Diethoxysilane formation by the disproportionation of triethoxysilane over heat-treated calcium hydroxide

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The disproportionation of triethoxysilane was carried out in a fixed-bed flow reactor over the solids obtained by heat-treating calcium hydroxide at various temperatures. In the disproportionation, the reaction proceeding to completeness to afford silane and tetraethoxysilane occurs to far lesser extent: predominantly diethoxysilane is obtained together with tetraethoxysilane. Dimethoxysilane is obtained by the disproportionation of trimethoxysilane also over the heat-treated calcium hydroxide.

Keywords: diethoxysilane, disproportionation, triethoxysilane, calcium hydroxide, dimethoxysilane, trimethoxysilane

1. Introduction

Many reports have, since long, been made on the disproportionation of trialkoxysilanes such as triethoxy- and trimethoxysilanes using a homogeneous or heterogeneous catalyst. Since the pioneering work by Friedel and Ladenburg [1], the disproportionation of triethoxysilane by treatment with a sodium ethoxide or hydroxide catalyst has been disclosed in the patent literature [2]. As for the trimethoxysilane disproportionation, the reaction proceeds over catalysts such as metal oxides, supported metals, active carbon, anion-exchange resins, active alumina, molecular sieves, and hydrotalcite-like materials [3,4]. The present authors have found that an alumina-supported potassium fluoride shows high catalytic activity for the trimethoxysilane disproportionation [5]. In any of the works reported so far, silane and tetraalkoxysilanes corresponding to the reactant trialkoxysilanes were obtained according to eq. (1), but dialkoxysilanes were not produced at all:

$$4(\mathrm{RO})_3\mathrm{SiH} \rightarrow \mathrm{SiH}_4 + 3(\mathrm{RO})_4\mathrm{Si}\,,\quad \mathrm{R} = \mathrm{C_2H_5} \text{ or } \mathrm{CH_3}\,. \tag{1}$$

Dialkoxysilanes can be a starting material for linear silicones, because of their having a one-dimensional structure, in contrast to trialkoxysilanes which give three-dimensional and highly cross-linked silicones.

In the present paper, efficient solid catalysts are reported, over which the disproportionation affording dialkoxysilane does proceed. Thus, according to eq. (2), diethoxysilane is obtained by the disproportionation of triethoxysilane over a heat-treated calcium hydroxide:

$$2(\mathrm{C_2H_5O})_3\mathrm{SiH} \rightarrow (\mathrm{C_2H_5O})_2\mathrm{SiH}_2 + (\mathrm{C_2H_5O})_4\mathrm{Si} \tag{2}$$

The aim of the present work is to examine the heat-treatment and the reaction conditions suitable for the diethoxysilane formation. The heat-treated calcium hydroxide is tested as a catalyst also for the disproportionation of trimethoxysilane to give dimethoxysilane.

2. Experimental

A 0.5 g portion of calcium hydroxide or magnesium hydroxide with high purity grade obtained from Kanto Chemical Co., Inc. was charged in a fixed-bed flow reactor (10 mm i.d.), and was heated under an inert-gas stream at 473–773 K for 1 h. The reactants, triethoxysilane and trimethoxysilane, were used as obtained from Shin-etsu Chemical Co., Ltd. Triethoxysilane (21.0 kPa) or trimethoxysilane (20.0 kPa) was fed into the reactor by a motor-driven syringe at 393 K. As internal standards were also fed propane (9.3 kPa) and heptane (7.0 kPa), the latter being mixed with the reactant. The reactor was operated under atmospheric pressure with an inert gas fed as balance. The contact time, W/F, ranged from 12 to 29 g h mol^{-1}. The effluent gas from the reactor was led to gas chromatographs through stainless-steel pipes and six-way stopcocks, 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

3.1. Disproportionation of triethoxysilane

Over the catalyst obtained by heat-treating calcium hydroxide at 573 K for 1 h, the reaction was carried out at 393 K with a contact time, W/F, of 24 g h mol^{-1}. The conversion of triethoxysilane, $(C_2H_5O)_3SiH$, as a function of time on stream is shown in figure 1. The reaction proceeded practically with a steady conversion of $(C_2H_5O)_3SiH$; a 12% conversion continued throughout 0.5–3.5 h of time on stream. Diethoxysilane, $(C_2H_5O)_2SiH_2$, was formed with a 5% yield during the time on stream. A 6% yield of tetraethoxysilane, $(C_2H_5O)_4Si$, continued, which was higher by 1% than the $(C_2H_5O)_2SiH_2$ yield. If the reaction proceeds according to eq. (2), the same yield of $(C_2H_5O)_4Si$ as that of $(C_2H_5O)_2SiH_2$ should be obtained. The 1% excess in $(C_2H_5O)_4Si$ yield can be a consequence of an actual occurring of the disproportionation to $(C_2H_5O)_4Si$ and silane. Thus, since this disproportionation gives $(C_2H_5O)_4Si$ and silane with a 3 : 1 molar ratio as expressed in eq. (3), silane is to be formed with a 0.3% yield:

