

# Direct synthesis of methyl dimethoxysilane from metallic silicon and methanol using copper(I) chloride catalyst

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## Abstract

When the reaction of metallic silicon with methanol in the presence of a small amount of thiophene was carried out at 653 K, methyl dimethoxysilane was formed together with trimethoxysilane and tetramethoxysilane, the selectivity for methyl dimethoxysilane being 22%. Further adding a small amount of trioxane, trimer of formaldehyde, to the reaction system improved the selectivity for methyl dimethoxysilane. This indicates that formaldehyde formed by the dehydrogenation of methanol takes part in methyl dimethoxysilane formation. The reaction of silicon with ethanol also gave a 14% selectivity of ethyl diethoxysilane with a 43% silicon conversion. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Direct synthesis; Organosilane; Metallic silicon; Methanol; Copper catalyst

## 1. Introduction

Methylchlorosilanes are produced directly from metallic silicon by the reaction with methyl chloride [1]. The direct synthesis of dimethyldichlorosilane is the key process for the production of silicone polymers. In almost all cases of organosilane syntheses directly from metallic silicon, an organic halides, such as methyl chloride and chlorobenzene, must be used as a reactant [1]. These reactions are not suitable as environmentally benign processes because the halides are poisonous and corrosive. Therefore, it is worth finding a new direct method with no use of halides to form organosilane.

Trimethoxysilane, which is not an organosilane, can also be synthesized from metallic silicon by the reaction with methanol using a copper catalyst [2–5]. A ratio of trimethoxysilane to tetramethoxysilane (by-product) in the products greatly depends on the conditions for preheating the mixture of silicon and copper(I) chloride catalyst as well as the reaction conditions [5]. When a small amount of thiophene, which is well-known as a poison of a metallic copper catalyst, was added to the

methanol feed, tetramethoxysilane formation was inhibited and trimethoxysilane was exclusively yielded [6]. This indicates that tetramethoxysilane is the secondary product formed by the reaction of trimethoxysilane and methanol over metallic copper formed during the silicon–methanol reaction [6].

To synthesize trimethoxysilane, generally the reaction of silicon with methanol is carried out below 600 K, since the reaction rate dramatically decreases above 600 K. Here, we report that in the presence of thiophene the reaction can proceed with a high rate above 600 K and that an organosilane, methyl dimethoxysilane, can be obtained together with trimethoxysilane. The effects of reaction variables on the selectivity and the yield of methyl dimethoxysilane were examined, and the mechanism of methyl dimethoxysilane formation was proposed.

## 2. Experimental

Silicon grains (45–63  $\mu\text{m}$ , purity 99.9%, impurities Fe: 0.008 wt%, Sb: 0.003 wt%) was washed by a 46% hydrogen fluoride aqueous solution for 1 h at room temperature to remove  $\text{SiO}_2$ -overlayers. The silicon grains (6.0 mmol) and copper(I) chloride grains (45–63

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$\mu\text{m}$ , purity 99.9%,  $\text{Cu}/(\text{CuCl} + \text{Si}) = 2.5\text{--}40$  wt%) were mixed vigorously in a small vial, and the mixture was placed in a quartz tube (i.d. 10 mm) in an atmospheric fixed-bed flow reactor. The mixture was preheated at 723 K for 1 h in a helium stream, before the mixture of methanol (28–83 kPa) and thiophene (0.35–30 kPa) vapors was fed to the reactor tube at 553–723 K. Amounts of products were analyzed by gas chromatograph every 10 min. The products were identified by  $^1\text{H-NMR}$  and GC-MS.

