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Catalysis by Synthetic Hydrotalcite-like Minerals in a Disproportionation of Trimethoxysilane

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The hydrotalcite-like mineral containing interlayer Cl^- or CH_3O^- anions catalyzed a reaction, $4\ (CH_3O)_3SiH \longrightarrow 3\ (CH_3O)_4Si + SiH_4$. Thus, for example, when 41 mmol of $(CH_3O)_3SiH$ was subjected to the reaction at 323 K for 6 h in the presence of 0.62 g of the mineral containing interlayer CH_3O^- anions (2.0 mmol of CH_3O^- anions), the conversion of $(CH_3O)_3SiH$ was 83%.

Hydrotalcite, $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, is one of the naturally occurring anionic clay minerals.1) Isomorphously substituted minerals, $Mg_6Al_2(OH)_{16}A^{n-}{}_{2/n} \cdot 4H_2O$ ($A^{n-} = Cl^-$, $NO_3{}^-$, $SO_4{}^{2-}$, etc.), generally referred to hydrotalcite-like minerals can be synthesized.2) Here, Mg^{2+} and Al^{3+} cations constitute positively charged hydroxide layers between which water molecules and A^{n-} anions are intercalated, the latter being anion-exchangeable.3) Hydrotalcite and the like thermally decompose into mixed oxides which are known to catalyze several reactions including aldol condensation.4)

Reactions of the exchangeable interlayer anions in the pristine minerals have been reported.5,6) Martin and Pinnavaia5) found that interlayer I^- anions in a hydrotalcite-like mineral, $Zn_2Cr(OH)_6I_2 \cdot 2H_2O$, function as a nucleophile which attacks butyl bromide to give butyl iodide. Halide exchange between organic halides has been demonstrated where interlayer Cl^- anions in a hydrotalcite-like mineral, $Mg_6Al_2(OH)_{16}Cl_2 \cdot 4H_2O$, catalyze the reaction.6)

Silane, SiH_4, is one of the important chemicals in semiconductor industry, since highly pure silicon is easily obtained by thermally decomposing SiH_4. Disproportionations of chlorosilanes, Cl_nSiH_{4-n},7) and of alkoxysilanes such as

$(C_2H_5O)_3SiH$[8)] and $(CH_3O)_3SiH$[9)] can afford SiH_4. The disproportionation reactions are catalyzed by bases; C_2H_5ONa[8)] is an effective homogeneous catalyst and anion-exchange resins such as Amberlyst A-21[7)] and Diaion PA-306[9)] containing exchangeable Cl^- or OH^- anions are effective as heterogeneous catalysts. Since hydrotalcite-like minerals contain exchangeable interlayer anions, they can be used as a catalyst in which interlayer anions work as a nucleophile.

The aim of this work is to demonstrate the catalytic disproportionation of $(CH_3O)_3SiH$ (Eq. 1) in the presence of a hydrotalcite-like mineral containing exchangeable Cl^- or CH_3O^- interlayer anions.

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

The hydrotalcite-like mineral, $Mg_6Al_2(OH)_{16}Cl_2{\cdot}4H_2O$, was synthesized from aqueous solutions of $MgCl_2{\cdot}6H_2O$, $AlCl_3{\cdot}6H_2O$, and NaOH (Mg^{2+}/Al^{3+} molar ratio= 3) at 433 K.[2)] The mineral containing CH_3O^- anions was obtained by anion-exchanging NO_3^- anions of $Mg_6Al_2(OH)_{16}(NO_3)_2{\cdot}4H_2O$ in a methanol solution of CH_3ONa (CH_3O^-/NO_3^- molar ratio= 10) at 338 K for 43 h. The materials thus synthesized were evacuated at 453 K for 2 h to drive out interlayer water molecules. A 5 g portion of $(CH_3O)_3SiH$ (41 mmol) was added into a flask containing 0.62 g of the minerals (2.0 mmol of interlayer anions) under a nitrogen atmosphere. The flask was equipped with a condenser cooled at 273 K. The reaction mixture was analyzed for $(CH_3O)_3SiH$ and $(CH_3O)_4Si$ by a gas chromatograph, using heptane as an internal standard.

