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Direct synthesis of alkyldialkoxysilanes by the reaction of silicon, alcohol and alkene using a high-pressure flow reactor

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Abstract

In the reaction of silicon, methanol and ethylene, use of a high-pressure flow reactor operating at 240°C at 0.86 MPa of ethylene and 0.18 MPa of methanol gave a 33% selectivity for ethyldimethoxysilane, which was much higher than that using an atmospheric-pressure flow reactor (8%) or using an autoclave (4%). The selectivity increased proportionally with the ethylene pressure below 0.5 MPa. This indicates that the addition of ethylene or methanol to a surface silylene intermediate determines the selectivity and that the ethylene addition is a first-order reaction. Above 0.5 MPa the slope of the selectivity change was smaller. By feeding propylene instead of ethylene, *n*- and *iso*-propyldimethoxysilanes were obtained as organosilanes with 15 and 2% of selectivity, respectively. The reaction of silicon, ethanol and ethylene resulted in 28% selectivity for ethyldiethoxysilane at 0.99 MPa of ethylene and 0.21 MPa of ethanol at 240°C. © 2001 Elsevier Science B.V. All rights reserved.

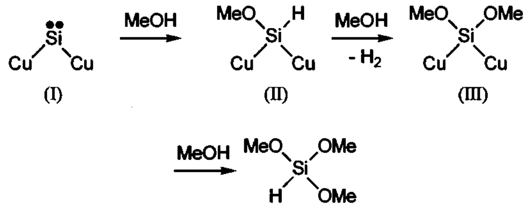
Keywords: Direct synthesis; Organosilane; Metallic silicon; Alcohol; Alkene; Copper catalyst

1. Introduction

A large amount of dimethyldichlorosilane, a monomer for silicone polymers, is industrially synthesized from metallic silicon and methyl chloride using a copper catalyst [1]. However, there is an environmental demerit in this reaction; the reactant, methyl chloride, and the products including hydrogen chloride as by-products are corrosive and harmful. Taking into account of the necessity of an anticorrosive reactor system and an environment, new methods of organosilane synthesis without halides are highly beneficial.

Methanol reacts with metallic silicon to afford trimethoxysilane using copper catalysts [2,3], such as copper(I) chloride [4,5]. We have found that the reaction of silicon with methanol in the presence of ethylene gives ethyldimethoxysilane (selectivity 8%) together with trimethoxysilane [6]. Additionally, use of butadiene instead of ethylene resulted in the formation of 1-methoxysilacyclopent-3-ene.

To explain the formation of trimethoxysilane in the silicon–methanol reaction and the formation of organosilane in the presence of ethylene or butadiene, the reaction mechanism involving silylene intermediate (I) was proposed. Eq. (1) shows the mechanism of trimethoxysilane formation.



(1)

Methanol reacts with surface silylene (I) on the silicon surface to form surface species (II), which is converted to species (III) by further reaction with methanol. Two Si–Cu bonds in the species (III) are simultaneously cleaved by attack of methanol to give trimethoxysilane. Ethylene or butadiene attacks surface silylene (I) to form silacyclopropane species (IV) or silacyclopent-3-ene species (V), and then finally ethyldimethoxysilane or 1-methoxysilacyclopent-3-ene is formed, respectively (Eq. (2)).

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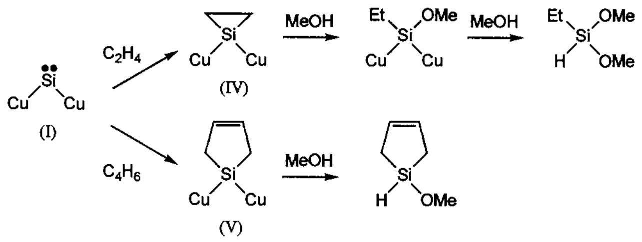


(2)

Adding allyl propyl ether instead of ethylene resulted in a 38% selectivity of allyldimethoxysilane [7]. This strongly indicates the intermediacy of silylene (I).