The selectivity and the yield of the product and the silicon conversion were defined as follows:

Selectivity (%)

$$= \frac{\text{Amount of the product (mmol)}}{\left(\text{Sum of amounts of silicon-containing products (mmol)}\right)} \times 100$$

$$\text{Yield (\%)} = \frac{\text{Amount of the product (mmol)}}{\left(\text{Amount of the silicon charged in the reactor (6 mmol)}\right)} \times 100$$

Silicon conversion (%)

$$= \frac{\text{Sum of amounts of silicon-containing products (mmol)}}{\text{Amount of the silicon charged in the reactor (6 mmol)}} \times 100$$

### 3. Results and discussion

#### 3.1. Time courses of the reaction

The reaction was carried out at 42 kPa of methanol pressure and 0.35 kPa of thiophene pressure at 653 K after the silicon–catalyst mixture was preheated at 723 K for 1 h. Methyltrimethoxysilane was formed together with dimethoxysilane, trimethoxysilane and tetramethoxysilane. Fig. 1 shows time courses of formation rates of three main products. All the rates increased with time on stream to the maxima and then decreased. The reaction stopped at 3 h and the silicon conversion reached 44%. The selectivities for methyltrimethoxysilane, dimethoxysilane, trimethoxysilane and tetramethoxysilane were 18%, 3%, 78% and 1%, respectively. On the other hand, without thiophene, the reaction hardly proceeded (4% of silicon conversion), however the selectivity for ethyltrimethoxysilane was 16%. This indicates that even the reaction without thiophene leads to methyltrimethoxysilane formation and that the addition of thiophene has an effect on preventing the reaction from stopping.

#### 3.2. Effect of various additives

Various sulfur-containing compounds instead of thiophene were used for the reaction of silicon with

methanol. The results are summarized in Table 1. All sulfur-containing compounds increased both the silicon conversion and the selectivity for methyltrimethoxysilane. 2-Methylthiophene and *n*-butyl mercaptan were more effective additives for improvement of the selectivity than thiophene, but the conversions were lower.

Triethylamine and pyridine were also used as the additives, since nitrogen-containing compounds are also poisons for metal catalysts [7]. These compounds did not raise the selectivity for methyltrimethoxysilane and the silicon conversions were almost zero.

These results indicate that sulfur is indispensable to improve of both the conversion and the selectivity and that thiophene is the most effective additives to obtain a high yield of methyltrimethoxysilane.

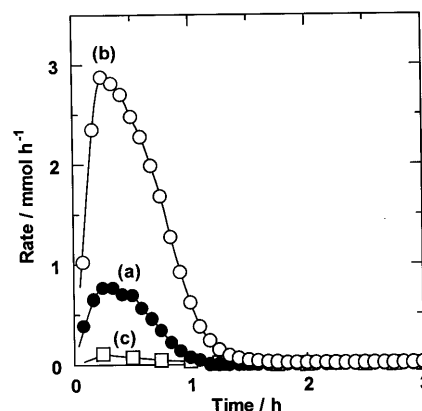


Fig. 1. Time courses of formation rates of methyltrimethoxysilane (a), trimethoxysilane (b), and tetramethoxysilane (c). Pretreating: 723 K for 1 h. Reaction conditions: silicon = 6.0 mmol, copper(I) chloride = 20 wt% (as copper metal), methanol pressure = 42 kPa, thiophene pressure = 0.35 kPa, reaction temperature = 653 K.

Table 1

Effect of various additives on the formation of methyltrimethoxysilane<sup>a</sup>

Additive	Silicon conversion (%)	Methyltrimethoxysilane selectivity (%)
Thiophene	47	17
2-Methylthiophene	38	20
<i>n</i> -Butyl mercaptan	33	21
<i>sec</i> -Butyl mercaptan	33	18
Ethyl sulfide	39	18
Thiophenol	33	18
Triethylamine	0	–
Pyridine	1	8
No additive	4	16

<sup>a</sup> Pretreatment and reaction temperature were 723 and 653 K, respectively. Methanol and additive pressure were 42 and 0.51 kPa, respectively.

