Catalytic conversion of organosilanes. 1. Disproportionation of alkylsilanes over solid acid and base catalysts

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Catalytic conversions of diethylsilane (E2), triethylsilane (E3) and diethyldimethylsilane (E2M2) were examined at 373–573 K in a closed recirculation reactor by using various solid acid and base catalysts. Basically two types of reaction were found: decomposition and disproportionation. Strongly acidic catalysts such as silica–alumina (SA), alumina and sulfated ZrO_2 (SO_3/ZrO_2) exhibited high disproportionation activity, while weakly acidic and basic catalysts showed low catalytic activity and gave mainly cracking products. The order of disproportionation reactivity of three silanes tested were E2M2 > E3 > E2 over SA and SO_3/ZrO_2, while it was E2 $\geqslant$ E3 > E2M2 over an alumina catalyst.

Keywords: Organosilane; disproportionation; oxide catalyst

1. Introduction

Although there are a long history and many works on the synthesis and conversion of hydrocarbons as well as those including hetero-atoms such as S, N and O, little research has been done on the heterogeneous catalytic conversions of organosilanes. Synthesis and conversion of organosilane derivatives are performed mainly in a homogeneous liquid phase by using Lewis acids such as $AlCl_3$, BF_3 and transition metal complexes. An example of the use of metal halides for the disproportionation of some alkylsilanes can be found in the earlier work by Russell [1,2].

Considering the increasing importance of applications of organosilanes in the fields of polymers, coupling reagents, silylic reagents, coatings etc., studies on the catalytic conversions of such compounds should be important. At present, an industrial organosilicon chemistry is based on alkylchlorosilanes and alkoxysi-

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lanes, both of which are synthesized by the reactions of Si with alkylchlorides and alcohol, respectively, by using Cu as a catalyst. As a fundamental investigation on the heterogeneous conversion of organosilanes, a transalkylation (disproportionation), a hydrosilylation such as an alkylation, a phenylation etc., and dehydrogenation will be target reactions. In this article, a study on the disproportionation of alkylsilanes was taken as a first candidate.

2. Experimental

Diethylsilane, triethylsilane and dimethyldiethylsilane purchased from Shinetsu Chemical Ind. Ltd. were purified by repeated freeze–thaw cycles and a trap-to-trap distillation using a conventional vacuum apparatus.

Silica–alumina was Nikki N631-L and alumina was JRC-ALO-4 which was a reference sample from Catalysis Society of Japan. An SO_3/ZrO_2 catalyst was prepared by immersing zirconium hydroxide in 1 N sulfuric acid, followed by washing, drying and calcining in air at 873 K for 3 h [3]. Zirconium pillared clay (Zr-PILC) was prepared by treating montmorillonite (MONT) with a 0.1 M aqueous solution of zirconium oxychloride under a reflux condition, followed by washing, drying at 383 K and calcining in air at 773 K for 16 h. Sulfate ion-treated Zr-PILC (AS/Zr-PILC) was prepared by treating 573 K calcined Zr-PILC with a 0.1 N aqueous solution of ammonium sulfate at room temperature, followed by drying and calcining in air at 873 K for 3 h.

Reactions were carried out at 373–573 K by using a closed recirculation reactor with a volume of 300 ml at an initial pressure of 30 Torr for E2 and E2M2 and 20 Torr for E3. Unless otherwise noted, the catalyst amount used was 200 mg. Prior to use, catalysts were first calcined in air at 873 K for 3 h and activated in vacuo at 773 K for 1 h.

Products were periodically withdrawn via a sampling loop which was connected with a reaction apparatus and were analyzed by a gas chromatograph equipped with a column of Gaskuropack 54 and an FID detector. At each sampling, about 1% of the substrate was removed for the analysis; however, this does not affect the product distributions.

3. Results and discussion

The gas phase reaction of alkylsilanes over the catalysts tested here was a decomposition (cracking) and a disproportionation (an alkyl exchange reaction). Figs. 1, 2 and 3 summarize the results of the reactions of E2M2, E2 and E3 at 573 K, respectively. Catalytic activity and selectivity were evaluated from the product distribution after 60 min reaction and expressed by mol g^{-1} min^{-1} and mol%, respectively.

