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Synthesis of methoxysilanes by the reaction of metallic silicon with methanol using copper(II) acetate as the catalyst

Masaki Okamoto, Naoki Mimura, Eiichi Suzuki and Yoshio Ono [1]

Department of Chemical Engineering, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152, Japan

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The reaction of methanol with silicon was studied using various copper compounds other than the halides. Copper(II) acetate and copper(I) oxide gave high silicon conversions (82%) though the selectivities for trimethoxysilane were low (< 19%). The selectivity was appreciably improved by addition of a small amount of thiophene or propyl chloride to the methanol feed.

Keywords: methoxysilanes; silicon; methanol; copper(II) acetate

1. Introduction

The copper-catalyzed reaction of silicon with methyl chloride to give methylchlorosilanes is well known. The direct synthesis of methylchlorosilanes is the most important in the silicon industry [1].

Silicon reacts also with methanol to afford tri- and tetramethoxysilane using copper catalyst [2,3]. Copper(I) chloride is a very effective catalyst. By properly selecting the reaction conditions and the pretreatment conditions of the silicon–copper(I) chloride mixture, the silicon conversion reached about 90% and the selectivity for trimethoxysilane was almost 100% [2,3]. However, when copper(I) chloride was used as the catalyst, chlorine-containing compounds are found in the products as impurities. Therefore, active catalysts, which do not contain halide ions, are highly desirable. In this work, the catalytic functions of various copper catalysts for the silicon–methanol reaction were compared, and the reaction with copper(II) acetate catalyst was further examined in detail.

2. Experimental

Silicon grains (6.0 mmol: 170 mg, purity 99.9%) and a copper compound (0.31

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[1] To whom correspondence should be addressed.

mmol) were mixed and the mixture was placed in a fixed-bed reactor, a quartz reactor (10 mm i.d.). The silicon–catalyst mixture was preheated at 473–673 K under a helium stream prior to the reaction. Methanol was fed with a motor-driven syringe. The reaction temperature was 453–653 K and the methanol pressure was 97 kPa (69 mmol h^{-1}). The products were analyzed every 3.5 min by gas chromatography.

3. Results and discussion

Table 1 shows the results obtained in the silicon–methanol reaction using various copper catalysts. The result for copper(I) chloride is also listed. The effects of the pretreatment conditions of the catalyst–silicon mixtures and the reaction temperature were examined for each catalyst system. The pretreatment and reaction temperature shown in table 1 are those which gave the highest silicon conversion for each catalyst. In all the cases, the silicon-containing products were trimethoxysilane and tetramethoxysilane; the other products were negligible. When copper(II) acetate or copper(I) oxide was the catalyst, a high silicon conversion (82%) was obtained, the selectivity for trimethoxysilane being low (<19%). Copper(I) thiocyanate, copper(II) sulfate, basic copper(II) carbonate or copper(II) nitrate (not listed in table 1) did not show any catalytic activity. Table 1 clearly shows that several copper compounds other than copper(I) chloride work as catalysts for the

Table 1
The silicon conversions and the selectivities for trimethoxysilane in the silicon–methanol reactions using various copper catalysts

Catalyst	Pretreatment temperature (K)	Reaction temperature (K)	Silicon conversion (%)	Selectivity for trimethoxysilane (%)
Cu_2O	523	523	82 (3.8 h)[a]	19
CuO	673	523	50 (4.3 h)[a]	57
$Cu(OCOCH_3)_2$[b]	–[f]	473	82 (4.0 h)[a]	8
$Cu(OCOH)_2$[c]	–[f]	473	11 (3.3 h)[a]	9
$CuC_8H_4O_4$[d]	–[f]	523	23 (3.1 h)[a]	21
CuC_2O_4[e]	523	523	1 (1.5 h)[a]	0
CuCl	513	513	88 (3.0 h)[a]	98

[a] Time at the end of the reaction.
[b] Copper(II) acetate.
[c] Copper(II) formate.
[d] Copper(II) phthalate.
[e] Copper(II) oxalate.
[f] Without pretreatment.
Pretreatment time: 1 h.

silicon–methanol reaction. However, the high selectivity for trimethoxysilane was not obtained with non-halide catalysts.

