Selective synthesis of triphenoxysilane by the reaction of metallic silicon with phenol using copper(I) chloride as the catalyst

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Abstract

When copper(I) chloride was used as a catalyst in the reaction of silicon with phenol, a high selectivity for triphenoxysilane ($HSi(OPh)_3$) (94%) was obtained, the other product being tetraphenoxysilane ($Si(OPh)_4$). Addition of a small amount of propyl chloride to the feed for poisoning metallic copper enhanced the selectivity for $HSi(OPh)_3$ without affecting the rate of silicon consumption. This result indicates that $HSi(OPh)_3$ is an exclusive primary product and that $Si(OPh)_4$ is formed by the secondary reaction between $HSi(OPh)_3$ and phenol. The reaction mechanism involving surface silylene intermediate is proposed for the formation of $HSi(OPh)_3$ as the sole primary product. The intermediacy of surface silylene was confirmed by adding ethylene in the silicon–phenol reaction to give rise to the trapped product ethyldiphenoxysilane, obtained in a 5.8% selectivity.

Keywords: Catalyst; Direct synthesis; Triphenoxysilane; Silicon; Phenol; Organosilane; Copper

1. Introduction

The reaction of metallic silicon with methyl chloride is a basis of the current silicon chemical industry [1]. Therefore, extensive studies have been made on this direct synthesis [1,2].

Metallic silicon also reacts with alcohols (ROH), methanol, ethanol, propyl alcohol and butyl alcohol, to afford trialkoxysilane ($HSi(OR)_3$) and tetraalkoxysilane ($Si(OR)_4$) [3–6]. We have reported that using copper(I) chloride as a catalyst, trialkoxysilanes are selectively obtained by the reactions of silicon with alcohols by properly selecting reaction conditions [5,6]. To explain the exclusive formation of trialkoxysilanes, we have proposed the following reaction mechanism, involving surface silylene intermediate [7]:
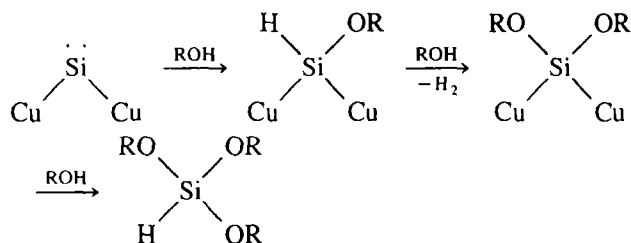
The intermediacy of silylene species was confirmed by the methanol–silicon reaction in the presence of alkenes such as ethylene [7,8] and allyl propyl ether [9]. For example, in the ethylene–methanol–silicon reaction, ethyldimethoxysilane ($HSi(C_2H_5)(OMe)_2$) was formed [7,8].

In contrast to the reaction with methyl chloride or alcohols, the reaction of metallic silicon with phenol has scarcely been reported. Kius and Waterman [10] reported that phenol reacted with silicon fused with metallic copper at 1273 K in a hydrogen atmosphere to form tetraphenoxysilane ($Si(OPh)_4$). Moreover, the yield of $Si(OPh)_4$ was very low (ca. 20%) and there was no formation of triphenoxysilane ($HSi(OPh)_3$), which is more valuable than $Si(OPh)_4$. There has been no report on the direct synthesis of $HSi(OPh)_3$.

In this work, we attempted the reaction of silicon with phenol using copper(I) chloride. The reaction was carried out by feeding phenol vapor to silicon–copper(I) chloride contact mass on the fixed-bed reactor. The effects of reaction variables on the reaction rate and the selectivity of the products were examined in detail. Ethylene was added to the system to trap a plausible silylene intermediate.

It is also shown that $Si(OPh)_4$ can be obtained exclusively with a high silicon conversion upon pretreating the contact mass at 723 K.

2. Experimental

Silicon grains (6.0 mmol; purity 99.9%) and copper(I) chloride grains (0.31 mmol) were mixed vigorously in a small vial. The sizes of both grains were sorted into 45–63 μm.

The mixture was placed in the fixed-bed reactor (quartz tube, inner diameter 10 mm). The mixture was heated to the reaction temperature (513–613 K), unless otherwise mentioned, and then phenol dissolved in di-isopropyl ether was fed to the reactor by a motor-driven syringe. Helium was also fed through a flow-meter. The sum of the flow rates of phenol, di-isopropyl ether and helium was 120 mmol h^{-1}. The products were introduced into a di-isopropyl ether trap at the exit of the reactor, and the solution was analyzed by gas chromatography every hour.

