

Catalytic Disproportionation of Alkylsilanes over Sulfated ZrO_2

Hideo FUJISAWA and Tsutomu YAMAGUCHI

Department of Chemistry, Faculty of Science, Hokkaido University,
Sapporo 060

Gas phase heterogeneous catalytic conversions of diethylsilane(E2), triethylsilane(E3) and diethyldimethylsilane(E2M2) were examined at 373 - 573 K in a closed recirculation reactor by using a sulfated $\text{ZrO}_2(\text{SO}_3/\text{ZrO}_2)$ catalyst. The catalyst exhibited high disproportionation activity even at 373 K.

Synthesis and conversion of organosilane derivatives are mainly carried in a homogeneous liquid phase using activating reagents such as AlCl_3 , BF_3 and transition metal complexes.

Since the application of organosilanes is now expanding in the fields of polymers, coupling reagents, silylic reagents etc., studies on the catalytic conversion of such compounds should have a strong importance. An example of the disproportionation of some alkylsilanes by using metal halides can be found in the earlier work by Russell.^{1,2)} Recently, Izumi et al. have demonstrated extensive works on the utilization of cation-exchanged montmorillonite in the liquid phase aldol reactions and Michael reactions using organosilicon reagents.³⁾

Thus, heterogeneous conversions of organosilanes, such as a transalkylation, a hydrosilylation, and a dehydrogenation draw our attention. In our preceding paper,⁴⁾ we reported a strong solid acid such as silica-alumina, alumina and a superacidic solid catalyst, SO_3/ZrO_2 , exhibited an activity for the disproportionation of alkylsilanes. Among them, the SO_3/ZrO_2 catalyst showed the highest activity for the reaction. Thus, we wish to report the catalytic performance of the SO_3/ZrO_2 catalyst for the disproportionation of alkylsilanes in more detail in this article.

Diethylsilane, triethylsilane and dimethyldiethylsilane purchased from Shinetsu Chemical Ind. Ltd. were purified by repeated freeze-thaw cycles and a trap-to-trap distillation by using a conventional vacuum apparatus. An SO_3/ZrO_2 catalyst was prepared by immersing zirconium hydroxide in 1 M sulfuric acid, followed by washing, drying and calcining in air.⁵⁾

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. The catalyst amount used was 100 mg. Prior to use, the catalyst was first calcined in air and activated in vacuo at 773 K. Products were analyzed by an on-line gas chromatography equipped with a column of Gaskuropak 54 and an FID detector. Catalytic activity and selectivity were evaluated from the product distribution after 35 min reaction and expressed by $\text{mol g}^{-1} \text{min}^{-1}$ and mol%, respectively. Sensitivity factors of reactants and products were determined experimentally.

The reaction of alkylsilanes over the SO_3/ZrO_2 catalyst was a disproportionation (an alkyl exchange reaction) and a decomposition (cracking), and was observable even at 373 K. Disproportionated products were ethylsilane(E1) and triethylsilane(E3) from E2. E1, E2, and tetraethylsilane(E4) were the products from E3. Tetramethylsilane(M4), ethyltrimethylsilane(E1M3), triethylmethylsilane(E3M1), and E4 were found as the products from E2M2. Product compositions were almost independent of the extent of conversion and the reaction time. In Fig. 1 compares the reactivity of three silanes. Because of the large difference in the reactivity of these compounds, the results were compared at the reaction temperature of 423 K for E2M2, and of 573 K for E2 and E3. Though the rate of decomposition was not so different for E2 and E3, and was slightly low for E2M2, the disproportionation reaction showed a strong dependence on the reactant structure. E2M2, which is saturated by alkyl groups, was most reactive over the SO_3/ZrO_2 catalyst, but this was not the case over alumina.⁴⁾ Alumina showed highest catalytic activity for E2, which is a less saturated compound, while SO_3/ZrO_2 was less active for this compound. Thus the order of the reactivity on SO_3/ZrO_2 was found to be $\text{E2M2} \gg \text{E2} \geq \text{E3}$, while that on alumina was $\text{E2} \geq \text{E3} > \text{E2M2}$. A different reactivity order over these catalysts may suggest the different types of reaction sequences are operative. Three types of the initiation steps can be

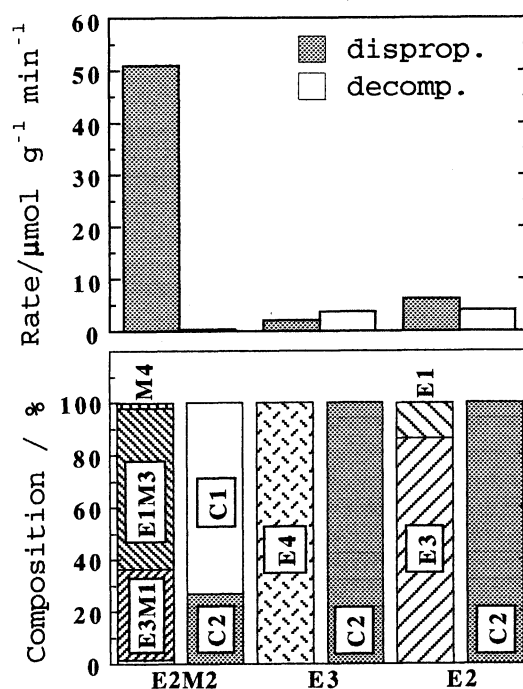


Fig. 1. Rate and product composition in alkylsilane conversion on SO_3/ZrO_2 .

