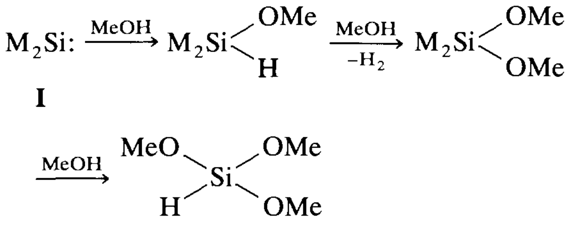
1. Introduction

The reaction of metallic silicon with methyl chloride into methylchlorosilanes is the most important reaction in the silicon industry. The drawback of this reaction is the corrosive nature of the reactant (CH_3Cl) and the products which include HCl. Therefore, the direct synthesis of organosilanes from metallic silicon without the use of halides is highly desirable.

Silicon reacts with methanol to afford $HSi(OCH_3)_3$ and $Si(OCH_3)_4$ in the presence of copper catalyst [1,2]. We have shown that $HSi(OCH_3)_3$ was selectively produced by properly selecting the pretreatment conditions of silicon–copper(I) chloride mixture and the reaction conditions [3]. Even when $Si(OCH_3)_4$ is appreciably formed, $HSi(OCH_3)_3$ is a sole primary product and $Si(OCH_3)_4$ is produced by the secondary reaction of $HSi(OCH_3)_3$ with methanol over metallic copper formed during the silicon–methanol reaction [3].

To explain the exclusive formation of $HSi(OCH_3)_3$, the intermediacy of surface silylene **I** in the formation of $HSi(OCH_3)_3$ was proposed (Eq. 1) [4].



$$\underset{\mathbf{I}}{M_2Si:} \xrightarrow{MeOH} M_2Si\begin{matrix}OMe\\H\end{matrix} \xrightarrow[-H_2]{MeOH} M_2Si\begin{matrix}OMe\\OMe\end{matrix} \xrightarrow{MeOH} \begin{matrix}MeO & & OMe\\ & Si & \\ H & & OMe\end{matrix} \qquad (1)$$

(M = Cu)

This mechanism also includes cleavage of the two Si–Cu bonds by attack of methanol in the last step.

We have reported that surface silylene **I** can be trapped by alkenes [3,4]. When methanol vapor (27 kPa) and ethylene (73 kPa) were fed to the mixture of silicon and copper(I) chloride packed in a fixed-bed reactor at 513 K, $HSi(C_2H_5)(OCH_3)_2$ (8%) was formed together with the main product $HSi(OCH_3)_3$ (92%). Based on the known chemistry of silylenes towards

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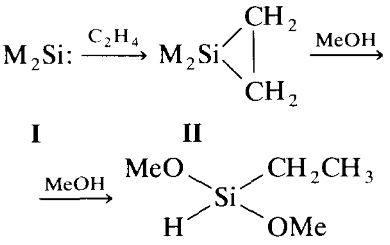
alkenes and alcohols [5–7], the following mechanism was proposed (Eq. 2):


(2)

(M = Cu)

Surface silylene **I** reacts with ethylene to form silacyclopropane species **II** on the surface. The species **II** is converted into ethylmethoxysilicon species **III** and then to $HSi(C_2H_5)(OCH_3)_2$ via methanolysis.

Allyl propyl ether showed higher trapping efficiency to produce $HSi(CH_2CH{=}CH_2)(OCH_3)_2$ in about 40% selectivity (the ratio of amount of $HSi(CH_2CH{=}CH_2)(OCH_3)_2$ to total amount of silane products) [8], the other products being alkoxysilanes. On the other hand, the selectivities for organosilanes were low in the reaction with simple alkenes. The selectivity for $HSi(C_2H_5)(OCH_3)_2$ never exceeded 10% in the reactions with ethylene under an atmospheric pressure. In this work, the liquid-phase reactions of silicon, methanol and ethylene in an autoclave were studied in order to obtain higher selectivity for organosilanes.