$$4(C_2H_5O)_3SiH \rightarrow SiH_4 + 3(C_2H_5O)_4Si \qquad (3)$$

In fact, as also shown in figure 1, the steady formation of silane with a 0.3% yield was observed. The total yield of $(C_2H_5O)_2SiH_2$, $(C_2H_5O)_4Si$, and silane was 11% in practical agreement with the conversion of $(C_2H_5O)_3SiH$, the material balance of silicon being complete during the reaction. In conclusion, the $(C_2H_5O)_3SiH$ disproportionation proceeds mainly according to eq. (2), and to a lesser degree according to eq. (3). The reaction expressed by the latter equation accounts for both the silane formation and the slightly higher yield of $(C_2H_5O)_4Si$ than the $(C_2H_5O)_2SiH_2$ yield.

The heat treatment of calcium hydroxide was carried out at various temperatures, 473–773 K, and the reactions were conducted under the same reaction conditions as those in figure 1. The results are shown in figure 2. For the 473 K heat treatment, the $(C_2H_5O)_3SiH$ conversion was 2%, and $(C_2H_5O)_2SiH_2$ and $(C_2H_5O)_4Si$ were formed, while silane was not at all. The yields of $(C_2H_5O)_2SiH_2$ and $(C_2H_5O)_4Si$ were both 1%. These results show that the reaction proceeds according to eq. (2). At an elevated heat-treatment temperature of 573 K, for which heat-treatment temperature the results have already been shown in figure 1, the $(C_2H_5O)_3SiH$ conversion developed to 12% and $(C_2H_5O)_2SiH_2$ and $(C_2H_5O)_4Si$ were formed with a yield of 5 and 6%, respectively. Together with $(C_2H_5O)_2SiH_2$ and $(C_2H_5O)_4Si$, silane was formed with a yield of 0.3%. The silane formation and the difference in the yields of $(C_2H_5O)_2SiH_2$ and $(C_2H_5O)_4Si$ became evident when the heat treatment had been carried out at 673 K. For this heat-treatment temperature, the $(C_2H_5O)_2SiH_2$ yield attained 14%, though as large an amount of silane as a 2% yield was formed simultaneously. Beyond a maximum in the $(C_2H_5O)_2SiH_2$ yield for the 673 K heat treatment, the $(C_2H_5O)_2SiH_2$ yield decreased to 5% and the silane yield remarkably increased to 12% at 773 K of the heat-treatment temperature. These $(C_2H_5O)_2SiH_2$ and silane yields practically account for the $(C_2H_5O)_4Si$ yield of 44%. The $(C_2H_5O)_3SiH$ conversion increased monotonously up to this heat-treatment temperature, at which it was 62%. In conclusion, the temperature of heat-treating calcium hydroxide is a factor determining whether the $(C_2H_5O)_3SiH$ disproportionation proceeds

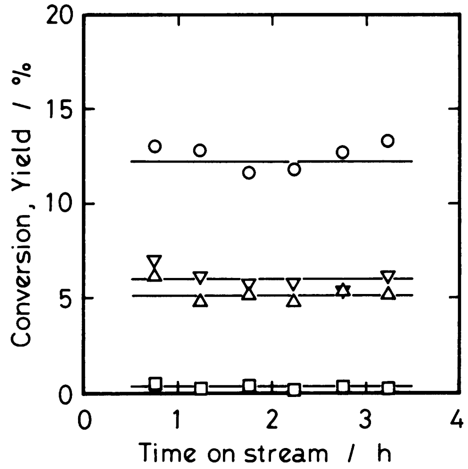

Figure 1. The conversion of triethoxysilane and the yield of products as a function of time on stream. Temperature of heat-treating $Ca(OH)_2 = 573$ K. Reaction conditions: reaction temperature = 393 K and $W/F = 24$ g h mol^{-1}. (○) Triethoxysilane conversion; (△) yield of diethoxysilane, (▽) tetraethoxysilane and (□) silane.

