Disproportionation of triethylsilane over CaY zeolite

Eiichi Suzuki, Youichi Nomoto, Masaki Okamoto and Yoshio Ono

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

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The disproportionation of triethylsilane over CaY zeolite was examined using a fixed-bed flow reactor. The reactions at 673–723 K gave diethylsilane and tetraethylsilane, the conversion of triethylsilane being 50%. Practically no hydrocarbons were included in the product. The effects of the degree of Ca^{2+} exchange and the reaction variables on the catalytic performance were examined.

Keywords: triethylsilane, disproportionation, CaY zeolite, acid-catalyzed reaction

1. Introduction

Since the pioneering work by Friedel and Ladenburg [1], who found that sodium shows catalytic activity for the disproportionation of triethoxysilane, various catalysts such as sodium ethoxide [2], anion-exchange resins [3], hydrotalcite-like materials [4], KF/Al_2O_3 [5,6] and heat-treated calcium hydroxide [7] have been reported for the disproportionations of triethoxy- and trimethoxysilane. The catalysts for the reaction extend to metal oxides, supported metals, active carbon, active alumina, and molecular sieves [3,8]. Among the catalysts reported, those having basic properties generally show relatively high activity.

For the disproportionation of alkylsilanes, quite different catalysts from those for the above-mentioned alkoxysilane disproportionations have been reported. Russell [9] found that metal halides such as aluminium chloride were the catalysts for the disproportionation of trimethylsilane and ethyltrimethylsilane. Fujisawa and Yamaguchi [10,11] found that strong solid acids such as silica–alumina, alumina, and a superacidic solid, sulfonated ZrO_2, show catalytic activity for the disproportionations of diethylsilane, triethylsilane, and diethyldimethylsilane. The difficulty in performing the disproportionation of alkylsilanes lies in accomplishing the reaction without the formation of hydrocarbons, for example, ethane and ethylene in the reactions using ethyl-substituted silanes as the reactant. Using zeolites such as HX, HY, and CaY zeolites, the reaction of diethyldimethylsilane occurs, and CaY gives far better results than the remaining two zeolites with respect to minimizing the formation of hydrocarbons [12].

In this work, the disproportionation of triethylsilane was found to proceed effectively, whereby hydrocarbons, i.e., ethane and ethylene, were practically not formed (equation (1)). Preliminary experiments by the present authors showed that Y zeolites ion-exchanged with alkaline earth metal, such as MgY, CaY, and BaY, gave a much higher activity than HY. Among the former three zeolites, MgY and BaY showed low activity and/or considerably high deactivation during the reaction in comparison with the catalytic performance of CaY.

$$2(C_2H_5)_3SiH \rightarrow (C_2H_5)_2SiH_2 + (C_2H_5)_4Si \qquad (1)$$

The aim of this work is to show the catalytic performance of CaY zeolite for the reaction, equation (1). Thus, the effects of the degree of Ca^{2+} ion exchange and the reaction variables on the catalytic performance were examined.

2. Experimental

Calcium-exchanged Y zeolites were prepared from NaY zeolite by ion exchange, the degree of ion exchange being 31–67% determined by atomic absorption spectroscopy. A 0.5 g portion of the CaY zeolite was loaded into the fixed-bed flow reactor (10 mm i.d.), and was heated under an inert gas stream at 833 K for 1 h. Triethylsilane (17.7 kPa) as obtained from Shin-etsu Chemical Co., Ltd. was fed into the reactor by a motor-driven syringe at 623–723 K. As internal standards, were also fed propane (9.3 kPa) and heptane (7.0 kPa), the latter being mixed with triethylsilane. The reactor was operated under atmospheric pressure with an inert gas fed as balance. The contact time, W/F, ranged from 4.8 to 23.6 $g\,h\,mol^{-1}$. The effluent gas from the reactor was led to gas chromatographs through stainless-steel pipes and six-way valves, and was analyzed every 30 min. The gas chromatographs were equipped with columns of Porapak S and SE-30 packed in 2 m long glass tubes (2.6 mm i.d.) and with thermal conduction detectors.