In the synthesis of ethyldimethoxysilane from silicon, methanol and ethylene, the selectivity for ethyldimethoxysilane is low (8%) using an atmospheric-pressure flow reactor. To improve the selectivity for ethyldimethoxysilane, the liquid-phase reaction in an autoclave had been studied [8]. Ethyldimethoxysilane and ethyltrimethoxysilane were formed as organosilanes together with trimethoxysilane and tetramethoxysilane. The liquid-phase reaction leads to a higher selectivity for the organosilanes (26%) than that obtained using an atmospheric-pressure flow reactor. In the liquid-phase reaction, ethyldimethoxysilane is converted into ethyltrimethoxysilane by the reaction with unreacted methanol over metallic copper and/or a wall of the reactor, because a contact time of ethyldimethoxysilane with methanol is much longer than that in a continuous flow reaction.

Gas-phase kinetics of the addition reaction of dihydrosilylene to ethylene has been studied by a couple of groups [9]. They have reported that the reaction rate of the addition is proportional to the ethylene pressure controlled below an atmospheric pressure. This strongly suggests that the selectivity for ethyldimethoxysilane increases proportionally to the ethylene pressure in the reaction of silicon, methanol and ethylene.

In this work, a high-pressure flow reactor was used for the reaction of metallic silicon with alcohol and alkene at an elevated alkene pressure in order to determine the dependence of the selectivity for organosilane on alkene pressure and to synthesize organosilanes with a high selectivity. Furthermore, the effects of reaction conditions on the selectivity and the yield of organosilane were examined. When propylene as an alkene was used, the formation of two kinds of propyldimethoxysilanes was expected. The effects of temperature and pressure were examined and the mechanism of propyldimethoxysilane formation was discussed.

2. Experimental

Silicon grains (99.9% purity, 45–63 μm) were washed by 46% HF solution for 1 h at room temperature (r.t.) to remove oxide overlayers. The silicon grains and copper(I) chloride grains (99.9% purity, 45–63 μm) were mixed vigorously in a small vial. The mixture containing 9 mmol of silicon and 10 wt % (as copper metal) of the copper catalyst was placed in a stainless-steel tubing (i.d. 9.3 mm) in a high-pressure fixed-bed flow reactor system. An inner wall of the reactor was coated with a thin silicon oxide layer to prevent the formation of copper alloy by the reaction of stainless steel with copper and the by-reactions of reactants and/or products over stainless steel. Prior to the reaction, the silicon–catalyst mixture was heated in a helium stream at 240°C for 1 h at atmospheric pressure, and then the flow was changed to a mixture of helium and ethylene and the total pressure was raised to 1.5 MPa by controlling a back-pressure regulator. Finally, methanol was fed into the reactor by a high-pressure liquid pump through a preheating zone for vaporizing methanol. The products were trapped for 15 min in ethylbenzene cooled by ice. Using 3-methylpentane as an internal standard, the products were analyzed every 15 min by a gas chromatograph equipped with a 2 m long glass column packed with SE-30 and a thermal conductivity detector.

A selectivity, a yield and a silicon conversion are defined by the following equations.

$$\text{Selectivity (\%)} = \frac{\text{Amount of the product (mmol)}}{\text{Sum of amounts of silicon-containing products (mmol)}} \times 100$$

$$\text{Yield (\%)} = \frac{\text{Amount of the product (mmol)}}{\text{Amount of the silicon charged in the reactor (9 mmol)}} \times 100$$

$$\text{Silicon conversion (\%)} = \frac{\text{Sum of amounts of silicon-containing products (mmol)}}{\text{Amount of the silicon charged in the reactor (9 mmol)}} \times 100$$

3. Results and discussion

3.1. Ethyldimethoxysilane synthesis from silicon, methanol and ethylene

3.1.1. Time course of the reaction

After the mixture of silicon and the catalyst was heated at 240°C for 1 h in a helium stream, the reaction of silicon, methanol and ethylene was carried out at 240°C. The total pressure was 1.0 MPa consisting of 0.15 MPa of methanol, 0.72 MPa of ethylene and 0.13 MPa of helium as a balance gas. Ethyldimethoxysilane and trimethoxysilane were formed together with small amounts of ethyltrimethoxysilane, methyldimethoxysilane and tetramethoxysilane. Fig. 1 shows the time courses of formation rates of the products and a cumulative silicon conversion. All the rates increased with reaction time toward maxima around 1 h and then decreased. The reaction stopped at 4.25 h and the silicon conversion reached 63%. A 30% selectivity for ethyldimethoxysilane was obtained, the product distribution being trimethoxysilane (61%), ethyltrimethoxysilane (4%), methyldimethoxysilane (3%) and tetramethoxysilane (2%). A much higher selectivity for ethyldimethoxysilane using a high-pressure flow reactor was obtained compared to 8 and 4% using an atmospheric-pressure flow reactor [6] and an autoclave [8], respectively. In the liquid-phase reaction, ethyldimethoxysilane was converted into ethyltrimethoxysilane by the reaction of ethyldimethoxysilane with methanol.

