

Slurry Phase Reaction of Elemental Silicon with Methanol in the Presence of Copper: Direct Synthesis of Trimethoxysilane

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Slurry phase reaction of elemental silicon with methanol has been studied in the presence of copper using a small amount of cuprous chloride as an activator in DBT (dibenzyltoluene) at various temperatures from 200 °C to 320 °C. Trimethoxysilane (**1a**) with a Si-H unit was obtained as the major product and tetramethoxysilane (**1b**) as the minor product. The reaction worked well using a 0.5 wt % CuCl as an activator. The optimum temperature for this direct synthesis of **1a** was 240 °C. Methoxysilanes were obtained in 95% yield with 81% selectivity to **1a** from 85% conversion of elemental silicon.

Key Words: Copper. Silicon. Methanol. Trimethoxysilane. Alkoxy silane

Introduction

Hydrosilanes with Si-H unit have been widely used as starting materials¹⁻⁴ for synthesizing organosilicon compounds through hydrosilylation with olefin in academic and industrial fields since it was discovered by J. L. Speier in 1957² that a hexachloroplatinic acid in *i*-propyl alcohol was a very effective catalyst for hydrosilylation.^{3,4} Even though hydrochlorosilanes has a long synthetic history⁵ and been well-established in academic and industrial filed,¹ they reacts easily with moisture to give off hydrogen chloride which is toxic for living system and rustic for iron devices. Generally organoalkoxysilanes are widely used as especially coupling agents in industrially application forms⁶ instead of organochlorosilanes. So an alkoxylation process for the conversion of organochlorosilanes to organpalkoxysilanes is required. Especially hydroalkoxysilanes are useful starting materials for the safe preparation of alkylalkoxysilanes with an epoxy unit,⁷ which are widely used as molding compounds in electronic industry, without a opening of epoxy-ring from the hydrosilylation reaction of trialkoxysilanes with epoxyated olefin such as allyl glycidyl ether and 4-vinyl-cyclohexyl epoxide.⁸ Therefore, much attention has been paid to the development of the direct synthesis for trialkoxysilanes with Si-H unit.^{9,11} There were some reports for the direct synthesis of alkoxy silanes with a Si-H starting from elemental silicon with methanol in the presence of copper compounds such as CuCl,^{9,11} CuCl₂,¹⁰ Cu₂O.⁹ Such Cu-compounds reacted easily with elemental silicon in a sintering step to give Cu₃Si phase,¹² which is known to be an active site,¹³⁻¹⁶ but eliminating undesirable compounds, tetrachlorosilane formed from the reaction of elemental silicon with copper[I, II] chlorides,^{9,11} and siloxanes from that with Cu₂O,⁷ respectively. In a large scale production, loss of elemental silicon through undesirable reaction is worth nothing. Thus we have studied a direct reaction of elemental silicon with methanol in the presence of copper metal using a small amount of copper compound as an activator.

We have previously reported the direct synthesis of hydrosilanes from the direct reaction of elemental silicon with a mixture of hydrogen chloride and activated organic chlorides such as *i*-propyl chloride,¹³ dichloromethane,¹⁴ and chloroform¹⁵ to give Si-H containing *i*-propyltrichlorosilane, bis-(chlorosilyl)methanes, and tris(chlorosilyl)methanes, respectively.¹⁶ This success in the direct synthesis of new Si-H containing organochlorosilanes prompted us to apply to the direct reaction of elemental silicon with methanol giving methoxysilanes, trimethoxysilane with a Si-H unit (**1a**) and tetramethoxysilane (**1b**). In this reaction, conversion of elemental silicon and selectivity to **1a** are important factors in a high yield production.

We wish to report the results obtained from the slurry phase reaction of elemental silicon with methanol in the presence of copper using a small amount of copper chloride as an activator in a stirred reactor at temperatures between 200 °C and 320 °C.

Results and Discussion

Reaction was carried out by feeding methanol into a slurry phase of a contact mixture of elemental silicon with Cu, prepared by preheating using a small amount of CuCl as an activator under a N₂ stream in a stirring-bed reactor of 330 °C for 2 h in DBT (dibenzyltoluene). Reaction mixtures were collected and distilled to give methoxysilanes **1a** and **1b** (eq 1). The composition of methoxysilanes was determined by GLC comparing with authentic samples **1a** and **1b**. The optimum conditions such as reaction temperature, a feeding rate of methanol, and activator for direct synthesis of trimethoxysilane starting from elemental silicon and methanol were studied in details.