3. Results and discussion

Using CaY zeolite with a degree of Ca^{2+} exchange of 67%, the reaction was carried out at 673 K. The conversion of triethylsilane, $(C_2H_5)_3SiH$, as a function of time on stream is shown in figure 1. The conversion changed a little up to 0.5 h of time on stream, after which it attained a steady value of 50% throughout 1–4 h. The yield of

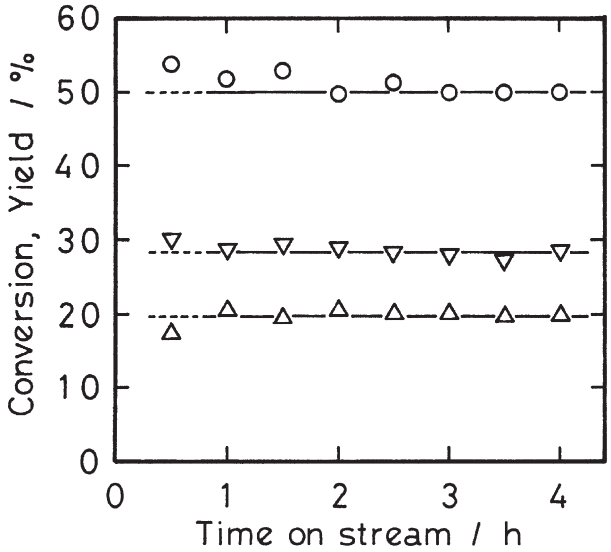

Figure 1. The conversion of triethylsilane and the yield of products as a function of time on stream. CaY zeolite (67% Ca^{2+}-exchanged) $= 0.500$ g. Reaction conditions: reaction temperature $= 673$ K, triethylsilane $= 17.7$ kPa, and $W/F = 23.6$ g h mol^{-1}. The conversion of triethylsilane (○), the yields of diethylsilane (△) and tetraethylsilane (▽).

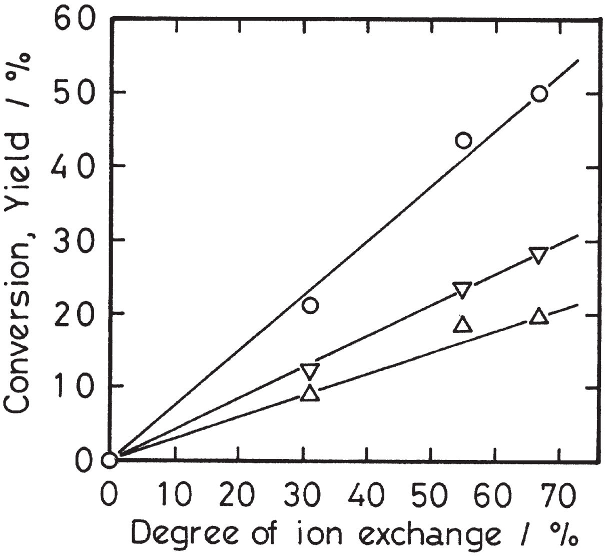

Figure 2. The effect of the degree of ion exchange on the conversion of triethylsilane and the yield of products. CaY zeolite $= 0.500$ g. Reaction conditions and symbols are the same as those in figure 1.

products, diethylsilane, $(C_2H_5)_2SiH_2$, and tetraethylsilane, $(C_2H_5)_4Si$, are also depicted in figure 1. The steady state yields were obtained for 1–4 h of time on stream, and were 20 and 28% for $(C_2H_5)_2SiH_2$ and $(C_2H_5)_4Si$, respectively. As a silicon-containing compound other than $(C_2H_5)_2SiH_2$ and $(C_2H_5)_4Si$, a small amount of SiH_4 was detected in the product. In the product, only trace amounts of C_2 hydrocarbons were detected. The yields of $(C_2H_5)_2SiH_2$ and $(C_2H_5)_4Si$ are in the ratio 1 : 1.4, which deviates from the expected ratio of 1 : 1 on the assumption that the reaction proceeds only according to equation (1). The deviation can be explained by taking into account the transformation of $(C_2H_5)_2SiH_2$ once formed into SiH_4 and $(C_2H_5)_4Si$ according to equation (2).

$$2(C_2H_5)_2SiH_2 \rightarrow SiH_4 + (C_2H_5)_4Si \qquad (2)$$

According to the calculation using the observed conversion of $(C_2H_5)_3SiH$ and yields of $(C_2H_5)_2SiH_2$ and $(C_2H_5)_4Si$, SiH_4 should be formed by 2.5% of the yield based on $(C_2H_5)_3SiH$ fed into the reactor. In fact, the molar amount of SiH_4 in the product was in the order of 10^{-2} of $(C_2H_5)_3SiH$. In conclusion, the reaction proceeds with a steady conversion of $(C_2H_5)_3SiH$, and practically no hydrocarbon is formed. In the subsequent figures, the steady values of the conversion and the yields will be shown.