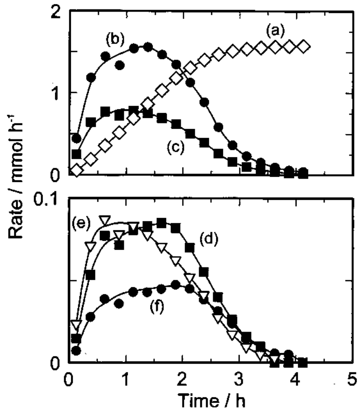


Fig. 1. Changes in the silicon conversion (a) and formation rates of trimethoxysilane (b), ethyldimethoxysilane (c), ethyltrimethoxysilane (d), methyltrimethoxysilane (e) and tetramethoxysilane (f) with reaction time in the reaction of silicon, methanol and ethylene. The pretreatment was carried out at 240°C for 1 h. The reaction temperature was 240°C. Methanol and ethylene pressures were 0.15 and 0.72 MPa, respectively.

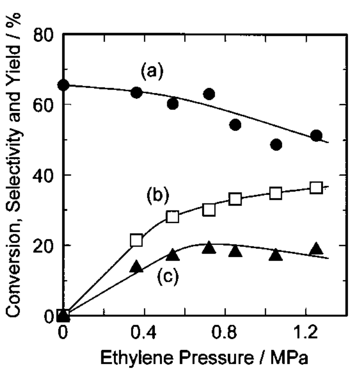


Fig. 2. Effect of ethylene pressure on the silicon conversion (a), the selectivity (b) and yield (c) of ethyldimethoxysilane. The pretreatment was carried out at 240°C for 1 h. The reaction temperature was 240°C. Methanol pressure was 0.15 MPa.

Even comparing with the sum of ethyldimethoxysilane and ethyltrimethoxysilane selectivities (26%) using an autoclave [8], a 30% selectivity for ethyldimethoxysilane using a high-pressure flow reactor was higher.

In our previous work, it has been reported that ethyltrimethoxysilane and tetramethoxysilane are secondary products formed by the reaction of ethyldimethoxysilane and trimethoxysilane with unreacted methanol over copper metal, respectively [8]. Low selectivities for ethyltrimethoxysilane and tetramethoxysilane indicate that use of the flow reactor depresses the secondary reactions.

We have found that the reaction of silicon with methanol at a higher reaction temperature (above 300°C) gives methyldimethoxysilane together with trimethoxysilane and that formaldehyde is a reaction intermediate for methyldimethoxysilane formation [10]. Formation of a small amount of methyldimethoxysilane was observed also in the silicon–methanol–ethylene reaction. It is plausible that the reaction at a high pressure leads to the formation of formaldehyde even at a low temperature and the consequent formation of methyldimethoxysilane.

3.1.2. Dependence of the selectivity for ethyldimethoxysilane on ethylene pressure

The effect of ethylene pressure is shown in Fig. 2. Ethylene pressure was varied from 0 to 1.25 MPa, while methanol pressure was kept at 0.15 MPa. Thus, total pressure was also changed from 1.0 to 1.4 MPa. With increasing ethylene pressure, ethyldimethoxysilane selectivity proportionally increased below 0.5 MPa. Above 0.5 MPa, the slope of the selectivity was smaller and the selectivity was 36% at 1.25 MPa. However, the silicon conversion gradually decreased with ethylene pressure. The yield of ethyldimethoxysilane increased and reached 19% at 0.72 MPa of ethylene pressure above, which it slightly decreased.

Kinetic studies of silylene addition reaction to ethylene have revealed that the addtion is a first-order reaction with respect to ethylene pressure at a low pressure [9]. As shown in Fig. 2, the selectivity for ethyldimethoxysilane proportionally increased with ethylene pressure below 0.5 MPa. According to Eqs. (1) and (2), the selectivity is governed by the reaction of surface silylene with ethylene or methanol. The linear relation between the selectivity for ethyldimethoxysilane and the ethylene pressure shows that the reaction of surface silylene with ethylene is a first-order reaction. This agrees with the literature of the kinetic study [9], indicating that surface silylene reacts with ethylene according to the same mechanism as vapor-phase silylene. On the other hand, above 0.5 MPa of ethylene pressure, the selectivity nonlinearly increased. At a higher pressure, ethylene probably adsorbed and oligomerized on the surface and consequently the selectivity may decrease.