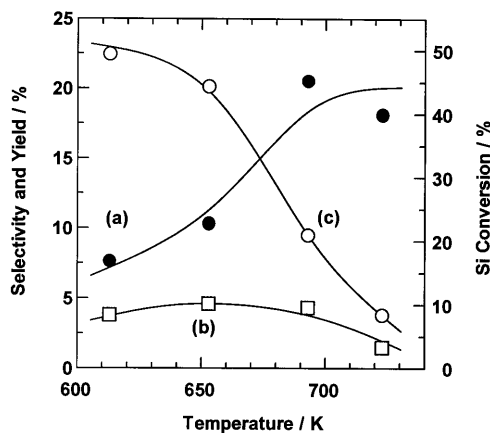


Fig. 2. Effect of reaction temperature on the selectivity (a), the yield (b) of methyltrimethoxysilane and the silicon conversion (c). Pretreating: 723 K for 1 h. Reaction conditions: silicon = 6.0 mmol, copper(I) chloride = 10 wt% (as copper metal), methanol pressure = 55 kPa, thiophene pressure = 1.8 kPa, reaction temperature = 653 K.

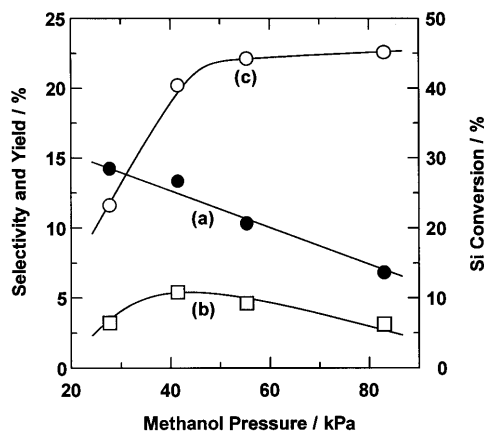


Fig. 3. Effect of methanol pressure on the selectivity (a), the yield (b) of methyltrimethoxysilane and the silicon conversion (c). Pretreating: 723 K for 1 h. Reaction conditions: silicon = 6.0 mmol, copper(I) chloride = 10 wt% (as copper metal), thiophene pressure = 1.8 kPa, reaction temperature = 653 K.

### 3.3. Effects of reaction conditions

In order to obtain a higher yield of methyltrimethoxysilane, the effects of reaction conditions were examined.

The effect of reaction temperature is shown in Fig. 2. The selectivity and the conversion significantly depended on reaction temperature. The selectivity for methyltrimethoxysilane increased with reaction temperature and reached 21% at 693 K, while the silicon conversion was lower at a higher temperature. At 723 K the conversion was very low (8%). The highest yield of methyltrimethoxysilane (5%) was obtained at 653 K.

The reaction was carried out at various pressures of methanol. The pressure of thiophene was held constant at 1.8 kPa. As shown in Fig. 3, the selectivity was lower

at a higher pressure of methanol. The conversion increased with methanol pressure to 45% at 83 kPa.

The amount of copper(I) chloride catalyst was varied. The results are shown in Fig. 4. Without use of copper chloride, the reaction did not proceed. The silicon conversion was the highest (40%) using 10 wt% of the catalyst. The selectivity for methyltrimethoxysilane increased with the catalyst amount. The yield of methyltrimethoxysilane reached constant value (7%) above 20 wt%.

Fig. 5 shows the effect of thiophene pressure. Methanol pressure was kept constant at 42 kPa. Without thiophene, the silicon conversion was very low but methyltrimethoxysilane was formed with a 16% selectivity. Addition of thiophene improved the selectivity for methyltrimethoxysilane. The selectivity increased with increase of thiophene pressure and reached 23% at 30

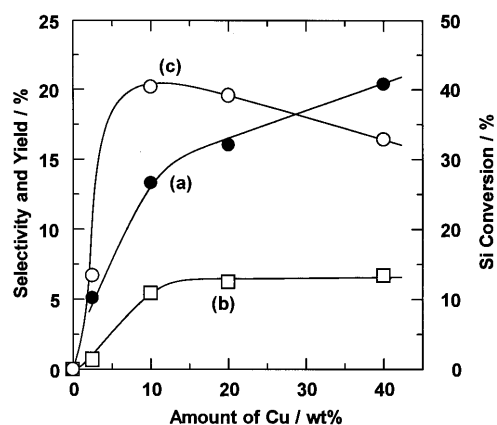


Fig. 4. Effect of the amount of copper(I) chloride on the selectivity (a), the yield (b) of methyltrimethoxysilane and the silicon conversion (c). Pretreating: 723 K for 1 h. Reaction conditions: silicon = 6.0 mmol, methanol pressure = 42 kPa, thiophene pressure = 1.8 kPa, reaction temperature = 653 K.