The reactions were carried out over CaY zeolites with various degrees of Ca^{2+} ion exchange under the same reaction conditions as those in figure 1. Results are shown in figure 2. At 0% of degree of ion exchange, namely using NaY zeolite as a catalyst, the reaction did not proceed at all. With increasing the degree of ion exchange to 67%, the $(C_2H_5)_3SiH$ conversion proportionally increased to 50%. The yields of $(C_2H_5)_2SiH_2$ and $(C_2H_5)_4Si$ also increased proportionally to the degree of ion exchange. At every degree of ion exchange, the total yield of $(C_2H_5)_2SiH_2$ and $(C_2H_5)_4Si$ was almost in accordance with the $(C_2H_5)_3SiH$ conversion, their yields being in the ratio 1 : 1.4, just as observed in figure 1. The CaY zeolite has been known to show acidity as evidenced by the observation of acidic hydroxyl groups upon an infrared absorption measurement [13]. These results indicate that a reaction mechanism involving acid sites of the zeolite is operative. In fact, over solid bases such as alumina-supported potassium fluoride, hydrotalcite heat-treated to be decomposed into mixed magnesium–aluminium oxide [14], and heat-treated hydroxides of magnesium and calcium, the disproportionation of $(C_2H_5)_3SiH$ actually did not proceed. Whether the initiation of the disproportionation of alkylsilanes takes place through a proton addition to the silicon atom occurring on the protonic acid sites or a hydride abstraction on the Lewis acid sites, depends on the nucleophilicity of the silicon atoms of the alkylsilanes [12]. For example, since the silicon atom of $(C_2H_5)_2Si(CH_3)_2$ is more nucleophilic than that of $(C_2H_5)_2SiH_2$, $(C_2H_5)_2Si(CH_3)_2$ is easily activated on the protonic acid sites. In the present work, $(C_2H_5)_3SiH$ is used as the reactant and may be moderately nucleophilic. Then, it is not surprising that $(C_2H_5)_3SiH$ is activated over CaY zeolite, over which the disproportionation is initiated through the protonation of the silicon atom of $(C_2H_5)_3SiH$.

In figure 3, the results of the reactions carried out at various contact times are summarized. The $(C_2H_5)_3SiH$ conversion was 24% at 4.79 g h mol^{-1} of contact time, and it increased monotonously and attained 50% at 23.6 g h mol^{-1} where the contact time is the same as that in figure 1. The yields of $(C_2H_5)_2SiH_2$ and $(C_2H_5)_4Si$ also increased with contact time. At a low contact time of 4.79 g h mol^{-1}, the two yields are close to each other, whereas at high contact times the difference in the two yields becomes apparent.

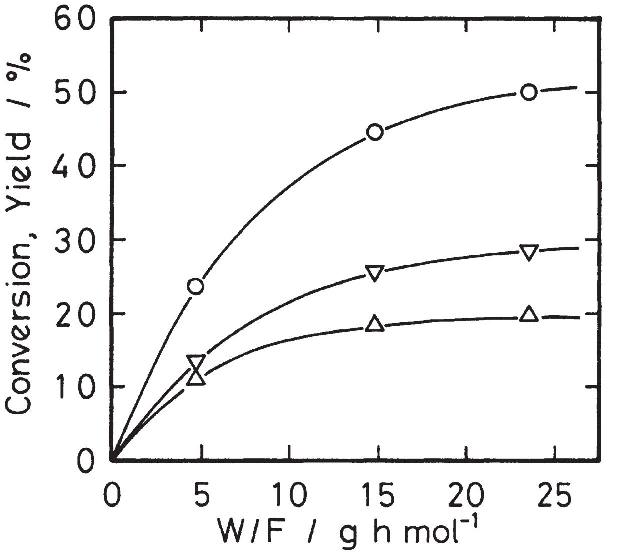

Figure 3. The conversion of triethylsilane and the yield of products at various contact times. CaY zeolite (67% Ca^{2+}-exchanged) = 0.500 g. Reaction conditions: reaction temperature = 673 K and triethylsilane = 17.7 kPa. Symbols are the same as those in figure 1.