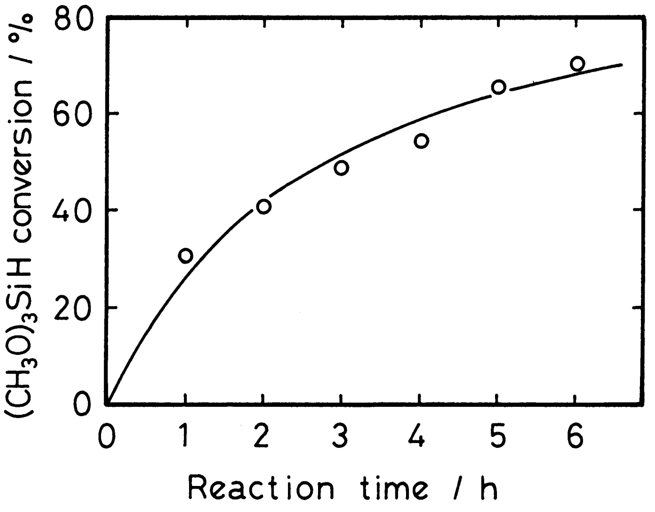

Fig. 1. Time course of $(CH_3O)_3SiH$ conversion. Reaction conditions: $(CH_3O)_3SiH$= 5 g (41 mmol), hydrotalcite-like mineral containing Cl^- ions= 0.62 g, and reaction temperature= 323 K.

Figure 1 shows a time course of $(CH_3O)_3SiH$ conversion for reactions in the presence of a hydrotalcite-like mineral containing interlayer Cl^- anions; the conversion was calcualted from the amount of unreacted $(CH_3O)_3SiH$. The conversion increased with the reaction time and was 70% at 6 h. We define the selectivity of the reaction as follows:

$$\text{Selectivity} = \frac{[\text{amount of } (CH_3O)_4Si \text{ produced}]}{(3/4) \times [\text{amount of } (CH_3O)_3SiH \text{ consumed}]} \times 100. \qquad (2)$$

At every reaction time shown in Fig. 1, the selectivity was 100%. This indicates that the disproportionation reaction proceeds according to Eq. 1.

Table 1 summarizes reaction-time ($\geq$ 6 h) dependences of the $(CH_3O)_3SiH$ conversion calculated from the amount of unreacted $(CH_3O)_3SiH$. Figures in parenthesis show the selectivity defined by Eq. 2.

The first entry in Table 1, obtained under the same reaction conditions as those in Fig. 1, shows that the conversion increased with reaction time beyond 6 h and attained 99% at 22 h. Selectivity, however, decreased, indicating that reactions other than Eq. 1 occur. The use of twice weight of the mineral (entry 2 in Table 1) or the elevation of reaction temperature (entry 3 in Table 1) gave

Table 1. Disproportionation of $(CH_3O)_3SiH$ with hydrotalcite-like minerals[a)]

Entry	Interlayer anion in mineral	Weight of mineral / g	Reaction temperature / K	Conversion (selectivity)[b)] / %			
				Reaction time / h			
				6	9	16	22
1	Cl^-	0.62	323	70 (100)	79 (92)	-	99 (72)
2	Cl^-	1.2	323	92 (95)	-	-	-
3	Cl^-	0.62	343	-	-	97 (78)	-
4	CH_3O^-	0.62	323	83 (100)	95 (95)	-	-

a) $(CH_3O)_3SiH$= 5 g (41 mmol).

b) for definition, see text.

the increased $(CH_3O)_3SiH$ conversion, while the selectivity was 95 or 78%. Deviation of the selectivity from 100% would be due to, for example, polymerization of $(CH_3O)_4Si$ into di- or higher-siloxanes by the action of undetectable amount of water.

The disproportionation is catalyzed also by a hydrotalcite-like mineral containing interlayer CH_3O^- anions, which gives a higher activity than the Cl^--containing mineral. Thus, as shown in entry 4 in Table 1, the $(CH_3O)_3SiH$ conversion was 83% at 6 h and 95% at 9 h, while the selectivity was 100 and 95%, respectively.

In conclusion, the hydrotalcite-like mineral containing CH_3O^- or Cl^- anions catalyzed a disproportionation of $(CH_3O)_3SiH$.

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