NOTES *Bull. Chem. Soc. Jpn.,* ***64****, 3445—3447 (1991)*

Direct Synthesis of Trimethoxysilane from Methanol and Hydrogen-Treated Silicon Using Copper(II) Chloride as a Catalyst

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(Received April 9, 1991)

Synopsis. When silicon, on which copper(II) chloride was supported, was pretreated under a hydrogen stream at 533 K and brought in contact with methanol at 533 K, trimethoxysilane was formed with an 89% selectivity and a complete silicon conversion in 5.5 h. Pits were formed on the silicon surface, and grew with increasing silicon conversion.

Trimethoxysilane is an important chemical, since various organosilicon compounds can be derived by the reactions of trimethoxysilane and organic compounds. By using a copper compound as a catalyst, trimethoxysilane has been obtained selectively from silicon and methanol. A selectivity of 80—90% for trimethoxysilane has been attained by adding methanol dropwise into a suspension of silicon and copper(I) chloride[1] or copper(II) hydroxide[2] in e.g. dodecylbenzene. By passing methanol vapor through a mixture of silicon–copper(I) chloride–zinc[3] or that of silicon–copper(I) chloride,[4] which was pretreated at 623 K, trimethoxysilane with a selectivity of 84—98% was also yielded.

It is presumed that the reduction of copper(I) chloride powder by silicon (Eq. 1) at the pretreatment stage is involved in the formation of active sites in a silicon–methanol reaction,[3,4] just as in the direct synthesis of methylchlorosilanes from methyl chloride and silicon–copper(I) chloride mixture:[5–8]

$$4\,\mathrm{CuCl} + \mathrm{Si} \longrightarrow 4\,\mathrm{Cu} + \mathrm{SiCl_4}. \qquad (1)$$

The copper thus formed in the atomic form must be very reactive towards silicon to form the alloy on the silicon surface. Copper compounds other than copper(I) chloride can therefore be used as a catalyst if they can be reduced to the active form.

This work concerns a direct synthesis of trimethoxysilane from silicon and methanol in which a copper-based catalyst is supported on silicon. Copper(II) chloride is chosen as the catalyst since it dissolves in methanol. We wish to report here that if the silicon–copper(II) chloride is pretreated under a hydrogen stream, a complete reaction of silicon with methanol to yield trimethoxysilane with high selectivity can be attained.

Experimental

Silicon (Soekawa Chemical Co., Ltd., 99.5% in purity) was used without any cleaning. The silicon was sieved into grains of 45-63 μm, washed with water, and immersed in a methanol solution of copper(II) chloride (Kanto Chemical Co., Inc., guaranteed reagent grade). Evaporation of methanol at room temperature gave a "silicon–copper(II) chloride contact mass", a 0.5 g portion of which was loaded in a fixed-bed flow reactor. After the pretreatment at 533—723 K for 1 h under a helium or hydrogen stream, methanol was fed at 533—553 K by a motor-driven syringe at a rate of 87 mmol $\mathrm{h^{-1}}$. The effluent gas was analyzed automatically every 2.5 min with a gas chromatograph (2 m-long SE-30 column).

Scanning electron micrographs (SEM) were taken using a Hitachi S-510 instrument with an acceleration voltage of 25 kV.

Results and Discussion

Silicon grains both before and after copper(II) chloride (Cu=2.5 wt.%) was supported were examined by a scanning electron microscopy. The silicon grains exhibited a rather smooth surface (Fig. 1a), while each grain of the contact mass had deposits of copper(II) chloride, as exemplified in Fig. 1b.

The formation of copper from the silicon–copper(II) chloride contact mass may be facilitated by hydrogen during the pretreatment stage, since hydrogen may reduce copper(II) chloride directly to copper or copper(I) chloride, which then undergoes reduction to copper, according to Eq. 1. Such an efficient conversion of copper(II) chloride to copper would lead to an enhanced