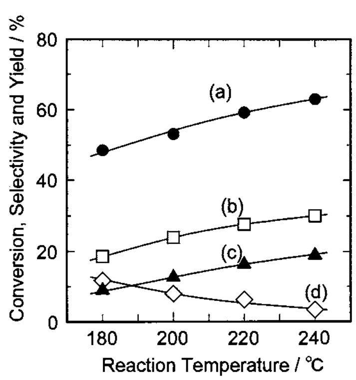


Fig. 3. Effect of reaction temperature between 180 and 240°C on the silicon conversion (a), the selectivity (b) and the yield (c) of ethyldimethoxysilane, and the selectivity for ethyltrimethoxysilane (d). The pretreatment was carried out at 240°C for 1 h. Methanol and ethylene pressures were 0.15 and 0.72 MPa, respectively.

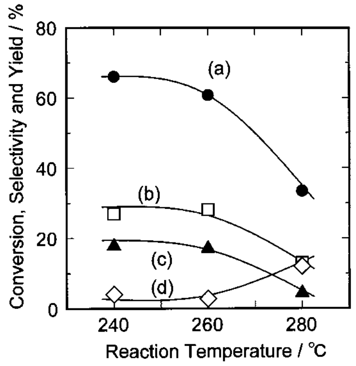


Fig. 4. Effect of reaction temperature above 240°C on the silicon conversion (a), the selectivity (b) and yield (c) of ethyldimethoxysilane, and the selectivity for ethyltrimethoxysilane (d). No pretreatment was carried out. Methanol and ethylene pressures were 0.15 and 0.72 MPa, respectively.

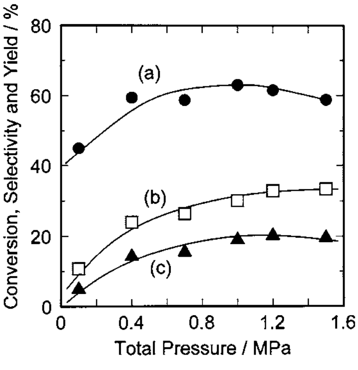


Fig. 5. Effect of total pressure on the silicon conversion (a), the selectivity (b) and yield (c) of ethyldimethoxysilane. The pretreatment was carried out at 240°C for 1 h. The reaction temperature was 240°C. The ratio of ethylene to methanol pressure was 0.72:0.13.

3.1.3. Effects of reaction conditions on the selectivity for ethyldimethoxysilane

After the silicon–catalyst mixture was pretreated at 240°C for 1 h, the reaction was carried out at various temperatures between 180 and 240°C. The results are shown in Fig. 3. The silicon conversion, the selectivity and the yield of ethyldimethoxysilane increased with increasing temperature, while ethyltrimethoxysilane selectivity decreased. We have reported that tetramethoxysilane is formed by a secondary reaction of trimethoxysilane with methanol over metallic copper in the silicon–methanol reaction [6]. It is highly plausible that ethyldimethoxysilane is a sole primary product as an ethylene-added organosilane and that a methoxylation of ethyldimethoxysilane with methanol results in the formation of ethyltrimethoxysilane [8]. The sum of ethyldimethoxysilane and ethyltrimethoxysilane selectivities was almost constant around 33%. This means that the selectivity for ethylene-added organosilanes does not depend on the reaction temperature.

The effect of the reaction temperature above 240°C was examined with no pretreatment. As shown in Fig. 4, the silicon conversion declined to 34% at 280°C and the selectivity and the yield of ethyldimethoxysilane were also low at 280°C. At 240 and 260°C, the sum of ethyldimethoxysilane and ethyltrimethoxysilane selectivity was almost same, while at 280°C it slightly decreased. The selectivity for secondary products, i.e. ethyldimethoxysilane and tetramethoxysilane, increased with the reaction temperature. Figs. 3 and 4 indicate that a high selectivity and a high yield of ethyldimethoxysilane are obtained at 240°C.

