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

Joon Soo Han,† Joo Hyun Cho,†‡ Myong Euy Lee,‡ and Bok Ryul Yoo†,*

†Organosilicon Chemistry Laboratory, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, Korea. *E-mail: bryoo@kist.re.kr
‡Department of Chemistry, Graduate School, Yonsei University, Seoul 120-749, Korea

Received November 25, 2008, Accepted January 19, 2009

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, Alkoxysilane

Introduction

Hydrosilanes with Si-H unit have been widely used as starting materials for synthesizing organosilicon compounds through hydrosilylation with olefin in academic and industrial fields since it was discovered by J. L. Speier in 1957 that a hexachloroplatinic acid in i-propyl alcohol was a very effective catalyst for hydrosilylation. Even though hydrochlorosilanes has a long synthetic history and been well-established in academic and industrial filed, 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 industrial application forms instead of organochlorosilanes. So an alkoxylation process for the conversion of organochlorosilanes to organopalkoxysilanes is required. Especially hydroalkoxysilanes are useful starting materials for the safe preparation of alkylalkoxysilanes with an epoxy unit, which are widely used as molding compounds in electronic industry, without a opening of epoxy-ring from the hydrosilylation reaction of trialkoxysilanes with epoxylated olefin such as allyl glycidyl ether and 4-vinyl-cyclohexyl epoxide. Therefore, much attention has been paid to the development of the direct synthesis for trialkoxysilanes with Si-H unit. There were some reports for the direct synthesis of alkoxysilanes with a Si-H starting from elemental silicon and methanol in the presence of copper compounds such as CuCl, CuCl2, Cu2O. Such Cu-compounds reacted easily with elemental silicon in a sintering step to give Cu3Si phase, which is known to be an active site, but eliminating undesirable compounds, tetrachlorosilane formed from the reaction of elemental silicon with copper[I, II] chlorides, and siloxanes from that with Cu2O, 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, dichloromethane, and chloroform to give Si-H containing i-propyltrichlorosilane, bis-(chlorosilyl)methanes, and tris(chlorosilyl)methanes, respectively. This success in the direct synthesis of 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.

\[
\text{Si} + \text{CH}_3\text{OH} \xrightarrow{\text{Cu}} \text{HSi(OCH}_3)_3 + \text{Si(OCH}_3)_4
\]

Effect of Reaction Temperature. Effect of reaction tem-
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 86% to 90% as the feeding rate of methanol increased from 0.25 mL/min to 0.5 mL/min. Amount of unreacted methanol recovered increased from 0 at a feeding rate of 0.25 mL/min to 15% 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.

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

<table>
<thead>
<tr>
<th>entry</th>
<th>reaction temp. (°C)</th>
<th>mixture (g)</th>
<th>reaction mixture</th>
<th>yield (%)</th>
<th>selectivity to 1a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>200</td>
<td>44.7</td>
<td>MeOH: 73 (267) 9 (26)</td>
<td>73</td>
<td>91</td>
</tr>
<tr>
<td>2</td>
<td>240</td>
<td>48.1</td>
<td>MeOH: 79 (311) 16 (51)</td>
<td>92</td>
<td>86</td>
</tr>
<tr>
<td>3</td>
<td>280</td>
<td>48.1</td>
<td>MeOH: 71 (280) 25 (79)</td>
<td>93</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>320</td>
<td>49.0</td>
<td>MeOH: 63 (253) 31 (100)</td>
<td>94</td>
<td>72</td>
</tr>
</tbody>
</table>

*50 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 %). GLC area % (mmol); a mixture of disiloxanes obtained in small amount is excluded for simplicity. Yields are based on amount of methanol used. Selectivity to 1a: sum of 1a and 1b.

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

<table>
<thead>
<tr>
<th>entry</th>
<th>feeding rate (mL/min)</th>
<th>reaction mixture (g)</th>
<th>reaction mixture</th>
<th>yield (%)</th>
<th>selectivity to 1a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.25</td>
<td>48.2</td>
<td>MeOH: 79 (312) 16 (51)</td>
<td>92</td>
<td>86</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>48.1</td>
<td>MeOH: 79 (311) 16 (51)</td>
<td>92</td>
<td>86</td>
</tr>
<tr>
<td>6</td>
<td>1.0</td>
<td>46.0</td>
<td>MeOH: 73 (275) 10 (30)</td>
<td>76</td>
<td>90</td>
</tr>
</tbody>
</table>

*50 mL (39.6 g, 1,238 mmol) of methanol was used at 240 °C by varying feeding rate a mixture of elemental silicon (90 wt %), Cu (9.5 wt %), and CuCl (0.5 wt %). GLC area percentage (mol); a mixture of disiloxanes obtained in small amount is excluded for simplicity. Yields are based on methanol used. Sum of 1a and 1b.

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, CuCl2, Cu2O, 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 directreaction 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
Optimization for Feeding Rate of Methanol in the Direct Synthesis of 1a. Direct reaction 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 the same time, dry nitrogen gas introduced at a rate of 200 mL/min. methanol used at each reaction temperature. The results are summarized in Table 1.

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” below, the contact mixtures were prepared using three different amounts of CuCl (0.25, 0.5, and 1.0 wt % based on solid reactants).
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 %.

**Acknowledgments.** This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy and partially by Korea Institute of Science and Technology.

**References**