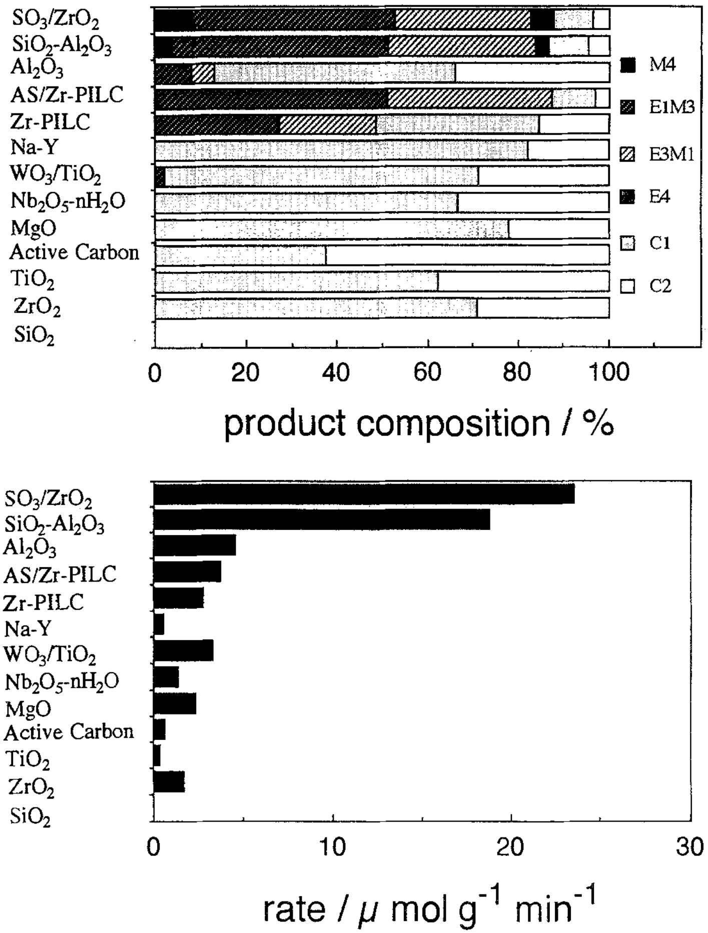

Fig. 1. Activity and selectivity in E2M2 reaction.

SA, SO_3/ZrO_2, alumina and AS/Zr-PILC were active for the disproportionation, while TiO_2, ZrO_2, MgO, WO_3/TiO_2, niobic acid, Na-Y, MONT, Zr-PILC and activated carbon were inactive for the disproportionation, instead a decomposition reaction occurred. SiO_2 was totally inactive and this also indicates the contribution from the non-catalytic, thermal reaction can be neglected. An SO_3/ZrO_2 catalyst, which is known as an extremely strong solid acid [3], was most active and gave about 50% conversion within 60 min. This catalyst catalyzed the disproportionation even at 373 K.

Oxide catalysts that are acidic, such as SA, SO_3/ZrO_2, and alumina, showed good catalytic activity, while the ones which have weak or no acidic character were inactive for the disproportionation reaction. Solid bases were inactive. Though WO_3/TiO_2 and niobic acid have an acidic character and are excellent catalysts for the olefin isomerization [4] and the olefin–aldehyde condensation reaction [5], they were inactive too. Considering the fact that strong solid acid

