

Intermediacy of surface silylene in the direct synthesis of methylchlorosilanes

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Abstract

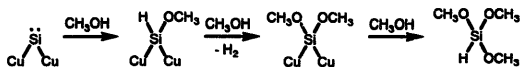
The reaction of silicon with methyl chloride was carried out in the presence of butadiene. The products consisted of 1,1-dichlorosilacyclopent-3-ene, 1-methyl-1-chlorosilacyclopent-3-ene and 1-chlorosilacyclopent-3-ene besides methylchlorosilanes. Silacyclopent-3-enes accounted for 25% of the whole products. The high selectivity for silacyclopent-3-enes indicates that surface silylene is the intermediate in the reaction of silicon with methyl chloride.

Keywords: Silylene; Catalysis; Alkyl halide; Silicon; Copper; Silane

1. Introduction

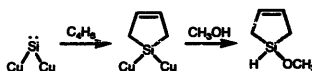
The direct synthesis of methylchlorosilanes from metallic silicon and methyl chloride is the most important process in the silicon industry [1]. Methylchlorosilanes, especially dimethyldichlorosilane, are raw materials for synthesizing silicone polymers. The mechanism of the reaction of silicon with methyl chloride has been examined by many workers [2,3]. However, the mechanism has not been firmly established yet.

Methanol also reacts with metallic silicon to afford trimethoxysilane and tetramethoxysilane in the presence of copper(I) chloride catalyst [4,5]. We have shown that trimethoxysilane was selectively obtained by properly selecting reaction conditions [5]. To explain the exclusive formation of trimethoxysilane, the following reaction mechanism involving surface silylene as a reaction intermediate was proposed [6].



We have verified the intermediacy of surface silylene in the silicon–methanol reaction by trapping surface silylene. For example, the reaction in the presence of butadiene as the trapping reagent gave a trapped product, 1-methoxysilacyclopent-3-ene, with a 3% selectiv-

ity besides trimethoxysilane [6]. The formation of 1-methoxysilacyclopent-3-ene is expressed by the following scheme.



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Here, surface silylene is supposed to be formed by the diffusion of Si atoms through copper overlayers on the silicon surface [6].

Using ethylene or allyl propyl ether instead of butadiene gave the trapped products ethyldimethoxysilane or allyldimethoxysilane respectively in higher yield [6–8].

In the reaction of metallic silicon with methyl chloride, several indications of silylene intermediates were reported.

Lewis et al. observed the strong signal of $m/z = 78$ in the mass spectrum of the products in temperature programmed desorption, when methyl chloride was chemisorbed on the Zn-doped Cu_3Si alloy [2]. They attributed the signal to silylene ($:\text{SiMeCl}$). They also showed that hydrogen can trap the silylene intermediate. The intensity of the signal of $m/z = 78$ was increased 6–15-fold when hydrogen–methyl chloride mixtures were used for the chemisorption [2]. Furthermore, they observed the formation of MeSiH_2Cl when the direct synthesis was carried out with methyl chloride and hydrogen at low methyl chloride conversion in a fixed-bed reactor [2]. From these facts, Lewis et al. proposed the intermediacy of the silylene in the direct synthesis.

Clarke and Davidson attempted to trap silylene intermediates with butadiene [9]. The pulse of the mixture of butadiene and methyl chloride was passed over the Si/Cu contact mass. They could observe the formation of silacyclopent-3-enes. They, however, refuted the importance of the silylene intermediates based on the low reactivity of the silylene species in the gas phase.

In this work, we attempted to trap surface silylene in the direct synthesis with butadiene under continuous flow conditions in a fixed-bed reactor to re-evaluate the role of silylene intermediates in the direct synthesis. The rates of formation of silacyclopent-3-enes, as well as methylchlorosilanes, were quantitatively determined.

