

## NOTES

## Catalytic Desulfurization

## XII. Similarity of Dehydrosulfurization of Ethanethiol and Dehydration of Ethanol over Alumina Catalyst

In a previous publication (1), two of us reported that alumina showed a high catalytic activity in the dehydrosulfurization of ethanethiol ( $C_2H_5SH$ ) to form ethylene, hydrogen sulfide, and diethyl sulfide. However, the mechanism was not clear. The molecular structure of ethanethiol is very similar to that of ethanol, and the mechanism of dehydration of ethanol over alumina has been extensively studied (2-6). The reaction is assumed to proceed via aluminium ethoxide as reaction intermediate (3-6). It was therefore considered important to compare the behavior and the adsorption states in the dehydrosulfurization of ethanethiol and the dehydration of ethanol over alumina in order to clarify the mechanism of the former reaction.

The behavior of both reactions with temperature and the adsorption state of both reactants over alumina were investigated, respectively, by the use of a conventional pulse reactor and by infrared spectroscopy, following the same methods as those described in our previous paper (7). The alumina catalyst was prepared by the hydrolysis of aluminium isopropoxide and then calcined at  $500^\circ C$  for 4 hr in air. The BET surface area was  $280 m^2/g$ .

For their experiments, finely powdered catalyst was pressed into a thin wafer (diameter, 2 cm) under  $1-3 tons/cm^2$ . After evacuation at  $250^\circ C$  for 2 hr in the ir cell, 200 Torr of ethanethiol or 100 Torr of ethanol were introduced at room tempera-

ture for 30 min. The gaseous phase was evacuated at room temperature for 30 min, and then ir spectra of adsorbed species were observed at the same temperature. Since no ir spectra of adsorbed species were observed on CaO and  $SiO_2$  following such a treatment, these oxides being inactive for the dehydrosulfurization of ethanethiol (1), it was concluded that physisorbed species were completely eliminated from the catalyst surface by this procedure. The ir spectra observed in this work are therefore attributable only to chemisorbed species.

Figure 1 shows the behavior of both catalytic reactions over alumina as a function of reaction temperature. Disproportionation products such as diethyl sulfide and diethyl ether were predominantly formed at lower reaction temperatures, but ethylene became the main product in both reactions as the reaction temperature increased. It was found that the behavior of dehydrosulfurization of ethanethiol over alumina is similar to that of the dehydration of ethanol, although ethanol showed a higher reactivity than ethanethiol over the catalyst. This similarity of behavior of both reactants over alumina catalyst suggests that the adsorption state and reaction mechanism in the dehydrosulfurization of ethanethiol are analogous to those of dehydration of ethanol.

The ir spectra obtained for both reactants when adsorbed on alumina and the assignments of the bands are shown in Fig. 2. The bands of the stretching and bending

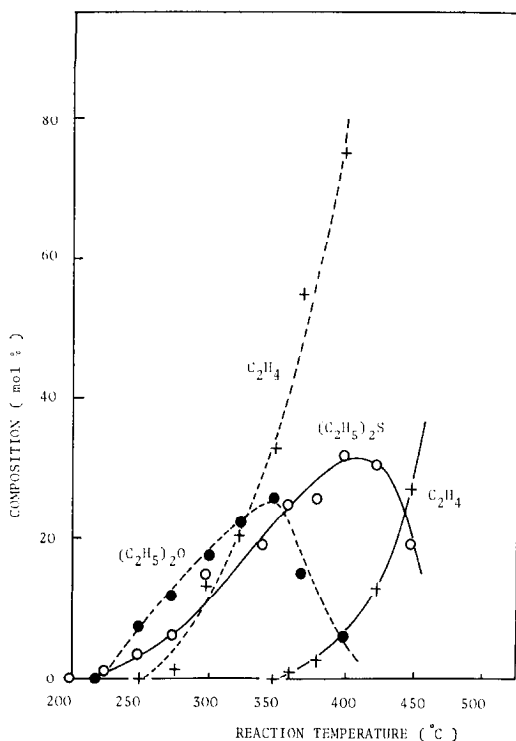


Fig. 1. Behavior of dehydrosulfurization of ethanethiol and dehydration of ethanol over alumina against reaction temperature. Experimental conditions: catalyst weight, 0.01 g; carrier gas (He) flow rate, 30 ml/min; sample injection, 2  $\mu$ l. —, dehydrosulfurization of ethanethiol; ----, dehydration of ethanol.

modes of the alkyl groups in the spectra of adsorbed ethanethiol and ethanol were observed in the neighborhood of 1380, 1450, and 2950  $\text{cm}^{-1}$ , respectively. The band of 3000–3500  $\text{cm}^{-1}$  in the hydroxyl group region of the catalyst background broadened after the adsorption of both reactants. The change of spectra in the hydroxyl group region indicates that both reactants interact with the surface hydroxyl group of alumina surface to form hydrogen bonds. The spectra are similar with both reactants, the main difference being the large absorption band at 1660  $\text{cm}^{-1}$  assigned to the carbonyl group which was observed in the spectrum of adsorbed ethanol. As it has been reported that aluminium ethoxide is formed when ethanol adsorbs onto alumina (3, 4, 6) and as the ir spectra of

adsorbed ethanol observed in this work are in agreement with those of aluminium ethoxide obtained by other authors (4, 6), it is assumed that adsorbed species like aluminium ethoxide are formed here. This is supported by the following facts.