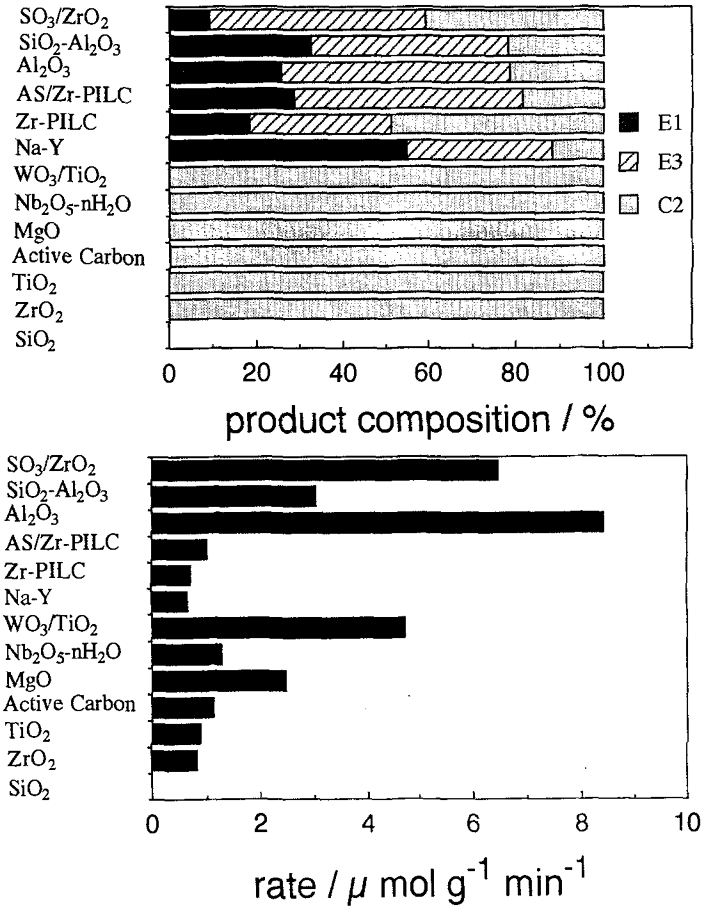

Fig. 2. Activity and selectivity in E2 reaction.

catalysts such as SA and SO_3/ZrO_2 are the good catalysts, acid strength required for the disproportionation reaction of organosilane compounds should be strong. In fact, a strong Lewis acid such as $AlCl_3$ was used [1,2] for the disproportionation reaction in the homogeneous media.

Since the calculated turnover frequency based on the amount of disproportionated products and the reported amount of acid sites [6] far exceeded unity in case of an alumina catalyst, the disproportionation reaction should be catalytic. Disproportionated products were ethylsilane (E1) and triethylsilane (E3) from E2. E1, E2 and tetraethylsilane (E4) are obtained from E3. Tetramethylsilane (M4), ethyltrimethylsilane (E1M3), triethylmethylsilane (E3M1) and E4 are the products from E2M2. Product compositions were almost independent of the extent of conversion and the reaction time. If the disproportionation reaction takes place exclusively, product ratios, E1/E3, M4/E4, E1M3/E3M1, E2/E4, should be unity, but the observed product ratios were not unity. Thus during the

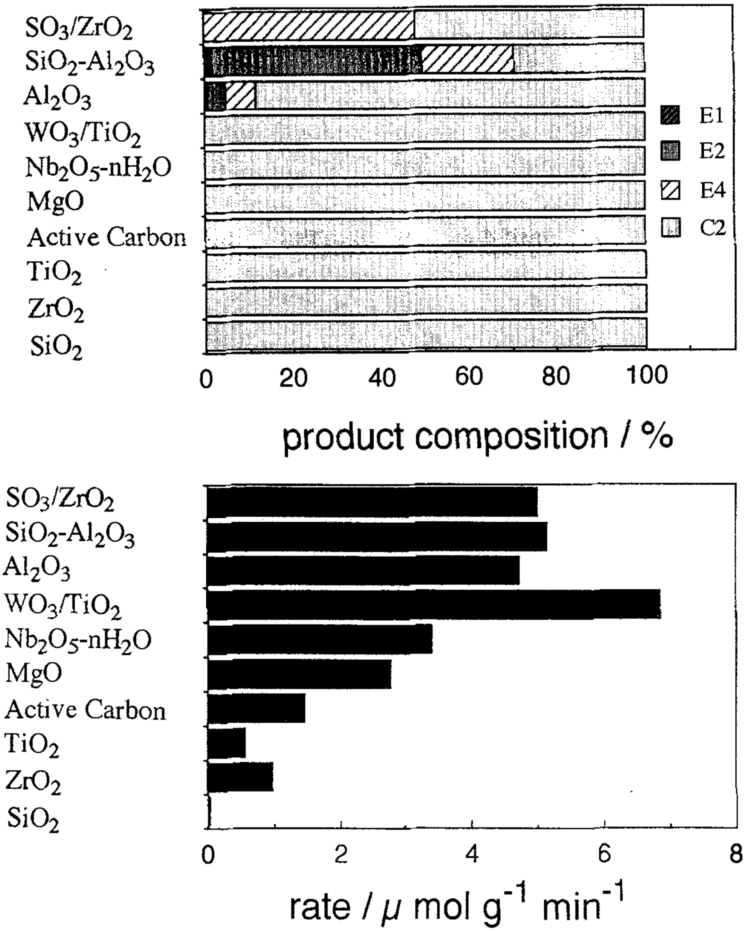

Fig. 3. Activity and selectivity in E3 reaction.

alkyl migration from one molecule to another, a part of the alkyl groups may be lost by forming lower hydrocarbons.