The reaction with copper(II) acetate was studied in more detail. When copper(I) chloride was used as the catalyst, both the reaction rate and the selectivity for trimethoxysilane greatly depended on the condition of the pretreatment of the silicon–copper(I) chloride mixture [1,2]. Here, in the case of the reaction with copper(II) acetate, one of the most active catalysts in table 1, the effect of the pretreatment condition on the reaction rate and the selectivity for trimethoxysilane was examined. Fig. 1 shows the time courses of the rate of methoxysilanes formation, the cumulative silicon conversion and the selectivity for trimethoxysilane when the pretreatment temperature was varied. Without the pretreatment of the silicon–catalyst mixture (fig. 1a), the rate of methoxysilanes formation increased with time and decreased through the maximum at 20 min. The silicon conversion reached

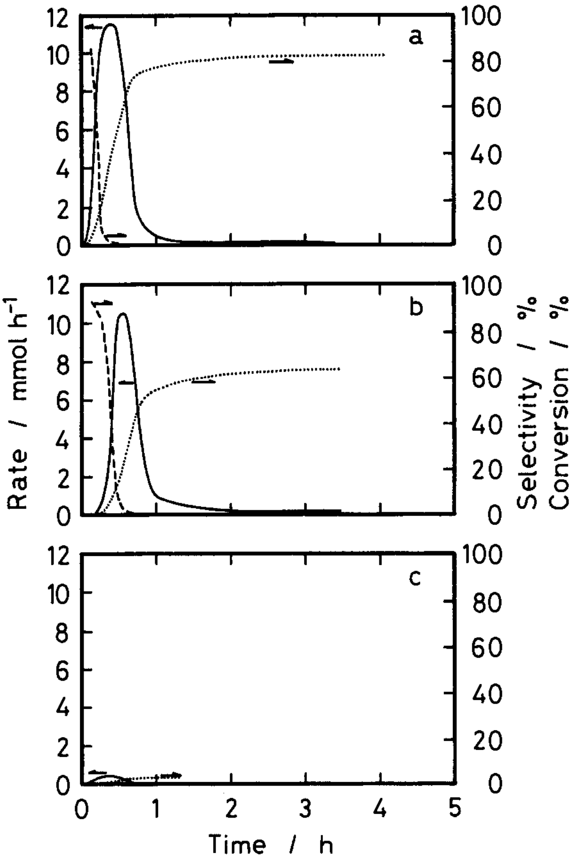

Fig. 1. Effect of the pretreatment temperature on the rate of methoxysilanes formation and the selectivity for trimethoxysilane, when copper(II) acetate was used as the catalyst: rate (——), selectivity (- - -), cumulative silicon conversion (. . .). Without pretreatment (a), pretreatment at 473 (b), 673 K (c) for 1 h. Reaction temperature: 473 K.

82% at 4 h when the reaction ceased, the average selectivity being very low (8%). When the silicon–catalyst mixture was pretreated at 473 K for 1 h (fig. 1b), the maximum of the reaction rate decreased and the silicon conversion was low (63%) and the selectivity for trimethoxysilane was also 8%. When the pretreatment was done at 673 K (fig. 1c), the reaction hardly occurred. The XRD analysis showed that the treatment of the silicon–copper(II) acetate mixture at this temperature resulted in the formation of metallic copper, though it was not observed at lower treatment temperatures. The very low silicon conversion under high-temperature pretreatment conditions may be related to the decomposition of the acetate into metallic copper.

The effect of the reaction temperature was also examined (see fig. 2). The reaction was started without any pretreatment of the silicon–catalyst mixture. The silicon conversion values were 82, 63, and 37%, at 473, 503, and 523 K, respectively.

