Disproportionation of trimethoxysilane over an alumina-supported KF catalyst

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An alumina-supported KF catalyst shows a high activity for the disproportionation of trimethoxysilane to give silane and tetramethoxysilane. Using KF (2–15 mmol g^{-1})/Al_2O_3, a 76% trimethoxysilane conversion was obtained for the reaction at 393 K in a fixed-bed flow reactor.

Keywords: silane, disproportionation, trimethoxysilane, potassium fluoride

1. Introduction

For producing a single crystal of silicon for manufacturing semiconductor devices, high purity is required of the polycrystalline silicon, a precursor of the single crystal. This requirement can be met by using silane, SiH_4, as a starting material for the polycrystalline silicon. Thermal decomposition of silane yields the polycrystalline silicon and hydrogen. Silane is obtained by reacting magnesium silicide, Mg_2Si, with hydrogen chloride or ammonium chloride, or by reacting silicon tetrachloride with lithium aluminium hydride. Disproportionation of chlorosilanes, Cl_nSiH_{4-n}, also gives silane [1].

The route to obtain silane under chlorine-free conditions has been reported. Thus, the disproportionation of alkoxysilanes, such as $(C_2H_5O)_3SiH$ [2] and $(CH_3O)_3SiH$ [3], gives silane and the corresponding tetraalkoxysilane. As the catalysts for the disproportionation reactions, homogeneous catalysts such as C_2H_5ONa are reported [2]. Heterogeneous catalysts can also be used, among which are included an anion-exchange resin, active alumina, molecular sieves, metal oxides, supported metals, and hydrotalcite-like materials [2,3]. Among many types of the heterogeneous catalysts reported, those having basic properties generally give relatively high catalytic performances.

Here, we wish to report that a basic catalyst, an alumina-supported KF, shows high activity for the disproportionation of $(CH_3O)_3SiH$:

$$4(CH_3O)_3SiH \longrightarrow SiH_4 + 3(CH_3O)_4Si \qquad (1)$$

2. Experimental

Trimethoxysilane (Shin-etsu Chemical Co., Ltd.) was used as obtained. Alumina (Merck, 90 aktiv)-supported KF catalyst was prepared by an impregnation method, the loading amount of KF being 1–15 mmol g^{-1}. The catalyst was loaded in a fixed-bed flow reactor (10 mm i.d.), and preheated at 573 K under a helium stream. Trimethoxysilane (21 kPa) was fed by a motor-driven syringe into the reactor at 353–453 K. Propane (9 kPa) and heptane (7 kPa) were also fed as internal standards for analysis of the effluent gas with gas chromatographs.

3. Results and discussion

The reaction was carried out using a KF(2 mmol g^{-1})/Al_2O_3 catalyst at 393 K. In fig. 1 is shown the change in the trimethoxysilane conversion with time on stream. After a slight decrease for 0.5–2 h of time on stream, a steady conversion of 72% continued for the following 2–4 h of time on stream. Only silane and tetramethoxysi-

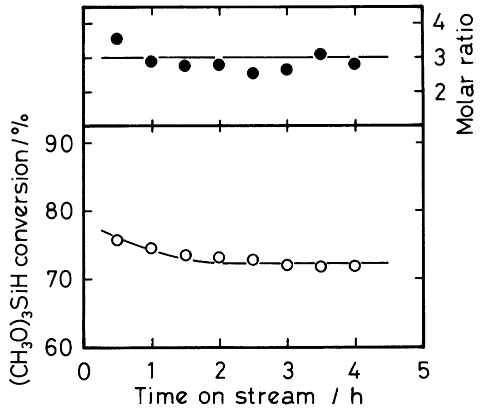

Fig. 1. Conversion of trimethoxysilane and molar ratio of tetramethoxysilane to silane as a function of time on stream. Catalyst: (KF(2 mmol g^{-1})/Al_2O_3 = 0.2 g, reaction conditions: $T = 393$ K, $(CH_3O)_3SiH = 21$ kPa (4.8 mmol h^{-1}), $W/F = 8.6$ g h mol^{-1}. (○) $(CH_3O)_3SiH$ conversion, (●) molar ratio of $(CH_3O)_4SiH$ to SiH_4.

lane were produced, and the molar ratio of tetramethoxysilane to silane is shown also in fig. 1. The ratio did not change practically throughout time on stream, and was very close to three. This shows that the reaction proceeds according to eq. (1).

Using the KF/Al_2O_3 catalysts with various loading amounts of KF, reactions were carried out under the same conditions as those in fig. 1. The results are shown in fig. 2. The pristine alumina with no KF supported gave 30% of conversion at 3 h of time on stream. Loading KF by 1 mmol g^{-1} had a remarkable effect of accelerating the reaction, and the conversion was 59%. At loadings of 2–15 mmol g^{-1}, the conversion did not change practically, and was 76%. Loading KF by 2 mmol g^{-1} is enough for obtaining high catalytic performance. Temperature dependence of the conversion was practically little; the reactions at 353–453 K using the 10 mmol g^{-1} loaded KF/Al_2O_3 catalyst gave the conversion of 76%. Fig. 3 shows the effect of contact time, W/F, on the trimethoxysilane conversion. The conversion increased with W/F and was constant (76%) at 4.3–8.6 g h mol^{-1}. The fact that the conversion does not change at large contact times might show that the reaction practically proceeds to an equilibrium over the KF/Al_2O_3 catalyst.