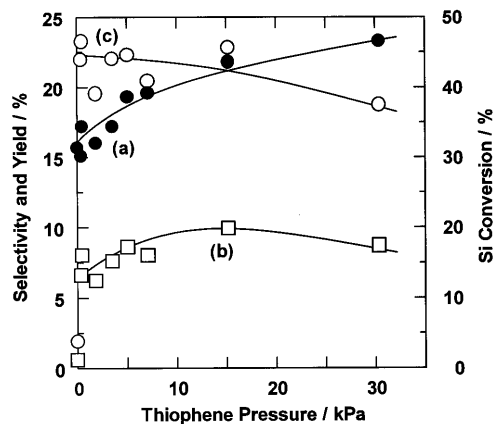
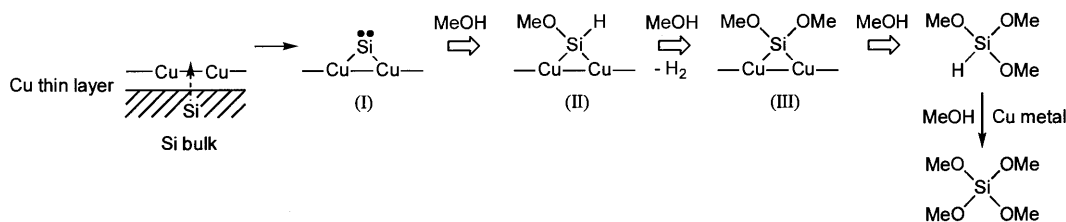


Fig. 5. Effect of thiophene pressure on the selectivity (a), the yield (b) of methyltrimethoxysilane and the silicon conversion (c). Pretreating: 723 K for 1 h. Reaction conditions: silicon = 6.0 mmol, copper(I) chloride = 20 wt% (as copper metal), methanol pressure = 42 kPa, reaction temperature = 653 K.



Scheme 1. Mechanism of trimethoxysilane formation.

kPa of thiophene pressure, while the silicon conversion decreased with increasing thiophene pressure. These results indicate that thiophene is not necessary for the formation of methyl dimethoxysilane, however influences the selectivity.

Under the optimal conditions for the highest yield of methyl dimethoxysilane, i.e. at 653 K at 42 kPa of methanol at 15 kPa of thiophene using 20 wt% of copper, methyl dimethoxysilane was obtained with a 10% yield. The silicon conversion and the selectivity for methyl dimethoxysilane were 46% and 22%, respectively.

### 3.4. Mechanism of methyl dimethoxysilane formation

We have reported the mechanism of trimethoxysilane formation involving a silylene intermediate [6] as shown in Scheme 1. Methanol reacts with surface silylene (I) to form surface species (II), which is converted into surface species (III) by an attack of methanol. Further, another methanol molecule attacks the species (III). Two silicon–copper bonds are simultaneously cleaved, and MeO and H are combined with the silicon atom to give trimethoxysilane. Silylene intermediate (I) are regenerated by diffusion of silicon atoms from the bulk to the copper layers on the surface. A part of copper layers are coagulated to form metallic copper, and the coagulation causes the deactivation of the catalyst. Tetramethoxysilane is formed by the reaction of trimethoxysilane and methanol over the metallic copper.

In the direct synthesis of methyl dimethoxysilane, methyl formate and formaldehyde were formed as non silicon-containing products. It is well-known that methanol is dehydrogenated over copper catalysts to form methyl formate and formaldehyde [8]. Thus, under the reaction conditions for methyl dimethoxysilane synthesis, the formation of methyl formate and formaldehyde must be caused by the dehydrogenation of methanol over metallic copper formed during the reaction. Fig. 6 shows the changes of the rates of formation of methyl dimethoxysilane, methyl formate and formaldehyde with time. Methyl formate was formed only during the formation of methyl dimethoxysilane, while formaldehyde was detected after methyl dimethoxysilane formation stopped. These facts suggest that methyl

formate and methyl dimethoxysilane are formed via the same intermediate and that formaldehyde participates in bonding methyl group to silicon atom.