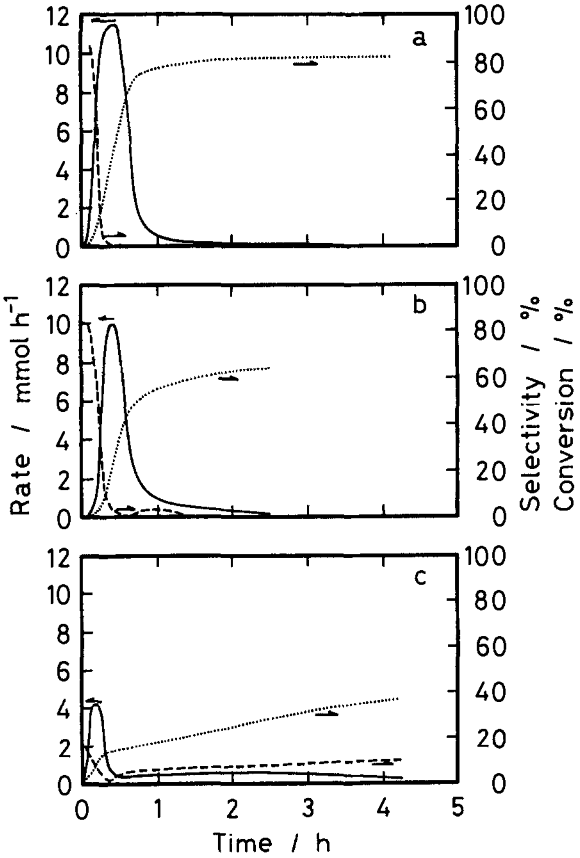

Fig. 2. Effect of the reaction temperature on the rate of methoxysilanes formation and the selectivity for trimethoxysilane, when copper(II) acetate was used as the catalyst: rate (——), selectivity (- - -), cumulative silicon conversion (. . .). Without pretreatment. Reaction temperature: 473 K (a), 503 K (b), 523 K (c).

Low reaction temperature led to high silicon conversion. However, when the reaction temperature was shifted stepwise during the reaction, the reaction rate was higher at higher reaction temperature. It follows that the reactive area on the silicon surface depends on the temperature where the reactions started in conformity with the effect of the pretreatment temperature. The selectivity for trimethoxysilane was low in every case (5–8%).

Fig. 3 shows the SEM image of the silicon surface when 25% of silicon was consumed. The pits were scattered on the surface. We have shown that the reaction proceeds from the area where Cu–Si alloy, such as Cu_3Si, has located and that the alloy may be a precursor of the reactive sites [3]. This indicates the formation of the alloy phase during the reaction. In fact, XRD analysis of the silicon–copper(II) acetate mixture after the reaction for 45 min indicated the presence of Cu_3Si as shown in fig. 4, where metallic copper also exists in the reacting system.

As described above, the selectivity for trimethoxysilane is low when copper(II) acetate is used as the catalyst. In the reaction of silicon with methanol catalyzed by copper(I) chloride, we have reported that trimethoxysilane is the sole primary product and that tetramethoxysilane is a secondary product formed by the reaction of trimethoxysilane with methanol over metallic copper formed during the reaction and that the selectivity for trimethoxysilane was enhanced upon addition of a small