The silicon conversion and selectivity are defined as follows:

Conversion (%)

$$= \frac{\text{the sum of moles of products [HSi(OPh)}_3 \text{ and Si(OPh)}_4]}{\text{moles of metallic silicon packed in the reactor}}$$

$\times 100$

Selectivity(%)

$$= \frac{\text{moles of HSi(OPh)}_3 \text{ produced}}{\text{the sum of moles of products [HSi(OPh)}_3 \text{ and Si(OPh)}_4]}$$

$\times 100$

3. Results and discussion

3.1. Effect of reaction temperature

The reaction of silicon (6.0 mmol) with phenol using copper(I) chloride catalyst was carried out at 533 K. HSi(OPh)$_3$ and Si(OPh)$_4$ were formed. Fig. 1 shows the changes in rate of formation of phenoxysilanes (HSi(OPh)$_3$ and Si(OPh)$_4$), cumulative silicon conver-
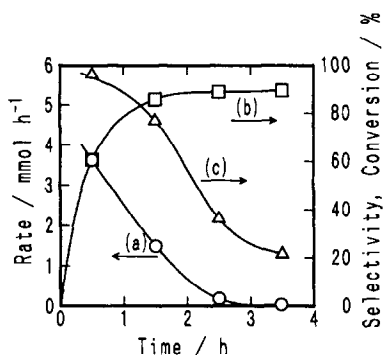

Fig. 1. Time courses of (a) the rate of phenoxysilane formation, (b) the cumulative silicon conversion and (c) the selectivity for HSi(OPh)$_3$ at 533 K. Silicon 6.0 mmol, copper(I) chloride 0.31 mmol, phenol 26 kPa.
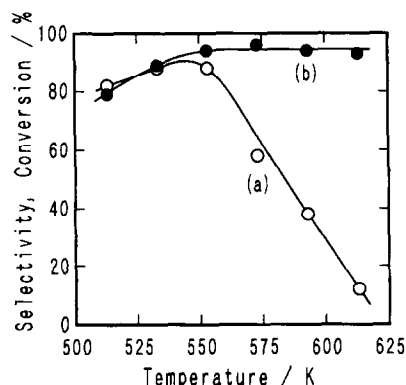

Fig. 2. Effect of reaction temperature on (a) the selectivity for HSi(OPh)$_3$ and (b) the silicon conversion. Silicon 6.0 mmol, copper(I) chloride 0.31 mmol, phenol 26 kPa.

sion and selectivity for HSi(OPh)$_3$ with time on stream. For the first hour, 3.7 mmol of silicon reacted, the main product being HSi(OPh)$_3$ (95% selectivity). The rate decreased with time and the reaction stopped after 4 h. The cumulative silicon conversion reached 85%. The selectivity for HSi(OPh)$_3$ decreased with time. The overall selectivity for HSi(OPh)$_3$ was 90% in 4 h.

The reactions were carried out at various temperatures. The results are shown in Fig. 2. The cumulative silicon conversion until the reaction stopped increased with increasing reaction temperature. Above 553 K, the conversion reached about 95%. The selectivity for HSi(OPh)$_3$ was lower at higher temperatures. The overall selectivity was very low (12%) at 613 K. The highest yield of HSi(OPh)$_3$ (84%) was obtained at 553 K, where the time course is shown in Fig. 1.

3.2. Effect of preheating the contact mass

The effect of preheating temperature on silicon conversion and selectivity was examined for the silicon–phenol reaction. The silicon–copper(I) chloride mixture was heated at 723 or 553 K for 1 h, and then the reaction was started by feeding phenol at a partial pressure of 26 kPa. At 723 K of preheating, the reaction ceased after 8 h, when the silicon conversion was 98%. The product was almost exclusively Si(OPh)$_4$. At 553 K of preheating, the reaction ceased after 4 h, where the silicon conversion was 78%. The selectivity for HSi(OPh)$_3$ was high at the beginning, but decreased with reaction time. The overall selectivity for HSi(OPh)$_3$ was 87%.

It is clear that the selectivity can be controlled by selecting the preheating temperature of the contact mass. This phenomenon is very similar to the one observed in the silicon–methanol reaction [5].

As described in the previous section, the silicon conversion was 94% and the selectivity for HSi(OPh)$_3$ was 89% without preheating treatment. Therefore, the

preheating treatment was not carried out for the rest of the experiments.

3.3. Effect of phenol pressure

The effect of phenol pressure on the reaction was examined. The phenol pressure was changed, while keeping the total feed rate at 120 mmol h^{-1} by changing the helium pressure. Fig. 3 shows the changes in selectivity for HSi(OPh)$_3$ and silicon conversion with phenol pressure. The selectivity for HSi(OPh)$_3$ increased with increasing phenol pressure and reached a maximum (89%) at 26 kPa. Above 26 kPa the selectivity decreased. The silicon conversion was 94% at 26–38 kPa. The highest yield of HSi(OPh)$_3$ (84%) was obtained at the phenol pressure of 26 kPa.