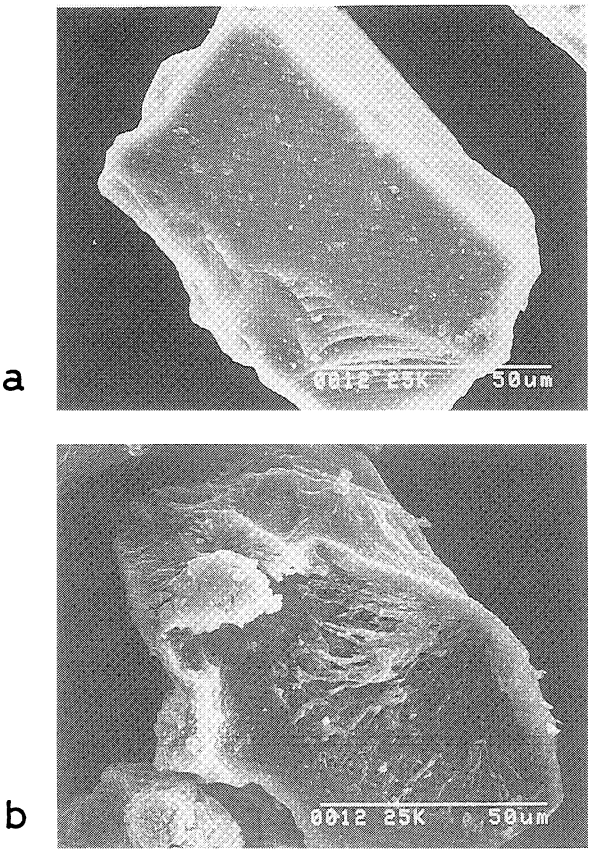

Fig. 1. Scanning electron micrographs of silicon and the silicon–$\mathrm{CuCl_2}$ contact mass. Silicon (a), silicon–$\mathrm{CuCl_2}$ contact mass (Cu=2.5 wt.%) (b). At 1000 magnifications.

reactivity of silicon. Then, the silicon-copper(II) chloride contact mass (Cu=2.5 wt%) was pretreated under a hydrogen stream at several temperatures (533—723 K) and tested for a reaction with methanol at 533 K. The enhancing effect of the hydrogen-pretretreatment on the reactivity of silicon is striking when the pretreatment is carried out at 533 K. Thus, with the hydrogen-pretreatment, a complete silicon conversion was attained in a reaction time of 5.5 h (Fig. 2a); with the helium-pretreatment, however, only 56% silicon conversion was obtained.

In Fig. 3, the rates of formation of methoxysilanes ($(CH_3O)_3SiH+(CH_3O)_4Si$) are plotted against the reaction time. For a pretreatment at 533 K, after an induction period the rate increased and attained a maximum beyond which it decreased, the silicon conversion attaining 100% in 5.5 h. With increasing temperature of the hydrogen-pretreatment, the induction period became shortened and eventually disappeared, and the conversions of silicon to methoyxysilanes decreased. The silicon conversion at 5 h was 72, 35, and 4% at 573, 623, and 723 K of the pretreatment temperature, respectively.

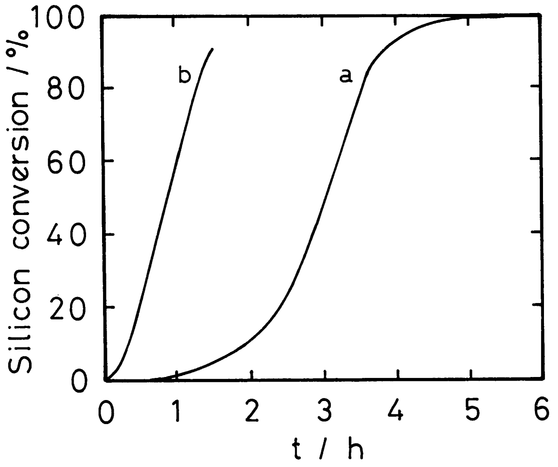

Fig. 2. Change in the cumulative silicon conversion with the reaction time. Pretreatment conditions: Silicon–$CuCl_2$ contact mass (Cu=2.5 wt.%) was pretreated under a hydrogen stream at 533 K (a) and 553 K (b) for 1 h. Reaction conditions: Reaction temperature=533 K (a) and 553 K (b), and CH_3OH=99 kPa.