2. Experimental

The pulverized silicon of 99.5% purity was obtained from Soekawa Chemical Co., Ltd. and washed with a 46% HF solution to remove oxide layers. The reactions were carried out in a 50 cm^3 autoclave. In a typical experiment, the mixture of silicon (18 mmol = 500 mg) and copper(I) chloride (0.2 mmol = 20 mg), methanol (54 mmol = 2.2 cm^3), toluene (5 cm^3) and ethylene (13 atm at room temperature: about 32 mmol) were put into the autoclave, and heated at 433 K for 3 h. The products were analyzed by a gas chromatograph.

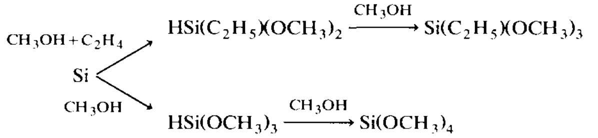
3. Results and discussion

3.1. Reaction of silicon, methanol and ethylene

3.1.1. Effect of solvents

The effect of solvents on the silicon conversion and the selectivity for ethylmethoxysilanes was examined. Silicon (18 mmol), copper(I) chloride (0.9 mmol), methanol (58 mmol), a solvent (2.4 cm^3) and ethylene (about 32 mmol) were heated at 433 K for 3 h. Table 1 summarizes the results.

When toluene was used as the solvent, the best result was observed. The selectivity for organosilanes $[HSi(C_2H_5)(OCH_3)_2 + Si(C_2H_5)(OCH_3)_3]$ was 26%, the other products being $HSi(OCH_3)_3$ (4%) and $Si(OCH_3)_4$ (70%). The silicon conversion calculated as the sum of the yields of the four products was 59%. The main organosilane was $Si(C_2H_5)(OCH_3)_3$. In the vapor phase reaction, $Si(C_2H_5)(OCH_3)_3$ was not found in the products. It is plausible to assume that $HSi(C_2H_5)(OCH_3)_2$ is a sole primary organosilane product and that $Si(C_2H_5)(OCH_3)_3$ is formed by the secondary reaction of $HSi(C_2H_5)(OCH_3)_2$ with methanol over metallic copper and/or the wall of the autoclave, since we have found that $Si(OCH_3)_4$ is formed by the secondary reaction of $HSi(OCH_3)_3$ and methanol over metallic copper [4]. The reaction pathway can be expressed by Eqs. 3 and 4.


(3)
(4)

Longer residence time of the primary products, $HSi(C_2H_5)(OCH_3)_2$ and $HSi(OCH_3)_3$, in the liquid-

Table 1
Effect of solvent on the reaction of silicon, methanol and ethylene

Solvent	Silicon conv. [a]/%	Selectivity/% EDMoS [b]	ETMoS [c]	Organosilanes [d]	TMoS [e]	QMoS [f]
Toluene	59	4	22	26	4	70
o-Xylene	49	5	20	25	6	69
Heptane	42	6	9	15	24	61
DEE [g]	46	1	5	6	8	86
Dioxane	12	0	12	12	11	77
DMF [h]	27	0	1	1	11	88
none	47	1	6	7	12	82

[a] Silicon conversion for 3 h. [b] $HSi(C_2H_5)(OCH_3)_2$, [c] $Si(C_2H_5)(OCH_3)_3$.
[d] $HSi(C_2H_5)(OCH_3)_2 + Si(C_2H_5)(OCH_3)_3$, [e] $HSi(OCH_3)_3$. [f] $Si(OCH_3)_4$.
[g] diethyl ether, [h] dimethylformamide.

Reaction conditions: solvent = 2.4 cm^3, methanol = 2.4 cm^3, silicon = 500 mg, ethylene = ca. 32 mmol, copper(I) chloride = 90 mg, reaction temperature = 433 K.