3.4. Reaction path to Si(OPh)$_4$

As described above, the selectivity for HSi(OPh)$_3$ depended very much on the reaction conditions such as temperature and preheating of the contact mass.

In the silicon–methanol reaction, we have reported that HSi(OMe)$_3$ is an exclusive primary product and that Si(OMe)$_4$ is the secondary product by reaction of HSi(OMe)$_3$ with methanol over metallic copper, which is formed during the reaction [7]. Addition of thiophene or alkyl chloride, which is a poison for metallic copper, to the methanol feed led to the high selectivity for HSi(OMe)$_3$ [7].

The XRD analysis of the contact mass showed that metallic copper was formed during the silicon–phenol reaction. Therefore, it is plausible that Si(OPh)$_4$ is produced by the reaction of HSi(OPh)$_3$ with phenol catalyzed by metallic copper.

In order to poison metallic copper, propyl chloride (1/30 of phenol) was added to the phenol feed. The results at 553 K are shown in Fig. 4. The selectivity increased sharply by adding propyl chloride. The over-
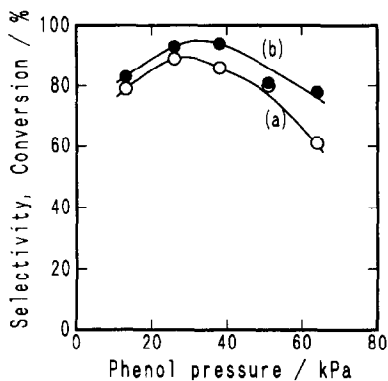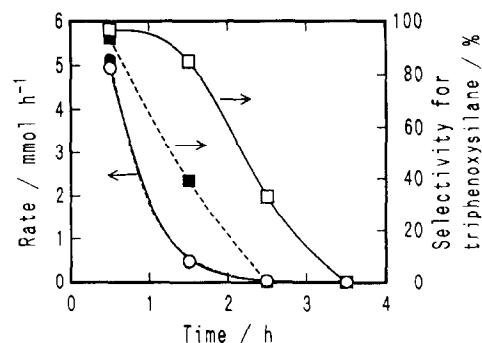
Fig. 4. Effect of addition of propyl chloride on the rate and selectivity for HSi(OPh)$_3$. Silicon 6.0 mmol, copper(I) chloride 0.31 mmol, phenol 26 kPa, reaction temperature 553 K. Solid lines: propyl chloride 0 kPa, rate (O), selectivity for HSi(OPh)$_3$ (□). Dashed lines: propyl chloride 0.87 kPa, rate (●), selectivity for HSi(OPh)$_3$ (■).

all selectivity increased to 95% in the presence of propyl chloride, while it was 89% in the absence of the chloride. In contrast to the selectivity, the reaction rate or silicon conversion was kept constant with or without propyl chloride. This indicates that propyl chloride does not affect the rate of formation of the primary product, but affects the conversion of the primary product to the secondary one.

In summary, the improvement in selectivity indicates that HSi(OPh)$_3$ is an exclusive primary product in the silicon–phenol reaction and that Si(OPh)$_4$ was formed by reaction of HSi(OPh)$_3$ with phenol by metallic copper.

3.5. Reaction mechanism

As described above, HSi(OPh)$_3$ and HSi(OMe)$_3$ are exclusive primary products in the silicon–phenol and silicon–methanol reactions respectively. Therefore, we propose the following reaction mechanism, which is similar to that for the silicon–methanol reaction [7]:
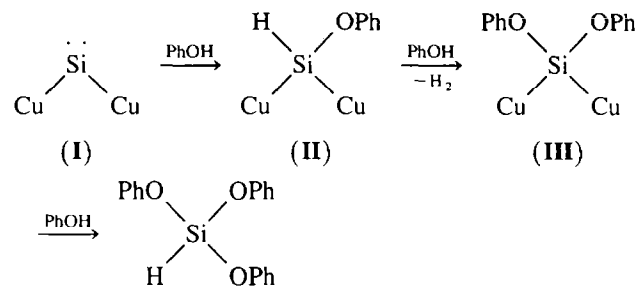
The surface silylene intermediate **I** was formed on the silicon–copper intermetallic phase during the silicon–phenol reaction. Surface silylene **I** reacts with phenol to form the surface species **II**, which is converted into species **III** by reacting further with phenol to substitute

Fig. 3. Effect of phenol pressure on (a) the selectivity for HSi(OPh)$_3$ and (b) the silicon conversion. Silicon 6.0 mmol, copper(I) chloride 0.31 mmol, reaction temperature 553 K.

PhO for H, accompanying desorption of hydrogen. The two Si–Cu bonds of the species **III** are then simultaneously cleaved by the attack of a phenol molecule to form HSi(OPh)$_3$.