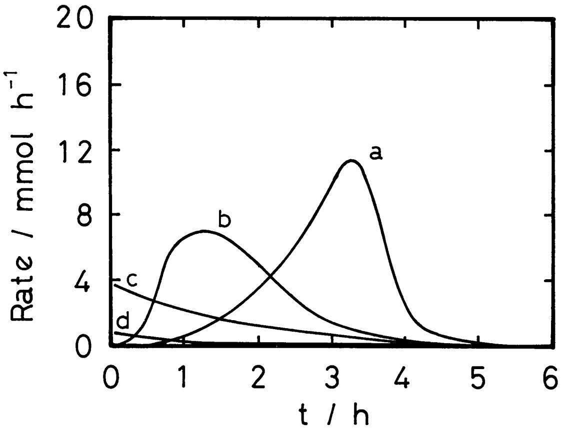

Fig. 3. Effect of hydrogen-pretreatment temperature on the change in the rate of formation of methoxysilanes ($(CH_3O)_3SiH+(CH_3O)_4Si$) with reaction time. Pretreatment conditions: Silicon–$CuCl_2$ contact mass (Cu=2.5 wt%) was pretreated under a hydrogen stream at 533 K (a), 573 (b), 623 K (c), and 723 K (d) for 1 h. Reaction conditions: Reaction temperature=533 K and CH_3OH=99 kPa.

We suppose that hydrogen facilitates the formation of copper on the silicon surface and that such a lower pretreatment temperature as 533 K is favorable for avoiding the agglomeration of the atomic copper and thus for the efficient reaction of the copper with silicon to form active sites for silicon–methanol reaction. A change in the morphology of the contact mass by the hydrogen-pretreatment at 533 K, however, was not detected by a SEM examination.

The selectivity for trimethoxysilane averaged over 5 h was 89, 93, 96, and 94% for pretreatments at 533, 573, 623, and 723 K, respectively.

A very efficient conversion of silicon was achieved at a higher reaction temperature of 553 K. Here, the contact mass (Cu=2.5 wt.%) was pretreated under a hydrogen stream at 553 K. Thus, as shown in Fig. 2b, in only a reaction time of 1.5 h, the silicon conversion attained 91%, the selectivity for trimethoxysilane averaged over the reaction time being 90%.

The change in the morphology of the reacting silicon grains with various levels of silicon conversion was examined. The silicon–copper(II) chloride contact mass (Cu=2.5 wt.%) was pretreated under a hydrogen stream at 533 K for 1 h and brought into contact with methanol vapor at 533 K for 0.6, 1, 3, and 4 h, the silicon conversion being 0.1, 1, 48, and 95%, respectively. The SEM images of the samples are shown in Fig. 4. A striking change in the morphology of silicon grains upon exposure to methanol was observed. Thus, the sample with a 0.1% of silicon conversion contained silicon grains with a pit, as exemplified in Fig. 4a.

With an increase in the silicon conversion, the number of silicon grains having detectable pits increased; silicon grains with irregular outlines accounted for the majority part of silicon grains, as shown Figs. 4b—d. The size of the pits develops with increasing silicon conversion. The silicon–methanol reaction does not occur uniformly on the silicon surface, but starts at areas scattered on the surface. The observation of pits on the silicon surface has a similarity to that in a silicon–methanol[9] or -methyl chloride[7,8] reaction using powdered copper(I) chloride as a catalyst, where active-site formation at the defects or pinholes of SiO_2 overlayer is postulated.

References

1) Japan Kokai Tokkyo Koho 55-28928 (1980); 55-76891 (1980); 57-108094 (1982); 62-96433 (1987).

2) United States Patent 4727173 (1988).

3) United States Patent 3072700 (1963); Deutsche Patent 1127338 (1960).

4) E. Suzuki and Y. Ono, *Chem. Lett.*, **1990**, 47.

5) R. J. H. Voorhoeve and J. C. Vlugter, *J. Catal.*, **4**, 123 (1965).