2. Experimental

Silicon grains and copper(I) chloride grains were sieved to 45–63 μm . The silicon grains were impregnated with zinc(II) chloride ($\text{Zn/Si} = 0\text{--}2\text{ wt.}\%$) as the promoter. The silicon grains (500 mg, 18 mmol) thus loaded with zinc(II) chloride were vigorously mixed with copper(I) chloride grains ($\text{Cu/Si} = 10\text{--}25\text{ wt.}\%$) in a small vial. The mixture was packed in the fixed-bed flow reactor (quartz tubing: i.d. 10 mm). After the pre-treatment of the mixture was carried out at 723 K in a helium stream for 10 min, methyl chloride (96 kPa) was fed to the reactor at 673 K for 0.5 h to activate the contact mass. After the activation the feed was changed from methyl chloride to a mixture of methyl chloride (32–64 kPa) and butadiene (32–64 kPa). The products were identified by GC-Mass and NMR. The products were analyzed by gas chromatography every 10 min.

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

Silicon conversion (%) =

$$\frac{\text{the sum of moles of products containing silicon atoms}}{\text{moles of silicon charged in the reactor}}$$

Selectivity (%) =

$$\frac{\text{moles of the corresponding product produced}}{\text{the sum of moles of products containing silicon atoms}}$$

Yield (%) =

$$\frac{\text{moles of the corresponding product produced}}{\text{moles of silicon charged in the reactor}}$$

3. Results and discussion

3.1. Time course of the reaction

The reaction of silicon with methyl chloride in the absence of butadiene was carried out at 673 K after the silicon-catalyst mixture was pretreated at 723 K for 10 min. The time courses of the rates of formation of the products are shown in Fig. 1. Dimethyldichlorosilane was formed as the main product, together with methyltrichlorosilane, methylchlorosilane, trimethylchlorosilane and dimethylchlorosilane. The rates increased with increasing time on stream. In particular, the rate of formation of dimethyldichlorosilane increased drastically in the first 15 min. After 4 h the rate of formation of methylchlorosilane increased remarkably, and between 5 and 7.5 h it became the main product. The average selectivities for dimethyldichlorosilane, methylchlorosilane, methyltrichlorosilane, dimethylchlorosilane and trimethylchlorosilane for 7.5 h were 47%, 21%, 21%, 7% and

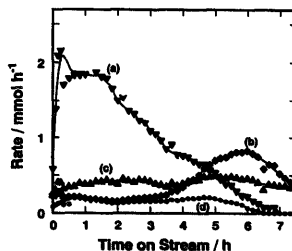


Fig. 1. Time courses of the formation rates of methylchlorosilanes in the reaction of silicon with methyl chloride at 673 K. The amounts of Cu and Zn were 20 wt.% and 1 wt.% respectively; the pressure of methyl chloride was 96 kPa. (a) Dimethyldichlorosilane, (b) methyltrichlorosilane, (c) methylchlorosilane, (d) dimethylchlorosilane.

4% respectively; 82% of silicon was consumed to form these silanes.

The reaction of silicon with methyl chloride in the presence of butadiene was carried out. Fig. 2 shows the changes in the rates of formation of the products with time on stream. After the pretreatment, the reaction started in a stream of methyl chloride under the same reaction conditions as shown in Fig. 1. In 0.5 h, 6% of silicon was converted into the silanes. The feed was changed from methyl chloride to the mixture of butadiene and methyl chloride at 0.5 h. In addition to the products trapped with butadiene (1-methyl-1-chlorosilacyclopent-3-ene (A), 1,1-dichlorosilacyclopent-3-ene (B) and 1-chlorosilacyclopent-3-ene (C)), methylchlorosilanes were also formed. Immediately after the change of the feed, 1-methyl-1-chlorosilacyclopent-3-ene was the main product among the trapped products. Both the rates of formation of 1,1-dichlorosilacyclopent-3-ene and 1-chlorosilacyclopent-3-ene were increased remarkably after 3.5 h and 4.5 h respectively. The fraction of silacyclopent-3-enes in the whole products between 0.5 h and 7.5 h was 10%. The yields of (A), (B) and (C) were 1.9%, 2.5% and 1.6% respectively. The rate of formation of methylchlorosilane increased compared with that in the absence of butadiene in Fig. 1. The formation of silacyclopent-3-enes suggests that surface silylene is the intermediate in the silicon–methyl chloride reaction. The mechanism of formation of silacyclopent-3-enes is speculated to be as follows:

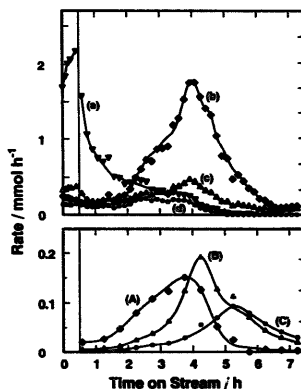
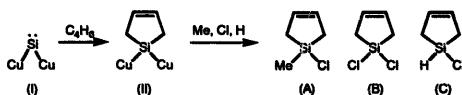
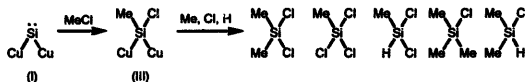


Fig. 2. Changes in the rates of formation of the products in the reaction of silicon, methyl chloride and butadiene at 673 K. The amounts of Cu and Zn were 20 wt.% and 1 wt.% respectively. The pressure of methyl chloride was 96 kPa between 0 and 0.5 h. After 0.5 h, the pressures of methyl chloride and butadiene were 64 kPa and 32 kPa respectively. (a) Dimethyldichlorosilane, (b) methylchlorosilane, (c) methyltrichlorosilane, (d) dimethylchlorosilane, (A) 1-methyl-1-chlorosilacyclopent-3-ene, (B) 1,1-dichlorosilacyclopent-3-ene, (C) 1-chlorosilacyclopent-3-ene.



Surface silylene (I) reacts with butadiene to form the surface species (II). The two Si–Cu bonds of the species (II) are cleaved and Si is combined with Me, Cl or H to form silacyclopent-3-enes. H may be originated from

the decomposition of methyl chloride and/or butadiene on the surface. The mechanism of formation of methylchlorosilanes was speculated.



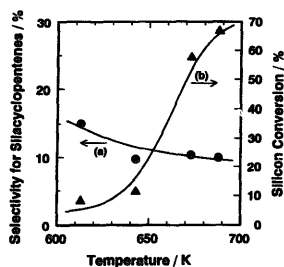


Fig. 3. The effect of reaction temperature on the selectivity for silacyclopent-3-enes (●) and the silicon conversion (▲). The amounts of Cu and Zn were 20 wt.% and 1 wt.% respectively. The pressures of methyl chloride and butadiene were 64 kPa and 32 kPa respectively. Reaction time: 0.5–7.5 h.

Methyl chloride attacks surface silylene (I) and dissociatively adsorbs on silicon to form the surface species (III), which, in turn, reacts with Me, Cl or H fragments to afford methylchlorosilanes. The change in the product distribution with time may be a reflection of the change in the distribution among Me, Cl and H species on the surface with time after adding butadiene to the feed.

3.2. Effects of the reaction conditions on the selectivity for silacyclopent-3-enes

In order to obtain a higher selectivity for silacyclopent-3-enes, the effects of the reaction conditions on the selectivity were examined.

Fig. 3 shows the selectivity for silacyclopent-3-enes and the silicon conversion at various reaction temperatures. When the reaction was carried out at 613 K the silicon conversion was very low (7%). The conversion was higher at higher temperatures, reaching 67% at 688 K. The selectivity for silacyclopent-3-enes decreased with increasing temperature.

The effect of butadiene to methyl chloride ratio on the selectivity for silacyclopent-3-enes was examined. The total pressure of butadiene and methyl chloride was

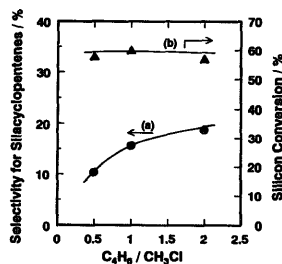


Fig. 4. The effect of the ratio of butadiene to methyl chloride on the selectivity for silacyclopent-3-enes (●) and the silicon conversion (▲). The amounts of Cu and Zn were 20 wt.% and 1 wt.% respectively. The reaction temperature was 673 K. Reaction time: 0.5–7.5 h.

kept at a constant value (96 kPa). The reaction temperature was 673 K. The results are shown in Fig. 4. The selectivity for silacyclopent-3-enes increased with increasing ratio. When the ratio was 2, the selectivity reached 17%. The silicon conversion was almost independent of the ratio (about 60%). The highest yield (9.6%) of the products trapped with butadiene was obtained when the ratio was 2.