Effect of Reaction Temperature. Effect of reaction tem-

Table 1. Reaction Temperature Effect on Direct Synthesis of **1a**.^a

| entry # | reaction temp. (°C) | reaction mixture | | | | yield (%) ^f | selectivity to 1a ^d |
|---------|---------------------|------------------|--------------------------------|-----------|-----------|------------------------|---------------------------------------|
| | | g (received) | percentage (mmol) ^b | | | | |
| | | | MeOH | 1a | 1b | | |
| 1 | 200 | 44.7 | 15 | 73 (267) | 9 (26) | 73 | 91 |
| 2 | 240 | 48.1 | 0.3 | 79 (311) | 16 (51) | 92 | 86 |
| 3 | 280 | 48.1 | - | 71(280) | 25 (79) | 93 | 80 |
| 4 | 320 | 49.0 | - | 63 (253) | 31 (100) | 94 | 72 |

^a50 mL (39.6 g, 1.238 mmol) of methanol was used at each reaction temperature, a mixture of elemental silicon (90 wt %), Cu (9.5 wt %), and CuCl (0.5 wt %). ^bGLC area % (mmol); a mixture of disiloxanes obtained in small amount is excluded for simplicity. ^cYields are based on the amount of methanol used. ^dSelectivity to **1a**: **1a**/sum of **1a** and **1b**.

Table 2. Effect of Feeding Rate of Methanol on Direct Synthesis of **1**.^a

| entry # | MeOH (mL/min) | reaction mixture (g) | percentage (mmol) ^b | | | yield ^c (%) | selectivity ^d (%) |
|---------|---------------|----------------------|--------------------------------|-----------------------|----------------------|------------------------|------------------------------|
| | | | MeOH | HSi(OMe) ₃ | Si(OMe) ₄ | | |
| 5 | 0.25 | 48.2 | - | 79 (312) | 16 (51) | 92 | 86 |
| 2 | 0.5 | 48.1 | 0.3 | 79 (311) | 16 (51) | 92 | 86 |
| 6 | 1.0 | 46.0 | 13 | 73 (275) | 10 (30) | 76 | 90 |

^a50 mL (39.6 g, 1.238 mmol) of methanol was added at 240 °C by varying feeding rate a mixture of elemental silicon (90 wt %), Cu (9.5 wt %), and CuCl (0.5 wt %). ^bGLC area percentage (mol); a mixture of disiloxane obtained in small amount is excluded for simplicity. ^cYield is based on methanol used. ^d**1a**/sum of **1a** and **1b**.

perature on the reaction of elemental silicon with methanol was studied at temperatures ranged from 200 to 320 °C. Reaction mixture, collected from each reaction at various reaction temperatures and fractional distilled to give methoxysilanes **1a** and **1b**. In addition to methoxysilanes, disiloxane compounds were formed in a small amount. Disiloxanes can be formed by the hydrolysis reaction of methoxysilanes with water formed by decomposition of methanol. The results are summarized in Table 1.

As shown in Table 1, total amount of reaction mixture increased from 44.7 g to 49.0 g as reaction temperature increased from 200 °C to 320 °C. The sum yield of methoxysilanes **1a** and **1b** based on methanol used increased from 73% to 94% as reaction temperature increased from 200 °C to 320 °C suggesting that reactivity of elemental silicon with methanol increases. The selectivity to **1a** decreased from 91% at 200 °C to 86% at 240 °C, 80% at 280 °C, 72% at 320 °C while amount of unreacted methanol recovered was decreased from 15% at 200 °C to 0.3% at 240 °C, then disappeared at 280 °C above. The results suggest that **1a** is formed at an early stage of this reaction and then converted to **1b** through a dehydrogenative methoxylation of **1a** with methanol. The yield of **1a** was the best at 240 °C and decreased at temperatures below or above 240 °C, while the sum yield of **1b** and **1b**, increased as reaction temperature increases.

It is interesting to note that the selectivity to **1a** was the highest at 200 °C and decreased at the temperatures above, probably due to conversion of **1a** to **1b** through dehydrogenative methoxylation of **1a** with methanol.

Feeding Rate of Methanol. In order to optimize the rate of feeding of methanol for synthesizing methoxysilane **1a**, the direct synthesis of **1a** was carried out at 240 °C by varying feeding rate from 0.25 mL/min to 1.0 mL/min. The results

obtained from the reaction are summarized in Table 2.

As shown in Table 2, as the feeding rate of methanol increased from 0.25 mL/min to 1.0 mL/min, amount of methanol recovered increased from 0 at a feeding rate of 0.25 mL/min to 13% at 1.0 mL/min, while total amount of reaction mixture decreased slightly from 48.0 g to 46.0 g. The sum yield of methoxysilanes **1a** and **1b** based on methanol used generally decreased from 92% to 76% while selectivity to **1a** increased from 86% to 90% as the feeding rate of methanol increased from 0.25 (or 0.5) mL/min to 1.0 mL/min. But the results obtained from a reaction with methanol at a feeding rate of 0.25 mL/min were similar to those from that of 1.0 mL/min, suggesting that the optimum feeding rate of methanol in the direct synthesis of **1a** was 0.5 mL/min in viewpoint of economical production.