There was no indication of the formation of water and carbon dioxide. This shows that oxygen atom, which originates from methanol consumed to form methyl group, remains in the mixture of silicon and catalyst. The oxygen atom is likely to react with silicon to form silicon dioxide, whose formation leads to a decrease of a silicon reactivity.

Trimer of formaldehyde, trioxane, was added to the mixture of methanol and thiophene. Fig. 7 shows the effect of trioxane on the selectivity for methyl dimethoxysilane. The selectivity increased from 16% to 20% by adding 50 Pa of trioxane, strongly indicating participation of formaldehyde in methyl dimethoxysilane formation. Above 50 Pa of trioxane, the selectivity was almost constant. The silicon conversion decreased a little by adding trioxane, however, at a high pressure of trioxane (410 Pa), the reaction stopped.

The speculated mechanism of methyl dimethoxysilane formation is shown in Scheme 2. Powder X-ray diffraction pattern of the silicon–catalyst mixture during the silicon–methanol reaction showed the formation of a metallic copper phase. Methanol is dissociatively ad-

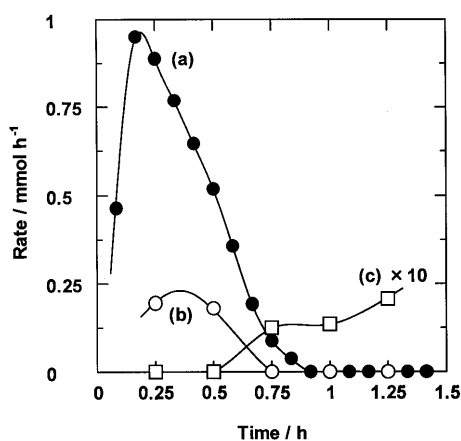


Fig. 6. Time courses of formation rates of methyl dimethoxysilane (a), methyl formate (b) and formaldehyde (c). Pretreating: 723 K for 1 h. Reaction conditions: silicon = 6.0 mmol, copper(I) chloride = 40 wt% (as copper metal), methanol pressure = 42 kPa, thiophene pressure = 1.8 kPa, reaction temperature = 653 K.

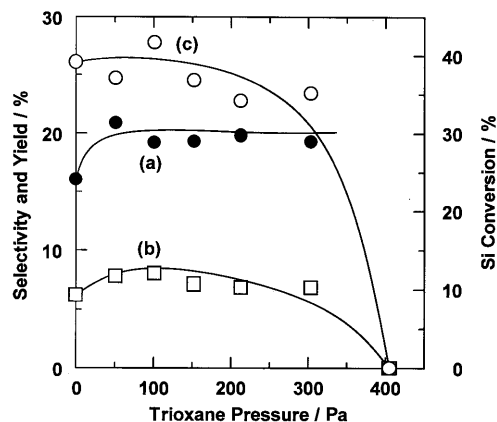


Fig. 7. Effect of trioxane pressure on the selectivity (a), the yield (b) of methyl dimethoxysilane and the silicon conversion (c). Pretreating: 723 K for 1 h. Reaction conditions: silicon = 6.0 mmol, copper(I) chloride = 20 wt% (as copper metal), methanol pressure = 42 kPa, thiophene pressure = 1.8 kPa, reaction temperature = 653 K.