In the spectrum of adsorbed ethanethiol shown in Fig. 2, the band of the  $-\text{CH}_2-\text{S}-$  group of adsorbed ethanethiol was observed at 1268  $\text{cm}^{-1}$  but that of the  $-\text{SH}$  group at around 2550  $\text{cm}^{-1}$  was not observed. The  $-\text{SH}$  group was, however, observed in the spectra of ethanethiol adsorbed on hydrogen-Y zeolite and metal-ion-exchanged Y zeolite which produce only ethylene and hydrogen sulfide as reaction products in the dehydrosulfurization of ethanethiol (7). The fact that the  $-\text{SH}$  group was not observed on alumina suggests that ethanethiol adsorbs with dissociation of the  $-\text{SH}$  group and forms an adsorption species like  $>\text{Al}-\text{S}-\text{C}_2\text{H}_5$ , which is similar in structure to aluminium ethoxide,  $>\text{Al}-\text{O}-\text{C}_2\text{H}_5$ . When ethanol adsorbs onto alumina with dissociation of the  $-\text{SH}$  group, the hydrogen atom of the  $-\text{SH}$  group is assumed to form a new hydroxyl group with a surface oxygen atom and, as a result, the hydroxyl group absorption in the range of 3000–3500  $\text{cm}^{-1}$  is broadened.

The spectrum of adsorbed ethanethiol disappeared with evacuation at 50°C for 30 min but that of adsorbed ethanol did not disappear with this treatment. This implies that the adsorption of ethanethiol onto alumina is not so strong, and the adsorption species of ethanethiol is more unstable than that of ethanol. However, this unstable adsorption species of ethanethiol on alumina would be able to become a reaction intermediate in the dehydrosulfurization of ethanethiol. The dehydrosulfurization of ethanethiol carried out in the pulse reactor showed that the reaction initiated at around 200°C, as shown in Fig. 1. However, diethyl sulfide and hydrogen sulfide desorbed from the catalyst surface at around 100°C in an experiment on thermal desorption of adsorbed ethane-

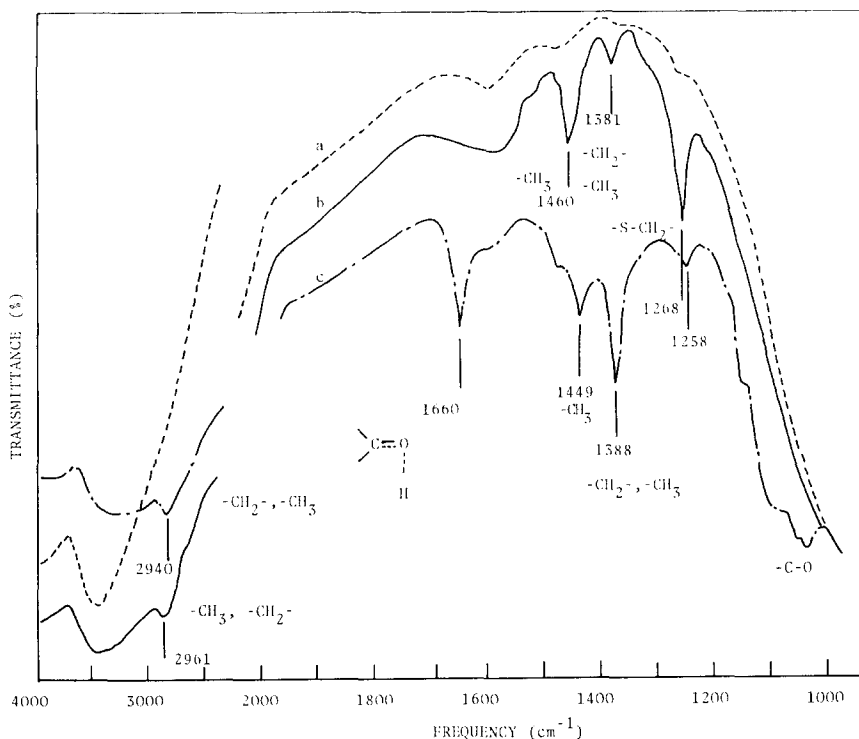


FIG. 2. Spectra of ethanethiol and ethanol on alumina: (a) Background; (b) exposed to 200 Torr of ethanethiol at room temperature, then pumped at room temperature; (c) exposed to 100 Torr of ethanol at room temperature, then pumped at room temperature.

thiol carried out in a static apparatus, in which the experimental conditions were very close to that of the ir spectroscopic study (8). Furthermore, the catalyst color changed from white to light yellow after the evacuation treatment at 50°C for 30 min following formation of the adsorbed species of ethanethiol at room temperature.

From these results, it can be considered that the adsorbed species of ethanethiol on alumina is already activated at around 50°C and would have the ability to become a reaction intermediate in the dehydro-sulfurization of ethanethiol over alumina catalyst. From the similarity of behavior and ir spectra of both reactants on alumina, it can be concluded that the dehydro-sulfurization of ethanethiol on alumina proceeds by a reaction mechanism analogous to the dehydration of ethanol on the same catalyst, in which the reaction intermediate is considered to be an aluminium ethoxide.

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MASATOSHI SUGIOKA  
TAKAYOSHI KAMANAKA  
KAZUO AOMURA

*Department of Chemistry  
Faculty of Engineering  
University of Hokkaido  
Sapporo, Japan 060*

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