Effect of CuCl as Activator: In order to reduce the loss of elemental silicon in sintering step of silicon with copper for preparing Cu₃Si phase, forming undesired products such as tetrachlorosilane or disiloxanes when Cu-compounds such as CuCl,^{9,11} CuCl₂,¹⁰ Cu₂O,⁹ etc. were used as catalyst in the direct synthesis of trimethoxysilane. Cuprous chloride, which is known as a best catalyst, gives relatively lots of tetrachlorosilane in a sintering reaction with elemental silicon. In a large scale production, loss of elemental silicon from undesirable reaction is worth nothing. Thus a direct reaction of elemental silicon with methanol in the presence of copper was carried out using a small amount of CuCl activator ranging from 0.25 wt % to 1.0 wt % based on total solid materials. The reaction worked well with a 0.5 wt % CuCl (entry no. 2) and above. The reaction of elemental silicon with methanol in the presence of copper (4.5 wt %) using CuCl (1.0 wt %) as an activator was carried out under the same reaction conditions of entry no. 2. The results were similar to those obtained from the reaction with a

0.5 wt % CuCl (entry no. 2). But a reaction using 0.25 wt % CuCl under the same reaction conditions of entry no. 2 showed that unreacted methanol was recovered (30%) and activity decreased slowly according to a reaction procedure. Considering that tetrachlorosilane is produced from the sintering of silicon and copper metal using a copper chloride, hydrogen chloride might be used as an activator in a sintering step. When HCl was used as an activator in place of CuCl, the direct reaction worked well. Although this reaction generally proceeds in good yields, but a little low of selectivity to **1a**, it was not preferable to the reaction with CuCl activator because extra HCl-controlling facility is needed.

In the direct synthesis of **1a**, purge of nitrogen gas helps **1a** escape safely out of reactor without decomposition of **1a**. Based on yield and selectivity of **1a**, the purging rate of nitrogen gas into reactor was good about 200 mL/min.

Preparation of 1a. When a large scale reaction of elemental silicon (285 g) with methanol (1.110 mL) was carried out for 37 h, 85% consumption of elemental silicon gave product mixture (991.0 g) consisting of **1a** (787 g, 6.4 mol) and **1b** (274.0 g, 1.80 mol). In order to check if a continuous reaction is possible, when new elemental silicon (240 g) was charged into the reactor above when about 85% of elemental silicon was consumed, the deactivation occurred. Thus once additional 0.5 wt % CuCl was added into the reactor, the reaction proceeded well again, but gave 60% selectivity to **1a** under the same conditions above, suggesting that CuCl was a useful activator for the direct synthesis of **1a**, but the selectivity to **1a** in a continuous process.

The optimum temperature of 240 °C in our system was slightly lower than that in other system.

It is interesting to note that the selectivity to **1a** was the highest at 200 °C and decreased at the temperatures above, probably due conversion of **1a** to **1b** through dehydrogenative methoxylation of **1a** with methanol.

Conclusions

Slurry phase reaction of elemental silicon with methanol has been studied in the presence of copper using a small amount of CuCl as an activator in DBT (dibenzyltoluene) medium at 240 °C gave trimethoxysilane in good yield. The optimum reaction temperature is 240 °C. The reaction worked well using a small amount of CuCl as an activator. The CuCl was a good activity enough for the synthesis of **1a** even though 0.5 wt % CuCl was used. Methoxysilanes **1a,b** were obtained in 96% yield with 81% selectivity to **1a** from 85% conversion of elemental silicon.

Experimental Section

Reagents and Physical Measurements. Anhydrous methanol (99.99%) was purchased from Solkatic Chemicals and used without further purification. Copper powder was purchased from Alcan Metal Powders (NJ, USA). Elemental silicon (Si, 98%; Fe, 0.50%; Ca, 0.25%; Al, 0.24%; C, 0.08%; S, 0.05%; P, 0.05%) was purchased from Samchuck Mining Co. (Kangwondo, Korea) or OSL-5-4855 (Si, 99.1%; Al,

0.29%; Ca, 0.037%; Fe, 0.30%; Ti, 0.035%) from Elkem Silicon (Oslo, Norway). The reaction products were analyzed by GLC using a packed column (10% SE-30 or SE-54 on 80-100 mesh chromosorb W/AW, 1/8 in. × 1.5 m) or a capillary column (SE-30, 30 m) with a Varian 3300 gas chromatograph, thermal conductivity detector, and Hitachi D-2500 integrator. Product yields were determined chromatographically with *n*-dodecane as an internal standard, if not described in details. Samples for characterization were purified by preparative GLC using a Donam system series DS 6200 gas chromatograph, thermal conductivity detector and a 4 m 1/8 in. stainless steel column packed with 20% OV-101 on 80-100 mesh chromosorb P/AW. NMR spectra were recorded on a Varian Unity Plus 600 (FT, 600 MHz, ¹H), Bruker AMX 500 (FT, 500 MHz, ¹H; 125 MHz, ¹³C), or a Varian Gem 300 (FT, 300 MHz, ¹H; 75 MHz, ¹³C) spectrometer in CDCl₃ solvent. Mass spectra were obtained using a Hewlett-Packard 6890 GC/MS.