3.6. Intermediacy of surface silylene

To confirm the intermediacy of surface silylene, trapping of surface silylene with ethylene was attempted, as in the case of the silicon–methanol reaction. If surface silylene was formed during the reaction, the following series of elementary reactions should lead to the formation of ethyldiphenoxysilane (HSi(C$_2$H$_5$) (OPh)$_2$):
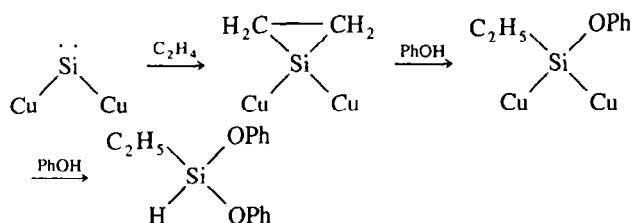
The reaction of silicon with phenol (26 kPa) in the presence of ethylene (40 kPa) was carried out at 513 K. HSi(C$_2$H$_5$)(OPh)$_2$ was formed together with HSi(OPh)$_3$ and Si(OPh)$_4$. The selectivity for HSi(C$_2$H$_5$)(OPh)$_2$ was 2.5%. The formation of HSi(C$_2$H$_5$)(OPh)$_2$ suggests that surface silylene is the intermediate in the silicon–phenol reaction.

Fig. 5 shows the selectivity for HSi(C$_2$H$_5$)(OPh)$_2$ and the silicon conversion at various pressures of ethylene. The phenol pressure was constant at 26 kPa. The selectivity proportionally increased with increasing ethylene pressure and reached 4.5% at 60 kPa. The fact that the increase in selectivity is proportional to the ethylene pressure indicates that the reaction of surface
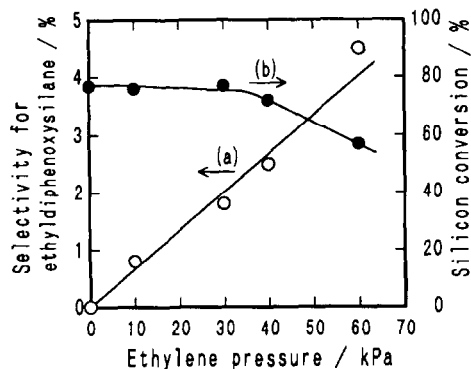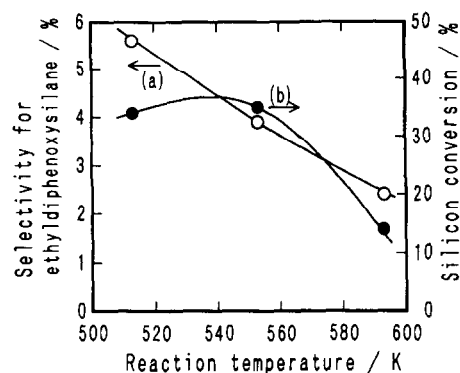

Fig. 6. Effect of reaction temperature on (a) the selectivity for HSi(C$_2$H$_5$)(OPh)$_2$ and (b) the silicon conversion. Silicon 6.0 mmol, copper(I) chloride 0.31 mmol, phenol 26 kPa, ethylene 81 kPa.

silylene with ethylene is competitive with the reaction with phenol. The silicon conversion slowly decreased from 80% to 57% with increasing ethylene pressure.

The effect of reaction temperature was also examined. The results are shown in Fig. 6. When the reaction temperature was 513 K, a high selectivity for HSi(C$_2$H$_5$)(OPh)$_2$ (5.8%) was obtained. The selectivity decreased markedly with increasing temperature. The silicon conversion was low (15%) at 593 K. A low reaction temperature (513 K) gave a high silicon conversion (33%), however, a very long reaction time (14 h) was necessary for the complete reaction. A high selectivity for HSi(C$_2$H$_5$)(OPh)$_2$ (5.8%) strongly indicates the intermediacy of surface silylene in the silicon–phenol reaction.

4. Conclusions

HSi(OPh)$_3$ was obtained in a high yield by the copper(I) chloride catalyzed reaction of metallic silicon and phenol. The reaction mechanism for the selective synthesis of HSi(OPh)$_3$ is essentially the same as that for the silicon–methanol reaction. Addition of ethylene to the silicon–phenol reaction gave HSi(C$_2$H$_5$)(OPh)$_2$ in a 5.8% selectivity. This indicates the intermediacy of surface silylene in the silicon–phenol reaction.

Si(OPh)$_4$ was also obtained exclusively with a high silicon conversion by pretreating the contact mass at 723 K.

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Fig. 5. Effect of ethylene pressure on (a) the selectivity for HSi(C$_2$H$_5$)(OPh)$_2$ and (b) the silicon conversion. Silicon 6.0 mmol, copper(I) chloride 0.31 mmol, reaction temperature 553 K, phenol 26 kPa.

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