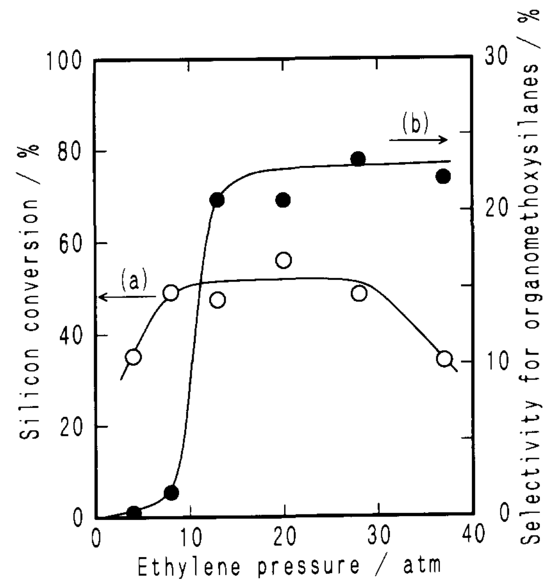


Fig. 1. Effect of ethylene pressure on the silicon conversion (a) and the selectivity for organomethoxysilanes (b) in the reaction of silicon, methanol and ethylene. Reaction conditions: silicon = 500 mg, copper(I) chloride = 20 mg, methanol = 2.2 cm^3 (54 mmol), toluene = 5 cm^3, reaction temperature = 433 K, reaction time = 3 h.

phase reaction tends to the increase of the final products, $Si(C_2H_5)(OCH_3)_3$ and $Si(OCH_3)_4$. o-Xylene was also a good solvent. Thus, the selectivity for the organosilanes was 25%, the silicon conversion being 49%. The selectivity for organoalkoxysilanes in the reactions in toluene or xylene was much higher than that (< 10%) in the vapor-phase reactions.

In the reaction in diethyl ether, dioxane, or dimethylformamide, the selectivity of the organosilanes was very low (< 12%) and the silicon conversion was also low, probably because adsorption of the polar molecules on the Cu–Si alloy surface prevents the formation of silylene intermediate on the surface. Without a solvent, the selectivity for the organosilanes was low (6.5%).

3.1.2. Effect of the ethylene pressure

The effect of the ethylene pressure on the silicon conversion and the selectivity for organomethoxysilanes is shown in Fig. 1, where the pressures are expressed as those measured at room temperature. Silicon (18 mmol), copper(I) chloride (0.2 mmol), methanol (54 mmol), toluene (5 cm^3) and ethylene (4–37 atm) were heated at 433 K for 3 h. The selectivity for organosilanes increased with increasing ethylene pressure and reached an almost constant value of 22% above 13 atm ethylene pressure. The silicon conversion was almost constant (50%) between 8 and 27 atm ethylene pressure. At 13 atm of the ethylene pressure, organosilanes were obtained with a yield of 11%, the products consisted of 12% $HSi(C_2H_5)(OCH_3)_2$, 9% $Si(C_2H_5)OCH_3)_3$, 24% $HSi(OCH_3)_3$ and 55% $Si(OCH_3)_4$.

3.1.3. Effect of the amount of methanol

Fig. 2 shows the effects of the amount of methanol on the silicon conversion and the selectivity for organomethoxysilanes in the fixed amount of toluene (5 cm^3). The silicon conversion increased with increasing amounts of methanol. The selectivity for organosilanes was higher at lower concentrations of methanol. When the methanol concentration was 18 mmol, the selectivity for organosilanes reached a high value (36%) and a small amount of diethylmethoxysilane (about 1%) was formed. Under this condition, the ratio of $HSi(C_2H_5)(OCH_3)_2$ to total amount of organosilanes was high (75%), the selectivity for $HSi(OCH_3)_3$ (32%) being the same as that for $Si(OCH_3)_4$. A low concentration of methanol gave a high selectivity for hydrosilanes ($HSi(C_2H_5)(OCH_3)_2$ and $HSi(OCH_3)_3$). The rates of the secondary reactions, hydrosilanes with methanol, are probably low at a low concentration of methanol.