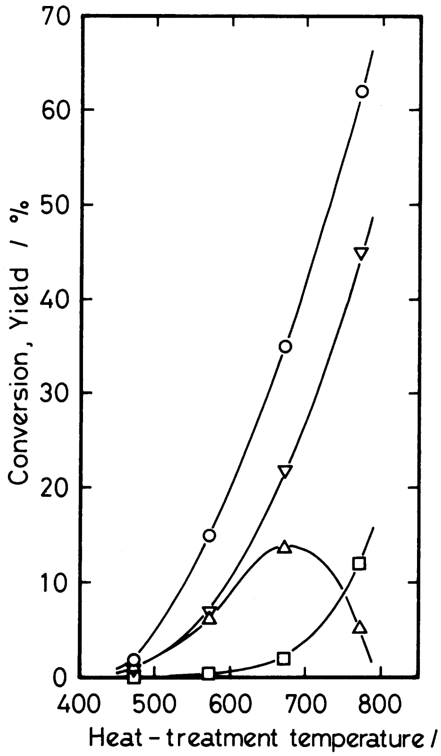

Figure 2. Effect of temperature of heat-treating calcium hydroxide on the conversion of triethoxysilane and the yield of products. Reaction conditions and symbols are the same as those in figure 1.

according to eq. (2) or eq. (3): the 573 K heat-treated calcium hydroxide is an effective catalyst for the $(C_2H_5O)_2SiH_2$ formation with the silane formation as highly suppressed as possible.

A powder X-ray diffraction pattern for the catalyst samples was attributable only to calcium hydroxide when the heat-treatment temperature was 473 or 573 K, while it consisted of a main profile for calcium hydroxide and an additional one for calcium oxide when the temperature was 673 K. For the 773 K heat-treatment, only the pattern assignable to calcium oxide was obtained. The heat-treatment of calcium hydroxide is accompanied by the appearance of basicity on the surface [6]. Thus, only relatively weak basic sites are generated by the 573 K heat-treatment, while both relatively weak and strong basic sites are formed above 673–773 K, in which temperature range the amounts of the basic sites increase and then decrease with the temperature. Among the solids derived from calcium hydroxide, a solid showing lower basicity than that of calcium oxide is an effective catalyst for the disproportionation of $(C_2H_5O)_3SiH$ to afford $(C_2H_5O)_2SiH_2$ and $(C_2H_5O)_4Si$. In fact, over calcium oxide, which had been heat-treated at 723 K, the $(C_2H_5O)_2SiH_2$ yield was only 8% under the same reaction conditions as those in figure 1.

Figure 3 shows the effect of contact time, *W/F*, on the catalytic performance of the 573 K heat-treated calcium hydroxide. With increasing contact time, the $(C_2H_5O)_3SiH$ conversion increased monotonously. Diethoxysilane was formed with the same yield as that of $(C_2H_5O)_4Si$ at the contact time of 12 and 20 g h mol^{-1}. In this region of contact time, no silane was formed at all. These results indicate that the reaction proceeds according to eq. (2). With further increase in the contact time to 29 g h mol^{-1}, the $(C_2H_5O)_2SiH_2$ yield increased, but at the same time, the silane formation became evident and increased. Corresponding to the silane formation, the difference in the yields of $(C_2H_5O)_4Si$ and $(C_2H_5O)_2SiH_2$ became evident. This difference is accounted for by the silane yield multiplied by three. This shows that the disproportionation according to eq. (3) is actually proceeding. In conclusion, at the low contact times, solely eq. (2) is operative, while at the high contact times the reaction proceeds mainly according to eq. (2) and simultaneously according to eq. (3) to a lesser degree.

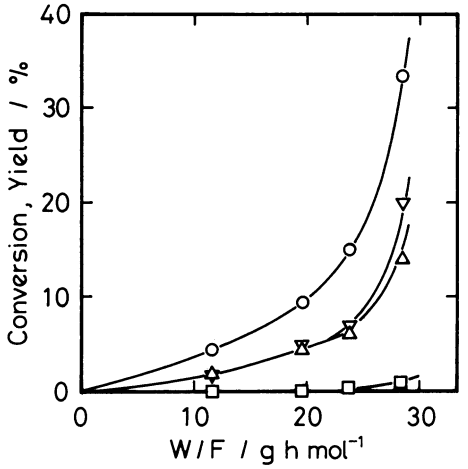

Figure 3. Effect of contact time on the conversion of triethoxysilane and the yield of products. Temperature of heat-treating $Ca(OH)_2 = 573$ K. Reaction conditions: reaction temperature = 393 K. Symbols are the same as those in figure 1.

Also over a heat-treated magnesium hydroxide, $(C_2H_5O)_2SiH_2$ is formed by $(C_2H_5O)_3SiH$ disproportionation. Using the 573 K heat-treated magnesium hydroxide as a catalyst, a 12% yield of $(C_2H_5O)_2SiH_2$ was obtained at 393 K with a contact time of 23 g h mol^{-1}. Similarly to the reaction using calcium oxide as a catalyst, magnesium oxide was a less effective catalyst for the formation of $(C_2H_5O)_2SiH_2$. Thus, only an 8% yield of $(C_2H_5O)_2SiH_2$ was obtained under the same reaction conditions as those for the reaction using the heat-treated magnesium hydroxide catalyst as mentioned above.