considered; a proton addition, a hydride abstraction, and a proton abstraction. In our previous work, we showed a typical solid base catalyst such as MgO and CaO did not show the activity for the reaction. Thus the proton abstraction can be neglected. Since the central Si atom of E2M2 is more nucleophilic than that of E2, the proton addition on a Si atom may be facile in E2M2. Thus the E2M2 reaction is favorable on a protonic catalyst. On the contrary,

if the reaction initiates via a hydride abstraction, E2 may be most reactive; E2 has two hydrogen atoms and is less sterically hindered. Alumina has both acidic and basic properties, however, its acidic properties is based on the Lewis acidity, and the conversion of the Lewis acid sites to the protonic acid sites does not take place. SO_3/ZrO_2 is also a Lewis acidic catalyst at a well-evacuated state, but the Lewis acid sites can be converted to the protonic sites. So the higher reactivity of the SO_3/ZrO_2 catalyst to E2M2 could be interpreted in terms of its high protonic acidity, though the detail of the reaction mechanism is left for the future investigations.

If the disproportionation reaction takes place exclusively, product ratios, E1M3/E3M1, M4/E4, E2/E4, and E1/E3, should be unity, but the observed product ratios were not. Thus during the alkyl migration from one molecule to another, a part of alkyl groups may be lost by forming lower hydrocarbons.

An optimization of the catalytic activity was performed by using the E2M2 reaction as a test reaction and by changing the pretreating conditions such as the treating concentration of sulfuric acid solution, the calcination temperature after the sulfation and the evacuation temperature prior to the reaction. An activation (calcination) temperature after the sulfation is known to have a remarkable influence on the catalytic activities.⁵⁾ In Fig. 2 illustrates the activity dependence on the activation temperature in the reaction of E2M2 at 423 K (150 °C) by using 100 mg of the catalyst which was prepared by the treatment of 1 M acid solution. It is clearly seen that an optimum temperature is found at 773 K (500 °C) and the catalytic activity is lost by the calcination at 973 K (700 °C). The disproportionation selectivity on the 573 K-calcined catalyst was low while the

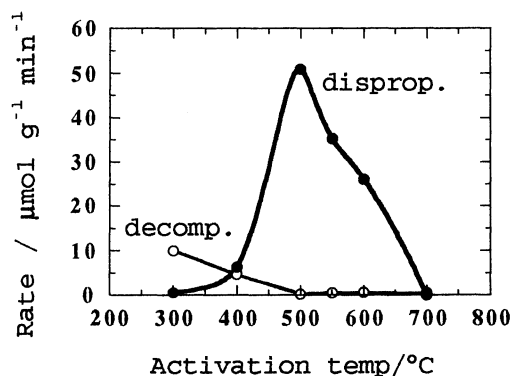


Fig. 2. Change of reaction rate by the activation temperature.

catalysts activated at 773 to 873 K (500 - 600 °C) gave a satisfactory results. The optimum temperature is slightly lower than that found in the benzophenone synthesis.⁵⁾ This may come from the difference of the type of reactions and thus the difference of the proper acid strength necessitated to catalyze the reactions.

The evacuation temperature prior to the reaction did not give strong influence on the catalytic activity; the catalytic activities after the 573 K- and 773 K-evacuation were the same for the E2M2 reaction.

An amount of sulfate ions fixed or the concentration of acid solution for the pretreatment is known to give a strong influence on the acidic properties of sulfated ZrO₂.^{6,7)} The effect of acid concentration on the E2M2 reaction was examined by changing the concentration in the range of utmost 1 M. The low concentration such as 0.01 to 0.05 M was ineffective, however, a steep increase in the disproportionation activity was found at the concentration of 0.1 M. Over this concentration the catalytic activity and selectivity were kept constant. Thus the acid concentration of 0.1 M is the lowest concentration to generate the effective acid strength for the E2M2 reaction.

Thus it was concluded that the heterogeneous gas phase disproportionation of alkylsilane derivatives was successfully performed at moderate temperatures over the catalyst which was treated by more than 0.1 M concentration of sulfuric acid, followed by the activation at 773 K (500 °C).

References

- 1) G.A.Russell, J. Am. Chem. Soc., **81**, 4815 (1959).
- 2) G.A.Russell, J. Am. Chem. Soc., **81**, 4825 (1959).
- 3) Y.Izumi, M.Kawai, H.Sakurai, M.Onaka, and K.Urabe, "Acid-Base Catalysis," ed by K.Tanabe et al., Kodansha Scientific, Tokyo (1989), p.21.
- 4) H.Fujisawa and T.Yamaguchi, Catal. Lett., in print.
- 5) T.Yamaguchi, Appl. Catal., **61**, 1 (1990).
- 6) K.Tanabe, T.Yamaguchi, K.Akiyama, A.Mitoh, K.Iwabuchi, and K.Isogai, Proc. 8th Intern. Congr. Catal., **5**, 601.
- 7) T.Yamaguchi, C.Nishimichi, and A.Kubota, Prepr. Div. Petr. Chem., ACS., **360**, 640 (1991).

(Received November 30, 1992)