3.1.4. Time course of the reaction

Silicon (18 mmol), copper(I) chloride, methanol (54 mmol), toluene (5 cm^3) and ethylene (13 atm at room temperature: about 32 mmol) were heated at 433 K. Fig. 3 shows changes in silicon conversion and selectivity for organomethoxysilanes with reaction time. The silicon conversion increased with time and reached

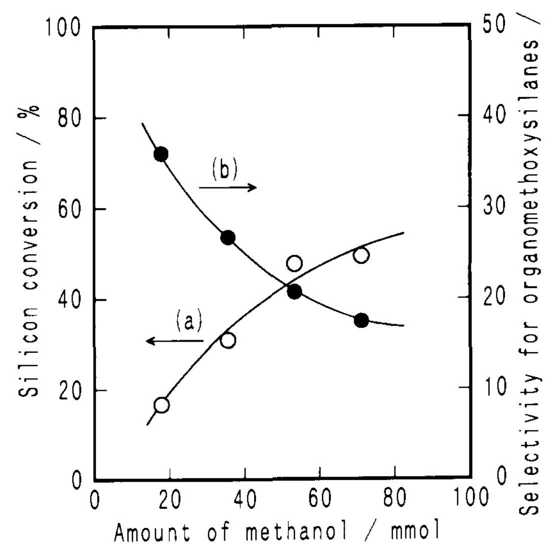


Fig. 2. Effect of amount of methanol on the silicon conversion (a) and the selectivity for organomethoxysilanes (b) in the reaction of silicon, methanol and ethylene. Reaction conditions: silicon = 500 mg, copper(I) chloride = 20 mg, ethylene = 13 atm (ca. 32 mmol), toluene = 5 cm^3, reaction temperature = 433 K, reaction time 3 h.

about 80% based on silicon at 7 h. The selectivity for organomethoxysilanes was constant at about 18% during the reaction. The selectivities for $HSi(C_2H_5)(OCH_3)_2$ and $HSi(OCH_3)_3$ were 16% and 53% at 2 h and 9% and 6% at 8 h, respectively. The selectivity for hydrosilanes ($HSi(C_2H_5)(OCH_3)_2$ and $HSi(OCH_3)_3$) decreased with time, indicating that $HSi(C_2H_5)(OCH_3)_2$ and $HSi(OCH_3)_3$, which are formed in the beginning of the reaction, are consumed to form $Si(C_2H_5)(OCH_3)_3$ and $Si(OCH_3)_4$, respectively, at the later stage by secondary reactions.

3.1.5. Effect of the reaction temperature

The reactions were carried out at various temperatures. The results are shown in Fig. 4. The reaction did not occur below 393 K. The silicon conversion increased with increasing reaction temperature. The highest selectivity for organomethoxysilanes was obtained at 433 K. The selectivity decreased with increasing temperature up to 433 K. Thus, the yield of organosilanes based on silicon was almost constant (10%) above 433 K. At a reaction temperature of 433 K, the selectivities for $HSi(C_2H_5)(OCH_3)_2$, $Si(C_2H_5)(OCH_3)_3$, $HSi(OCH_3)_3$ and $Si(OCH_3)_4$ were 12%, 9%, 24% and 55%, respectively.

3.2. Reaction of silicon, ethanol and ethylene

The reaction using ethanol instead of methanol was carried out. The products were $HSi(C_2H_5)(OC_2H_5)_2$, $Si(C_2H_5)(OC_2H_5)_3$, $HSi(OC_2H_5)_3$ and $Si(OC_2H_5)_4$. At 433 K, the yield of ethoxysilanes was very low (22%) over 3 h. We have shown that the rate of the reaction of silicon with ethanol is slower than that with methanol [9]. To obtain a higher silicon conversion, the reaction temperature was raised. When the reaction temperature was 453 K, the total yield of ethoxysilanes reached 90% in 5 h, the product distribution being 4% of $HSi(C_2H_5)(OC_2H_5)_2$, 6% of $Si(C_2H_5)(OC_2H_5)_3$, 28% of $HSi(OC_2H_5)_3$ and 62% of $Si(OC_2H_5)_4$. The selectivity for organoethoxysilanes was low (10%) at higher reaction temperatures.