3.2. Diethoxysilane formation in relation to reaction mechanism

Upon the coordination of basic sites such as fluoride ions on a KF/Al_2O_3 catalyst to hydrosilanes, the silicon expands its coordination number from four to five to form pentacoordinate species. These hypervalent species are more reactive than the ordinary tetracoordinate silicon compounds, and capable of reacting with carbonyl compounds to invoke hydrosilylations [7,8]. Also on the basic sites of a metal oxide such as CaO, pentacoordinate species is derived from cyanotrimethylsilane. By its reaction with carbonyl compounds the cyanosilylations [9], and with epoxides the ring openings [10], are known to proceed. Alkoxysilanes are also transformed into reactive species by the action of basic sites; for example, triethoxysilane activated over KF [11] or CaO [12] reacts with aldehydes or ketones to yield hydrosilylated products. For the reactions exemplified above, the reaction mechanism involving nucleophiles, which are released from the pentacoordinate species and then attack electrophiles, has been proposed.

The present authors suppose that the reaction mechanism involving the pentacoordinate species on the catalyst surface is operative in the reaction reported here. The silicon of a $(C_2H_5O)_3SiH$ molecule is coordinated by a basic site of the catalyst, followed by releasing a nucleophile, $C_2H_5O^-$. The $C_2H_5O^-$ ion thus formed attacks the silicon of another $(C_2H_5O)_3SiH$ molecule adsorbed on the catalyst. By this attack, replacement of H^- with $C_2H_5O^-$ occurs, and $(C_2H_5O)_4Si$ and H^- ion are formed. This H^- ion attacks the silicon to form a new Si–H bond and a $C_2H_5O^-$ ion. Repetition of this replacement of $C_2H_5O^-$ with H^- results in the formation of $(C_2H_5O)_2SiH_2$ or silane. The fact that the yield of $(C_2H_5O)_2SiH_2$ is preponderant over that of silane is indicative of the disproportionation proceeding to less completeness.

3.3. Disproportionation of trimethoxysilane

In all the works in which the disproportionation of trimethoxysilane, $(CH_3O)_3SiH$, was carried out, dimethoxysilane, $(CH_3O)_2SiH_2$, was not obtained at all, but the products were only tetramethoxysilane, $(CH_3O)_4Si$, and silane [3–5]. As described in the preceding section, when a heat-treated calcium hydroxide is used as a catalyst, $(C_2H_5O)_2SiH_2$ can be obtained from $(C_2H_5O)_3SiH$ by its disproportionation reaction. Then, the heat-treated calcium hydroxide was tested as a catalyst for the disproportionation of $(CH_3O)_3SiH$, aiming at the production of $(CH_3O)_2SiH_2$.

The heat treatment was carried out at 573 K, and the reaction was conducted at 393 K with a contact time of 22 g h mol^{-1}. Dimethoxysilane was obtained with a 9% yield together with $(CH_3O)_4Si$ and silane of which the yields were 31 and 7%, respectively. The 22% difference in the yields of $(CH_3O)_2SiH_2$ and $(CH_3O)_4Si$ is accounted for practically by the silane yield multiplied by three. These results show that the reaction proceeds according to eqs. (4) and (5) similarly to eqs. (2) and (3) for the $(C_2H_5O)_3SiH$ disproportionation described in the preceding section:

$$2(CH_3O)_3SiH \rightarrow (CH_3O)_2SiH_2 + (CH_3O)_4Si \quad (4)$$

$$4(CH_3O)_3SiH \rightarrow SiH_4 + 3(CH_3O)_4Si \quad (5)$$

4. Conclusion

Diethoxysilane is produced from triethoxysilane by its disproportionation when a hydroxide of calcium or magnesium is heat-treated and used as a catalyst. When the heat treatment is carried out at 573 and 673 K, diethoxysilane is obtained with yields of 5 and 14%, respectively, at 393 K. In the reactions with the heat-treatments at 673–773 K, the reaction to afford silane and tetraethoxysilane becomes evident. The contact time is also a key factor for the diethoxysilane formation. At too high contact times the silane yield predominates over the diethoxysilane yield; reactions at moderate contact times of 22–24 g h mol^{-1} give good results. The solid, which is obtained by heat-treating calcium hydroxide at 573 K and shows low basicity, is an effective catalyst for the diethoxysilane formation. This solid is effective as a catalyst also for the dimethoxysilane formation in the disproportionation of trimethoxysilane. The reaction at 393 K gives dimethoxysilane with a 9% yield.

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