6) R. J. H. Voorhoeve, "Organohalosilanes: Precursors to

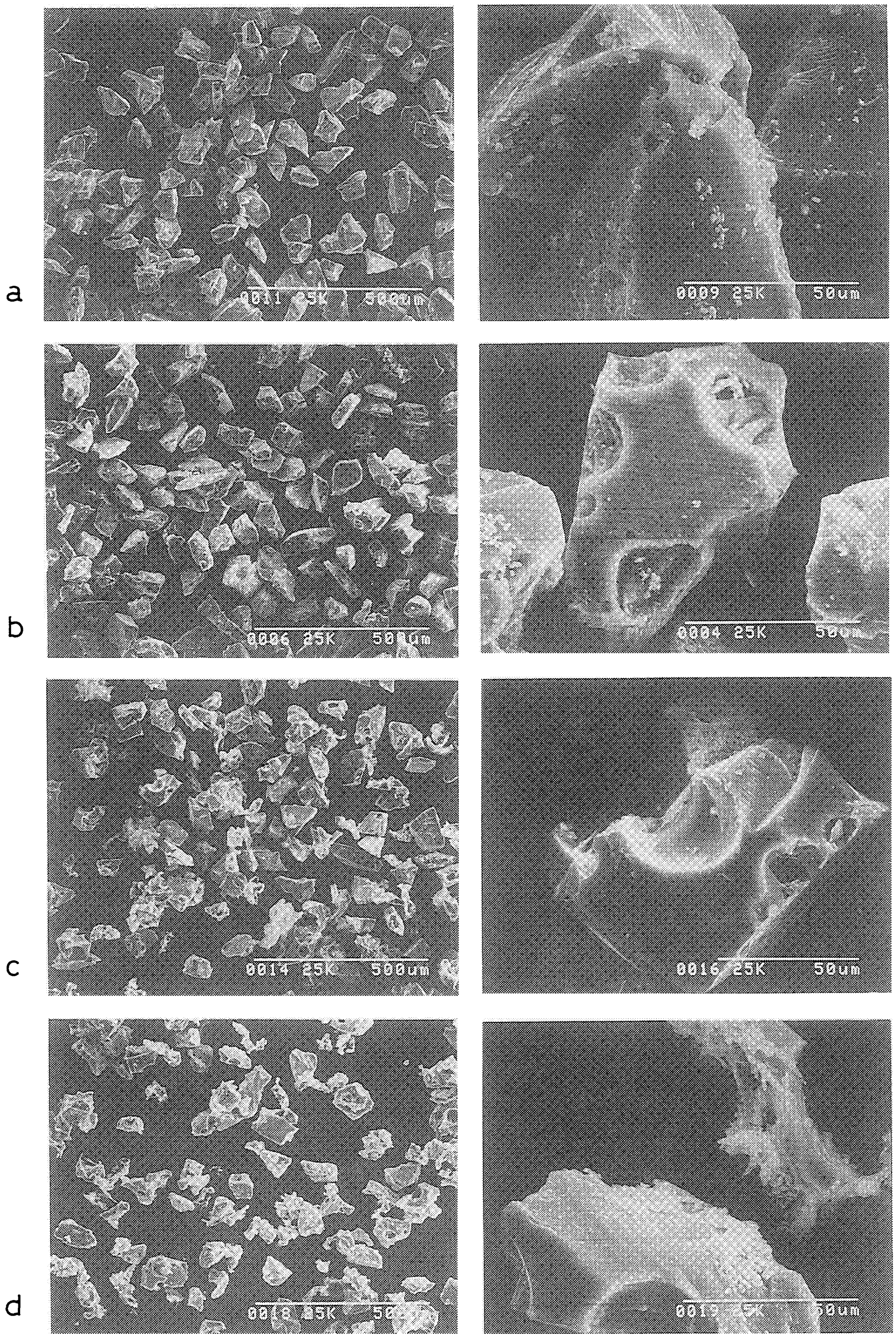

Fig. 4. Scanning electron micrographs of reacting silicon grains with various levels of silicon conversion. Pretreatment conditions: Silicon–$CuCl_2$ contact mass (Cu=2.5 wt%) was pretreated under a hydrogen stream at 533 K for 1 h. Reaction conditions: CH_3OH=99 kPa, reaction temperature=533 K, and reaction time=0.6 h (a), 1 h (b), 3 h (c), and 4 h (d). The left and right plates were obtained at 40 and 1000 magnifications, respectively.

Silicone," Elsevier, Amsterdam (1967).

7) W. F. Banholzer, N. Lewis, and W. Ward, *J. Catal.,* **101**, 405 (1986).

8) W. F. Banholzer and M. C. Burrell, *J. Catal.,* **114**, 259 (1988).

9) E. Suzuki and Y. Ono, *J. Catal.,* **125**, 390 (1990).