Some of the catalysts, which have been claimed in the former reports [3] to show the activity for the disproportionation of trimethoxysilane, were tested for the reaction under the same conditions as those in fig. 1. Over silica–alumina, Ru(0.5 wt%)/Al_2O_3, and Pt(0.5 wt%)/Al_2O_3, the reaction proceeded to give conversion of 20, 23, and 42%, respectively. Catalysts having basic properties were also tested. With MgO–Al_2O_3 (prepared by heating hydrotalcite, $Mg_6Al_2(OH)_{16}\,CO_3{\cdot}4H_2O$, at 723 K) and a hydrotalcite-like material having OH^- interstitial anions, $Mg_6Al_2(OH)_{16}(OH)_2{\cdot}4H_2O$, conversions of 56 and 37% were obtained, respectively. In conclusion, KF/Al_2O_3 reported here to show a 76% conversion is a highly effective catalyst.

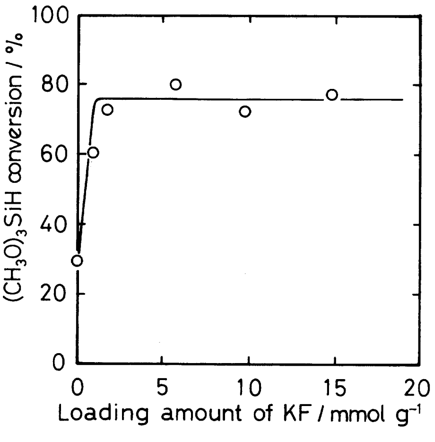

Fig. 2. Effect of loading amount of KF on the trimethoxysilane conversion. Catalyst: KF(2 mmol g^{-1})/Al_2O_3 = 0.2 g, reaction conditions: $T = 393$ K, $(CH_3O)_3SiH = 21$ kPa (4.8 mmol g^{-1}), $W/F = 8.6\,g\,h\,mol^{-1}$.

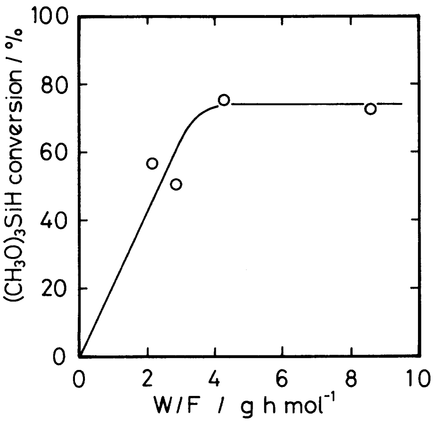

Fig. 3. Effect of contact time on the trimethoxysilane conversion. Catalyst: KF(2 mmol g^{-1})/Al_2O_3, reaction conditions: $T = 393$ K, $(CH_3O)_3SiH = 21$ kPa (4.8 mmol h^{-1}).

On the occurrence of the high catalytic activity of KF/Al_2O_3 as a solid base, fluoride ions are known to play a role of basic sites. Ando et al. [4] and Clark et al. [5] have reported that when KF is loaded on alumina the fluoride ions are present on the alumina surface in a coordinately unsaturated state. Upon the coordination of fluoride ions to hydrosilanes, a pentacoordinate silicon species is formed, which is capable of reacting with carbonyl compounds to invoke hydrosilylations [6,7]. Calcium oxide, a basic oxide, also activates cyanotrimethylsilane to invoke cyanosilylations of carbonyl compounds [8] and ring openings of epoxides [9]. For all the reactions exemplified above to occur, intermediacy of pentacoordinate silicon species has been postulated. The same postulation has been applied also to the reactions of alkoxysilanes such as triethoxysilane with aldehydes or ketones over KF [10] or CaO [11] to yield hydrosilylated products. The present authors suppose that the reaction mechanism involving the pentacoordinate silicon species on the catalyst surface is operative in the reaction reported here. Firstly, the fluoride ions on the surface coordinate with silicon of a trimethoxysilane molecule followed by releasing a nucleophile, CH_3O^-. The CH_3O^- ion thus formed attacks silicon of another trimethoxysilane molecule adsorbed on the catalyst. By this attack, replacement of H^- with CH_3O^- occurs, and tetramethoxysilane and H^- ion are formed. This H^- ion attacks the silicon to form a new Si–H bond and a CH_3O^- ion. Repetition of this replacement of CH_3O^- with H^- results in the formation of silane.

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