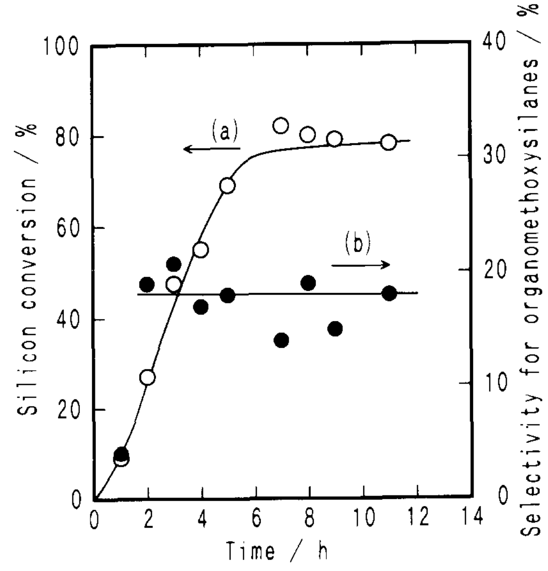


Fig. 3. Changes in the silicon conversion (a) and the selectivity for organomethoxysilanes (b) with reaction time in the reaction of silicon, methanol and ethylene. Reaction conditions: silicon = 500 mg, copper(I) chloride = 20 mg, methanol = 2.2 cm^3 (54 mmol), ethylene = 13 atm (ca. 32 mmol), toluene = 5 cm^3, reaction temperature = 433 K.

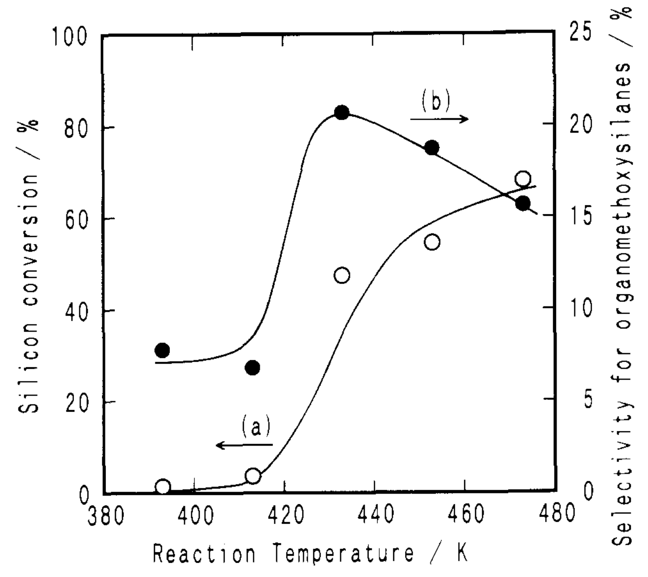


Fig. 4. Changes in the total yield of methoxysilanes (a) and the selectivity for organomethoxysilanes (b) with reaction temperature in the reaction of silicon, methanol and ethylene. Reaction conditions: silicon = 500 mg, copper(I) chloride = 20 mg, methanol = 2.2 cm^3 (54 mmol), ethylene = 13 atm (ca. 32 mmol), toluene = 5 cm^3, reaction time = 3 h.

4. Conclusions

The direct reaction of silicon with methanol and ethylene in an autoclave results in the formation of organosilanes, $HSi(C_2H_5)(OCH_3)_2$ and $Si(C_2H_5)(OCH_3)_3$, besides $HSi(OCH_3)_3$ and $Si(OCH_3)_4$. The selectivity for the organosilanes (26%) was higher than that (8%) obtained in the vapor-phase reactions. The use of a high pressure of ethylene and a low concentration of methanol in toluene or o-xylene results in higher selectivities. When ethanol was used instead of methanol, $HSi(C_2H_5)(OC_2H_5)_2$ and $Si(C_2H_5)(OC_2H_5)_3$ were formed besides $HSi(OC_2H_5)_3$ and $Si(OC_2H_5)_4$, but the selectivity for organoethoxysilanes was low (10%).

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