Reactor: The reactor was made of a 1.8 L plate bottomed Pyrex glass, 11 cm inner diameter and 19 cm length, with a 4 necked glass cover, and equipped with a mechanical stirrer with the four blade axial impeller through a center neck and with a condenser connecting a receiver cooled by ethylene glycol at -15 °C. Reaction temperature was measured with a thermocouple (type K) which was placed inside through a hole at the glass cover. The flow rate of N₂ gas was controlled by a Matheson 603 flow meter.

General Procedure for Preparation of the Contact Mixture of Elemental Silicon with Copper Using CuCl. A mixture of metallic silicon (100-325 mesh, 285.0 g), copper metal (13.5 g), copper(I) chloride (1.5 g), and DBT (600 g) was placed in the reactor. A mixture was sintered at 330 °C for 2 h with stirring under dry nitrogen flush at a rate of 200 mL/min. Some volatiles, mainly tetrachlorosilane, were formed at an early stage of sintering process.

The contact mixtures prepared by this procedure were used in all reactions except for study on "effect of activator for preparation of contact mixture of silicon with copper" below.

Study on the Effect of Reaction Temperature on the Direct Synthesis of 1a. Direct synthesis of **1a** was carried out by adding methanol into a contact mixture (300 g) in DBT (600 g) in a rate of 0.5 mL/min at various temperatures between 200 °C and 320 °C in a temperature interval of 40 °C. At same time, dry nitrogen gas introduced at a rate of 200 mL/min, methanol was used at each reaction temperature. The results are summarized in Table 1.

Optimization for Feeding Rate of Methanol in the Direct Synthesis of 1a. Direct reaction was carried out by adding 50 mL methanol into a contact mixture (300 g) in DBT (600 g) at 240 °C at different feeding rate of methanol ranging from 0.25 to 1.0 mL/min at a rate of 200 mL/min under dry nitrogen flush. The results are summarized in Table 2.

Effect of CuCl Activator in Preparation of Contact Mixture of Silicon with Copper. Using the same procedure described in "general procedure for preparation of the contact mixture of elemental silicon with copper using CuCl" the contact mixtures were prepared using three different amounts of CuCl (0.25, 0.5, and 1.0 wt % based on solid reactants). The each contact

mixture was tested by reaction with 50 mL methanol at a rate of 0.5 mL/min at 240 °C under the same conditions above. The reaction worked well with a 0.5 wt % CuCl (entry no. 2) and above. The reaction of elemental silicon with methanol in the presence of copper (4.5 wt %) using CuCl (1.0 wt %) as an activator gave similar results obtained from the reaction with a 0.5 wt % CuCl (entry no. 2). But a reaction using 0.25 wt % CuCl showed that unreacted methanol was recovered (30%) and activity decreased slowly as a reaction proceeded.

When 500 mL of gaseous hydrogen chloride was used as an activator instead of CuCl in a sintering step of contact mixture. The reaction proceeded well, but selectivity to **1a** was a little low (74%) compare to the results obtained from the reaction with CuCl activator.

General Procedure for the Direct Synthesis of 1a. Into a 300 g contact mixture of silicon with copper was fed methanol at a rate of 0.5 mL/h using a metric pump at 240 °C. At the same time nitrogen gas was introduced at a rate of 200 mL/min. About 2 min after starting the reaction, it was observed that the reaction temperature was raised slightly due to the exothermic nature of the reaction and then the liquid product was collected at the receiver. After a 37 h of reaction, 991.0 g of the product mixture was collected in receiver cooled to -15 °C. The mixture was fractional distilled to give **1a** (787 g, 6.4 mol) and **1b** (274.0 g, 1.80 mol). In addition to methoxy-silanes, 37 g of high boilers consisted of 1,1,3,3-tetramethoxydisiloxane (26%), pentamethoxydisiloxane (61%), hexamethoxydisiloxane (6%), and etc were obtained.

For a continuous reaction, after about 85% of elemental silicon was consumed under the same reaction conditions above, the temperature cooled down to room temperature with no feeding of methanol and new elemental silicon (240 g) and 0.5 wt % CuCl (1.5 g) was charged into the reactor, sintered at 330 °C for 2 h. Then a reaction was carried out by the same procedure of direct synthesis of **1a** above. The reaction proceeded well again, but selectivity to **1a** went down 60% wt % and production of disiloxanes mixture was increased to 30 wt %.

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