sorbed on the metallic copper to form methoxy species and H species. The methoxy species on copper surface (IV) is dehydrogenated to produce adsorbed formaldehyde (V), which is converted into methyl species (VI) and  $\text{CH}_2\text{O}_2$  bidentate species (VII) by the reaction with neighboring methoxy species. Methyl species reacts with adjoining surface species (II), which is an intermediate for formation of trimethoxysilane, to form methylmethoxy silicon species (VIII). Finally, methanol attacks the surface species (VIII) and methyl dimethoxysilane is formed. On the other hand, the reaction of the  $\text{CH}_2\text{O}_2$  bidentate species (VII) with methoxy surface species leads to methyl formate. Formaldehyde is desorbed from the species (V). When trioxane is fed to the mixture of methanol and thiophene, the amount of the species (V) increases, and finally the yield of methyl dimethoxysilane

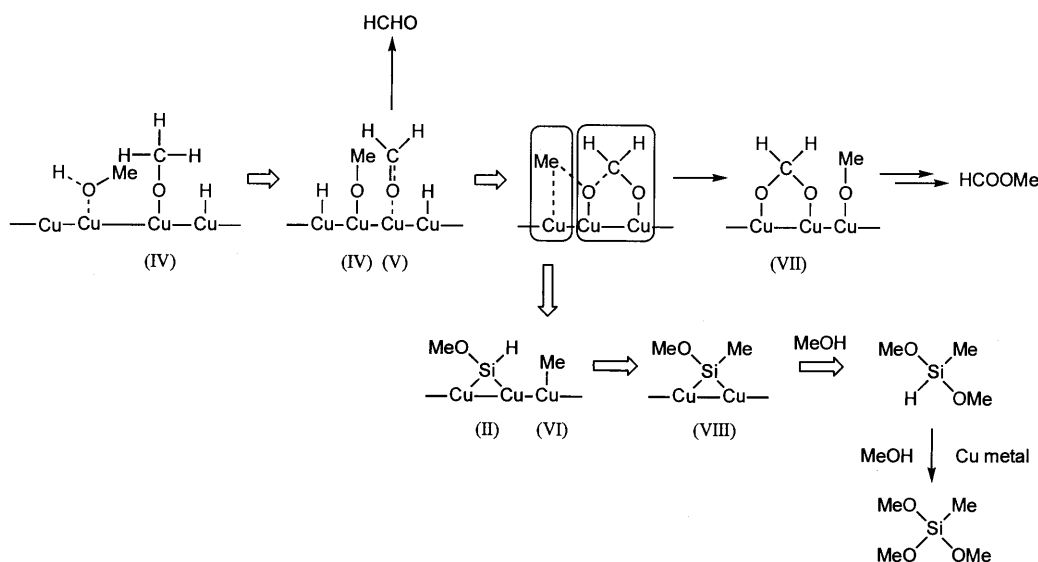
increases. However, as mentioned above, a large amount of trioxane resulted in inhibiting the formation of the whole methoxysilanes, probably because of coverage of the copper surface with the aldehyde. In the synthesis of triethoxysilane, addition of acetaldehyde completely stopped the formation of triethoxysilane [9]. As shown in Fig. 5, adding a small amount of thiophene significantly increased the silicon conversion from 4% to 44%. Thiophene added poisons metallic copper so that the formation of formaldehyde on the copper surface can be diminished. This leads to the increase of the silicon conversion.

### 3.5. Synthesis of ethyldiethoxysilane by the reaction of silicon with ethanol

It has been reported that ethanol also reacts with metallic silicon to afford triethoxysilane and tetraethoxysilane [3,9]. In the reaction of ethanol (81 kPa) in the presence of thiophene (12 kPa) at 613 K, ethyldiethoxysilane (selectivity 14%) was obtained together with ethylethoxysilane (2%), ethyltriethoxysilane (2%), diethoxysilane (4%), triethoxysilane (75%) and tetraethoxysilane (3%). The silicon conversion reached 43%.

## 4. Conclusions

Methyl dimethoxysilane and ethyldiethoxysilane were obtained directly from metallic silicon by the reaction of methanol and ethanol, respectively, in the presence of a small amount of thiophene. Thiophene prevents stopping the reaction and improves the selectivity for organosilanes. This is a new reaction with no use of halides for synthesis of organosilanes.



Scheme 2. Mechanism of methyl dimethoxysilane formation.

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