The effect of the amount of CuCl was also examined. A constant amount of ZnCl₂ (1 wt.%) was used as the promoter. Fig. 5 shows the changes of the selectivity and the silicon conversion with the amount of Cu. When a larger amount of Cu was used, the conversion was higher, but the selectivity was lower. Thus, the highest yield of silacyclopent-3-enes (9.6%) was obtained by using 20 wt.% of Cu.

The amount of ZnCl₂ as a promoter also affected the silicon conversion. Fig. 6 shows the results using various amounts of ZnCl₂. Without the use of Zn the reaction did not proceed. A loading of 0.5 to 1.0 wt.% ZnCl₂ to silicon gave a high silicon conversion, but a further increase of the loading to 2 wt.% slightly decreased the conversion. The selectivity for silacyclopent-3-enes was hardly affected by the amount of the promoter.

The best result with a high selectivity and a high

Table 1
Product distribution in the best reaction conditions for a high yield of silacyclopent-3-enes

6%	48%	11%	10%	6%	10%	9%
25%						

The amounts of Cu and Zn were 20 wt.% and 1 wt.% respectively. The reaction temperature was 673 K. The pressures of methyl chloride and butadiene were 13 kPa and 83 kPa respectively. The silicon conversion was 55%. Reaction time: 0.5–7.5 h

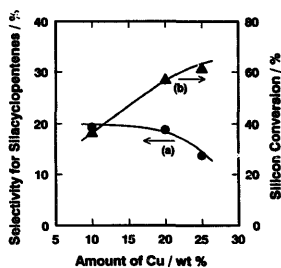


Fig. 5. The effect of the amount of Cu on the selectivity for silacyclopent-3-enes (●) and the silicon conversion (▲). The amount of Zn was 1 wt.%. The reaction temperature was 673 K. The pressures of methyl chloride and butadiene were 32 kPa and 64 kPa respectively. Reaction time: 0.5–7.5 h.

yield of silacyclopent-3-enes is shown in Table 1. Under the conditions described in Table 1, 55% of silicon was consumed between 0.5 to 7.5 h. The selectivity for silacyclopent-3-enes was 25%.

As described above, although Clarke and Davidson found silacyclopent-3-enes as products when they in-

jected a mixture of butadiene and methyl chloride over the Si/Cu contact mass, they refluxed the intermediacy of silylenes based on the low reactivity of gaseous silylenes [9]. However, the results from the pulse experiments did not afford enough analytical data for a quantitative discussion. The high trapping efficiency of the intermediates by butadiene suggests strongly that surface silylene is a real intermediate in the direct synthesis.

4. Conclusions

Silicon mixed with copper(I) chloride as the catalyst reacts with methyl chloride to afford methylchlorosilanes. To confirm the intermediacy of surface silylene in the reaction of silicon with methyl chloride, butadiene was added to the methyl chloride feed as a trapping reagent. 1-Methyl-1-chlorosilacyclopent-3-ene, 1-chlorosilacyclopent-3-ene and 1,1-dichlorosilacyclopent-3-ene were produced in addition to methylchlorosilanes. The selectivity for the silacyclopent-3-enes was as high as 25%. This indicates that surface silylene is the intermediate in the reaction of silicon with methyl chloride.

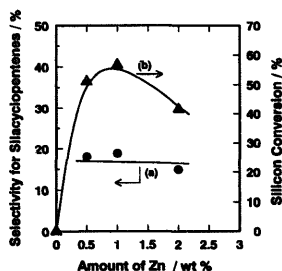


Fig. 6. The effect of the amount of Zn on the selectivity for silacyclopent-3-enes (●) and the silicon conversion (▲). The amount of Cu was 20 wt.%. The reaction temperature was 673 K. The pressures of methyl chloride and butadiene were 32 kPa and 64 kPa respectively. Reaction time: 0.5–7.5 h.

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