Fig. 5 shows the effect of total pressure. The ratio of ethylene to methanol pressure maintained 0.72:0.15. The selectivity increased with total pressure and 33% selectivity was obtained at 1.5 MPa. The silicon conversion also increased to 63% and then slightly decreased above 1.0 MPa. At 1.2 MPa the maximum yield of ethyldimethoxysilane (20%) was obtained, the silicon conversion and the ethyldimethoxysilane selectivity being 62 and 33%, respectively.

3.2. *n*-Propyldimethoxysilane synthesis from silicon, methanol and propylene

The reaction of silicon, methanol and propylene was carried out using the high-pressure reactor. The changes of the silicon conversion and formation rates of products with reaction time are shown in Fig. 6. *n*-Propyldimethoxysilane, *iso*-propyldimethoxysilane and *n*-propyltrimethoxysilane as propylene-added products were formed together with trimethoxysilane, tetramethoxysilane, methyldimethoxysilane and methyltrimethoxysilane. The *n*-propylsilane was a main product among the propylsilanes. *n*-Propyldimethoxysilane selectivity was 14%, the silicon conversion being 59%.

Fig. 7 shows the effect of propylene pressure. The *n*-propyldimethoxysilane selectivity increased in proportion to propylene pressure and attained 14% at 0.6

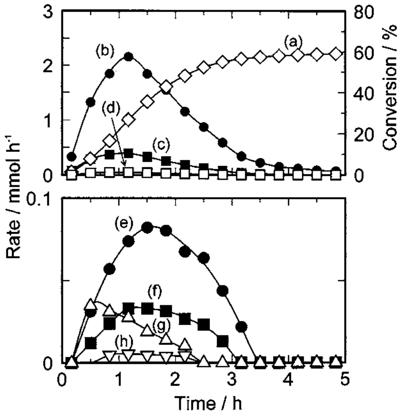


Fig. 6. Changes in the silicon conversion (a) and formation rates of trimethoxysilane (b), *n*-propyldimethoxysilane (c), *iso*-propyldimethoxysilane (d), tetramethoxysilane (e), *n*-propyltrimethoxysilane (f), methyldimethoxysilane (g) and methyltrimethoxysilane (h) with reaction time in the reaction of silicon, methanol and propylene. The pretreatment was carried out at 240°C for 1 h. The reaction temperature was 240°C. Methanol and propylene pressures were 0.10 and 0.60 MPa, respectively.

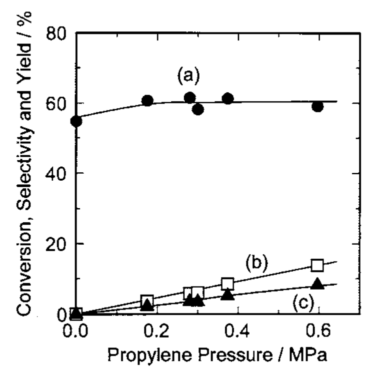


Fig. 7. Effect of propylene pressure on the silicon conversion (a), the selectivity (b) and yield (c) of *n*-propyldimethoxysilane. The pretreatment was carried out at 240°C for 1 h. The reaction temperature was 240°C. Methanol pressure was 0.10 MPa.

MPa. This result also indicates that the addition of propylene to surface silylene is a first-order reaction. The silicon conversion was almost constant around 60%. The ratio of *n*-propyl to *iso*-propyldimethoxysilane did not depend on the pressure, and was around 9.

The effect of the reaction temperature is shown in Fig. 8. The pretreatment of the silicon–catalyst mixture was carried out for 1 h at the same temperature as the reaction. The *n*-propyldimethoxysilane selectivity increased with the temperature and reached 14% between 220 and 240°C and the formation of *n*-propyldimethoxysilane almost stopped at 280°C. The silicon conversion reached 59% at 240°C and then decreased. The maximum of *n*-propyldimethoxysilane yield was 8% at 240°C. The ratio of *n*-propyl to *iso*-propyldimethoxysilane significantly changed with the reaction temperature. The ratio was very high (10) at 220°C, however, an increase of temperature decreased the ratio to 4 at 280°C. When methanol pressure was reduced to a half (52 kPa) at 240°C, both *n*-propyldimethoxysilane selectivity and the silicon conversion increased to 15 and 82%, respectively. A 12% of *n*-propyldimethoxysilane yield was obtained.