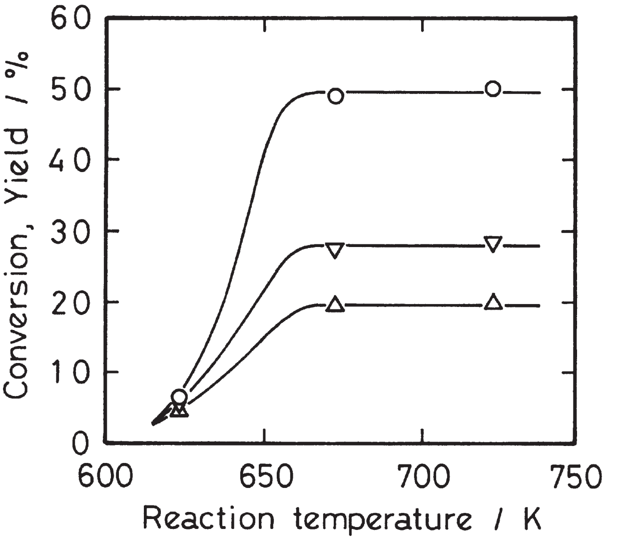

Figure 4. The conversion of triethylsilane and the yield of products at various reaction temperatures. CaY zeolite (67% Ca^{2+}-exchanged) = 0.500 g. Reaction conditions: triethylsilane = 17.7 kPa and W/F = 14.8 g h mol^{-1}. Symbols are the same as those in figure 1.

At low contact time, the reaction proceeds more essentially according to equation (1) and the reaction of equation (2) proceeds little compared with the reaction at high contact times. These results support the assumption that the transformation of $(C_2H_5)_2SiH_2$ according to equation (2) is a secondary reaction.

At various temperatures reactions were carried out using the CaY zeolite with a 67% Ca^{2+} exchange, the contact time being 23.6 g h mol^{-1}. The reactions were carried out at relatively high temperatures of 623–723 K, because Fujisawa and Yamaguchi [12] have found that $(C_2H_5)_3SiH$ does not readily diffuse in the pores of Y-type zeolite at low temperatures in the disproportionation of $(C_2H_5)_2SiH_2$ to yield $(C_2H_5)_3SiH$ and $(C_2H_5)_4Si$. Results are shown in figure 4. At 623 K the conversion of $(C_2H_5)_3SiH$ was only 7%, above which temperature the conversion increased drastically and attained 50% at 673–723 K. In this temperature region, the yield of $(C_2H_5)_2SiH_2$ and $(C_2H_5)_4Si$ was 20 and 28%, respectively, the ratio of the yields being again 1 : 1.4. Besides $(C_2H_5)_2SiH_2$ and $(C_2H_5)_4Si$, a small amount of SiH_4 comparable to that in figure 1 was formed. In addition, only a trace amount of C_2 hydrocarbons was detected in the product. In conclusion, elevation of the reaction temperature has an enhancing effect on the conversion of $(C_2H_5)_3SiH$; even at high temperatures, an almost 100% selectivity for the disproportionation is attained. This advantage has never been encountered in the disproportionation of alkylsilanes [10–12]. The stability of alkylsilane against the formation of hydrocarbons even at high reaction temperatures might be due to the fact that the alkylsilane is in contact with the catalyst for shorter times in the flow reactor as used in this work than in the closed-circulation reactor of the previous works [10–12].

4. Conclusion

The disproportionation of $(C_2H_5)_3SiH$ proceeds over CaY zeolite effectively, whereby practically no hydrocarbons such as ethylene and ethane are formed, the selectivity for the disproportionation being almost 100%. The reactions at 673–723 K under fixed-bed flow conditions with a contact time of 24 g h mol^{-1} give 50% conversions of $(C_2H_5)_3SiH$. The disproportionated products are primarily $(C_2H_5)_2SiH_2$ and $(C_2H_5)_4Si$ in an equimolar amount. A small part of $(C_2H_5)_2SiH_2$ thus formed undergoes further disproportionation giving equimolar amounts of SiH_4 and $(C_2H_5)_4Si$ as secondary products.

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