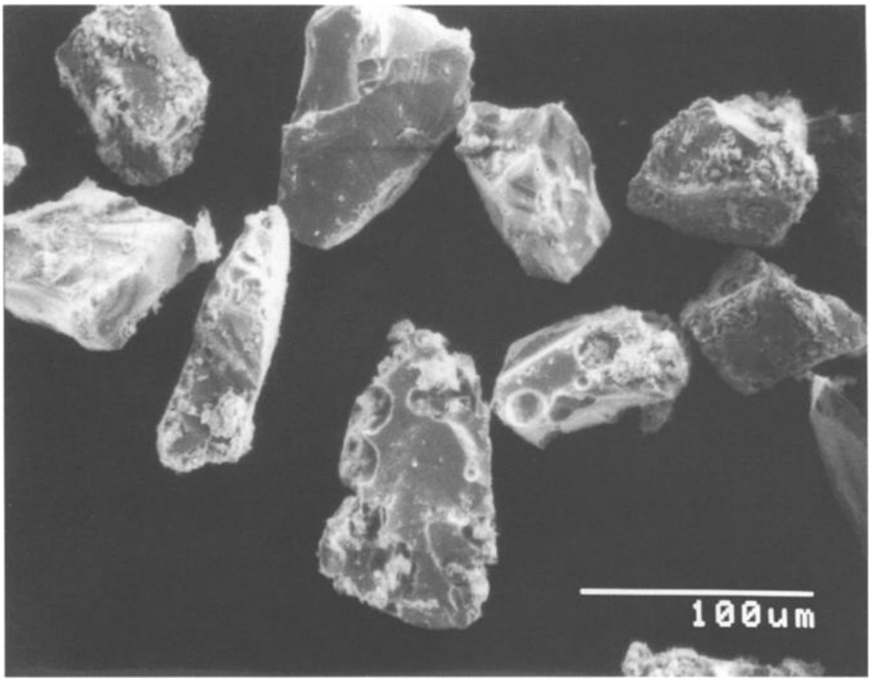

Fig. 3. SEM image of silicon surface when 25% of silicon conversion was consumed. Without pretreatment, reaction temperature = 473 K, reaction time = 45 min. Magnification ×150.

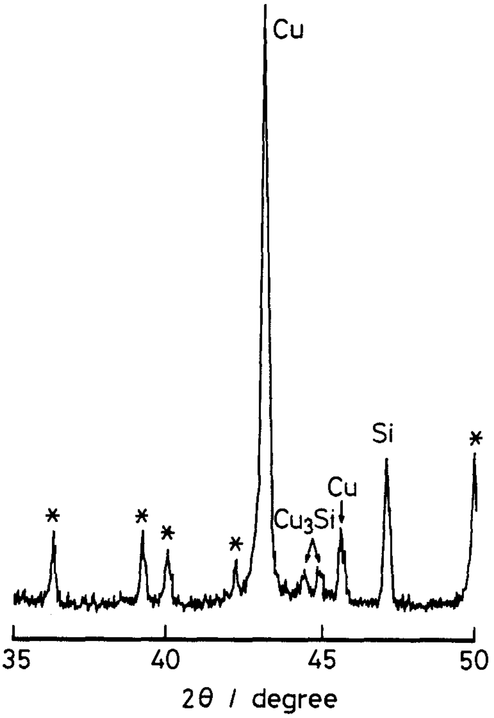

Fig. 4. XRD pattern of the silicon–copper(II) acetate mixture after the reaction for 45 min. Peaks with asterisk are attributable to diffractions due to silica sand packed in the evaporation zone of the reactor.

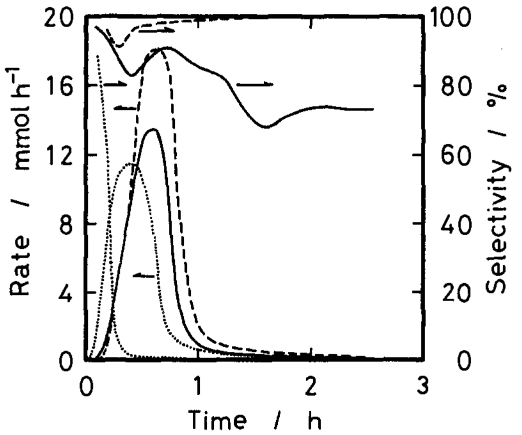

Fig. 5. Effects of thiophene and propyl chloride on the rate of methoxysilanes formation and the selectivity for trimethoxysilane. Without pretreatment, reaction temperature: 473 K, methanol: 97 kPa, thiophene (——) or propyl chloride (- - -): 1.9 kPa, no additive (. . .).

amount of thiophene or alkyl chloride, which adsorbs on copper surface to inhibit the secondary reaction [4]. As shown in fig. 4, the formation of metallic copper was confirmed by XRD. It follows that the low selectivity of copper(II) acetate catalyst is ascribed to the secondary reaction on the copper formed during the catalysis.

In order to improve the selectivity for trimethoxysilane, a small amount (2 mol%) of thiophene was added to the methanol feed. The result is shown in fig. 5. The selectivity improved to 86%, the silicon conversion being 61%. Thus, a reasonably high silicon selectivity together with high silicon conversion could be attained in a non-halide system.

Addition of propyl chloride (2 mol%) also resulted in a very high selectivity for trimethoxysilane (98%), as shown in fig. 5. This again indicates that the formation of tetramethoxysilane is caused by metallic copper.

References

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