Besides the disproportionation reaction, a decomposition took place. The decomposition product from E2 and E3 was C_2 hydrocarbons, while those from E2M2 were C_1 and C_2. Except for the case on active carbon catalyst, the production of C_1 always exceeded that of C_2. This may suggest that an electrophilic attack on a methyl–Si bond is more facile than on an ethyl–Si bond. Though attack on an electrophile on a saturated carbon atom is not observed for hydrocarbons, examples are reported to show the ease of electrophilic attack on an alkyl–Si bond. One example can be seen in the conversion of phenylalkylsilanes, where the relative rates of cleavage of $C_6H_5 > CH_3 > C_2H_5$ have been observed toward aluminum iodide [7].

Fig. 4 compares the reactivity of three alkylsilanes over SA, SO_3/ZrO_2 and alumina for the disproportionation and the decomposition reaction. The order

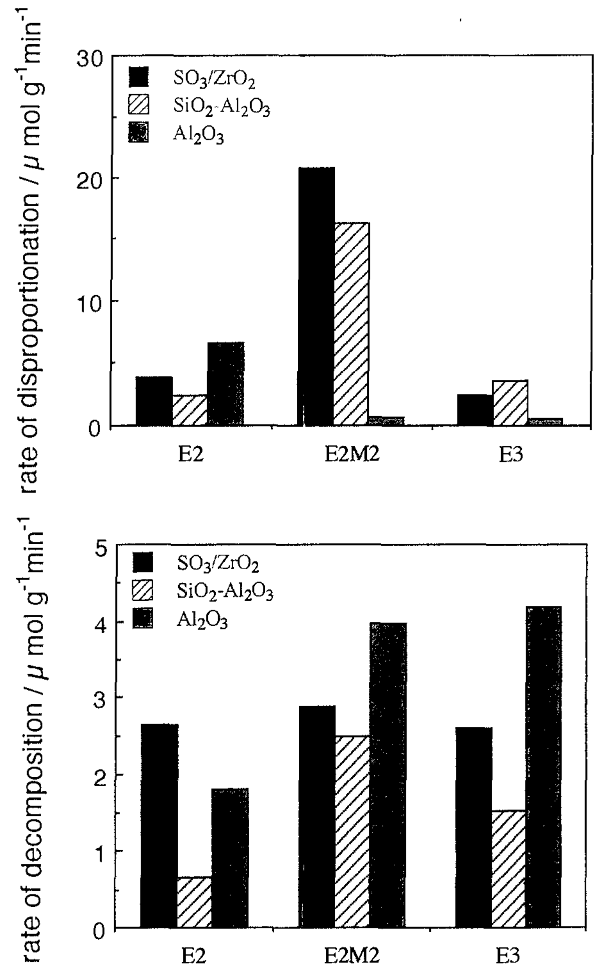

Fig. 4. Relative reactivity of three reactants in disproportionation.

of the reactivity is not the same. As is shown in fig. 4, the disproportionation reaction showed a strong dependence on the reactant structure. Though E2M2, which is saturated by alkyl groups, was quite reactive over SA and SO_3/ZrO_2 catalysts, this is not the case over alumina. Alumina showed highest catalytic activity for E2, which is a less saturated compound, while SA and SO_3/ZrO_2 were less active. Thus the order of the reactivity on SA and SO_3/ZrO_2 is E2M2 $>$ E3 $\geqslant$ E2, while that on alumina is E2 $\geqslant$ E3 $>$ E2M2.

Considering the fact that the disproportionation took place over solid acid catalysts, a possible reaction intermediate is a cationic one. In the case of hydrocarbons, a carbonium ion, which is produced by the addition of a proton to a hydrocarbon, and a carbenium ion, which is formed by the abstraction of a hydride ion from an organic molecule, are proposed. In case of organosilicon compounds, a siliconium ion, which is produced by the addition of a proton, and a silicenium ion, which is produced by the abstraction of a hydride ion, are the possible intermediates. A different reactivity order over the acid catalysts found here suggests different types of reaction intermediates are operative.

Over SA and SO_3/ZrO_2, alkyl-saturated reactants were more reactive, while over alumina, less saturated reactants were reactive. Thus, we tentatively propose that the proton addition could be an initiation step in case of SA and SO_3/ZrO_2, while a hydride abstraction could be an initiation step over alumina. An alkyl substitution to the central Si atom may enhance the electron density on Si, and hence enhances the proton affinity. The formation of a siliconium ion may be easier than the formation of a carbonium ion because the penta-coordinated intermediate is more facile to be produced in silicon compounds. Alumina is a typical Lewis type solid acid and shows no protonic property. So, in cases of E2 and E3, the first step may be a hydride abstraction, while in case of E2M2 the initiation step may be a coordination of an alkyl group to an electron-deficient Lewis site.

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