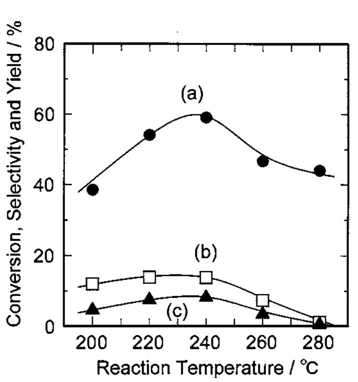
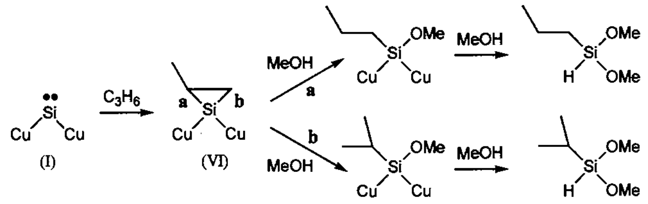


Fig. 8. Effect of reaction temperature on the silicon conversion (a), the selectivity (b) and yield (c) of *n*-propyldimethoxysilane. The pretreatment was carried out for 1 h at the same as the reaction temperature. Methanol and propylene pressures were 0.10 and 0.60 MPa, respectively.

The speculated mechanism of propyldimethoxysilanes formation is shown in Eq. (3).



(3)

Propylene reacts with surface silylene (I) to form methylsilacyclopropane species (VI), which is attacked by methanol to cleave either Si–C bond **a** or **b** in the species (VI). Cleavage of bond **a** or **b** governs a selectivity for the propylsilanes. If bond **a** is cleaved, then *n*-propylsilane is formed. On the other hand, cleavage of bond **b** leads to the formation of the *iso*-propylsilane. It has been reported that 1-methyl-1-phenyl-2-hexylsilacyclopropane produced by the reaction of methylphenylsilylene and 1-octene is methanolyzed to form 2-(methylphenylmethoxysilyl)octane, an *iso*-product; *iso*-/*n*-ratio is 7.0 [11]. When allyltrimethylsilane is used instead of 1-octene, 1-trimethylsilyl-2-(methylphenylmethoxysilyl)propane, which is an *iso*-product, is mainly obtained [11]. These results do not correspond with the result of methanolysis of species (VI), probably because of difference between a gas-phase and a surface methanolysis. We have reported that the reaction of silicon, hydrogen chloride and propylene for synthesizing propyldichlorosilanes gives mainly *iso*-propyldichlorosilane [12]. Key steps of organosilane formation in the silicon–HCl–propylene and silicon–methanol–propylene reactions are same, i.e. the reaction of surface silylene with propylene. The selectivity for *n*- or *iso*-product is determined by a kind of molecule attacking the species (VI) and the reaction temperature. In the silicon–methanol–propylene reaction, the *iso*-/*n*-ratio was constant when the propylene pressure was changed. This result indicates that propylene addition is not the step for determination of the selectivity for *iso*- or *n*-product. This is in agreement with the reaction mechanism shown in Eq. (3).

3.3. Ethyldiethoxysilane synthesis from silicon, ethanol and ethylene

Ethyldiethoxysilane was obtained with a high selectivity by the reaction of silicon, ethanol and ethylene. When the reaction was carried out at 0.99 MPa of ethylene and 0.21 MPa of ethanol at 240°C, ethyldiethoxysilane with a 28% selectivity was formed together with triethoxysilane (61%), tetraethoxysilane (2%), ethyltriethoxysilane (5%), diethylethoxysilane (3%) and diethyldiethoxysilane (1%). The silicon conversion was 46% and the yield of ethyldiethoxysilane was 13%.

4. Conclusions

Use of a high-pressure flow reactor enhanced the selectivity for organosilane in the reaction of silicon, alcohol and alkene. The reaction of silicon, methanol and ethylene under high-pressure conditions resulted in 33% selectivity for ethyldimethoxysilane, which is much higher than that under atmospheric conditions or using an autoclave reactor. The examination of the relation between the selectivity for alkyldimethoxysilane and alkene pressure revealed that the addition of surface silylene intermediate to alkene is a first-order reaction and that the mechanisms of the reactions of alkene with vapor-phase silylene and surface silylene are the same. Use of propylene gave *n*-propyldimethoxysilane as a main product among organosilanes, the selectivity for *n*-propyldimethoxysilane being 15%. The silicon–ethanol–ethylene gave ethyldiethoxysilane with 28% selectivity.

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