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Ethanol Dehydration on Alumina Catalysts

I. The Thermal Desorption of Surface Compounds

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The surface ethoxide on alumina made by ethanol adsorption was desorbed by heat treatment, with the desorbed species analyzed by mass spectrometry. Below 135°C the main components of the desorbed species by the thermal treatment were ethanol, diethyl ether, and ethylene, whereas only ethylene was obtained above 135°C. There was no difference in the infrared spectra which correlates with the change in product distribution. As the concentration of the surface ethoxide was increased, the formation of diethyl ether was favored at the low-temperature region. On the contrary, the formation of ethylene was suppressed with the increased concentration of both the surface ethoxide and the surface hydroxyl group. At the high-temperature region, however, ethylene was the only product without regard to the surface concentration. A diethyl ether molecule is formed from two surface ethoxide groups. The ethylene formation may take place by hydrogen abstraction from the methyl group of the surface ethoxide by the exposed oxide ion adjacent to the surface ethoxide. The structure of the ethanol adsorption on silica gel was investigated for comparison. The dehydration of ethanol over silica-alumina is also discussed.

INTRODUCTION

The dehydration of alcohol over alumina has been investigated extensively (*1*, *2*). Topchieva *et al.* (*3*) suggested that the surface ethoxide ($C_2H_5O\text{–}Al<$) changed into ethylene and diethyl ether for ethanol dehydration, however, Bremner (*4*) or Brey and Krieger (*5*) proposed an oxonium ion ($C_2H_5O^+H_2$) or a carbonium ion ($C_2H_5^+$) as the reaction intermediate. These ionic mechanisms were opposed, however, by Pines and Haag (*6*), who explained the dehydration of 1-butanol over alkali-containing alumina catalysts with a concerted mechanism.

The molecular structure of ethanol chemisorbed on alumina has been studied by Arai *et al.* (*7*), Greenler (*8*), Naito (*9*), Uvarov (*10*), and Triebmann *et al.* (*11*) by means of infrared spectroscopy. All these authors identified the surface compound on alumina as ethoxide ($C_2H_5O\text{–}Al<$), since an excellent accordance with aluminum ethoxide in the infrared absorption spectrum was observed.

It is the intent of this paper to pursue the behavior of the surface ethoxide on the alumina catalyst by means of infrared spectroscopy and mass spectrometry in order to elucidate the reaction mechanism of diethyl ether or ethylene formation from the surface ethoxide.

EXPERIMENTAL

Apparatus. The experimental apparatus for this investigation was the same as was used in the previous paper (*7*). The catalyst could be heated and exposed to a vacuum or a variety of gaseous atmosphere *in situ.* The fine powder of alumina gel or silica gel was pressed at 7000–10000 kg/cm^2 into thin wafers, 9 × 18 mm and 0.13–0.17 mm thick, with a weight of approximately 15 mg/cm^2. The evacuation above 400°C was done at the upper part of the cell, around which a furnace was placed far away from the light beam path. The setting of samples was well reproducible in this operation. The infrared spectra were measured up to 300°C, as the sample cell in the light beam was wound with a tape heater.

Materials. Alumina gel, silica gel, and silica-alumina were the same as used in the previous paper (*12*). The alumina gel samples were prepared by the hydrolysis of aluminum isopropoxide and were calcined in air at 550°C for 7 hr. The BET surface area (N_2 adsorption) was 170 m^2/g. The silica gel samples were prepared by the hydrolysis of ethyl orthosilicate and were calcined in air at 550°C. The BET surface area (N_2 adsorption) was 600 m^2/g. The silica-alumina cracking catalyst (SA-1) (SiO_2 87%, Al_2O_3 13%, Shokubai Kasei Co.) was calcined in air at 550°C for 7 hr. The BET surface area (N_2 adsorption) was 540 m^2/g. The silica-alumina cracking catalyst (SA-2) (SiO_2 73%, Al_2O_3 27%, Shokubai Kasei Co.) was calcined in air at 550°C for 7 hr. The BET surface area (N_2 adsorption) was 310 m^2/g.

Ethanol (G.R.) was distilled twice over magnesium metal under diminished pressure in order to remove the water, and then degassed through several freeze–thaw cycles.

Procedures. The alumina samples were evacuated ($\sim 10^{-5}$ mm Hg) at 550°C for 5 hr at the upper part of the infrared cell at first, slipped down to the light beam part of the cell, and then heated at various temperatures before the addition of a certain amount of ethanol. After the adsorption equilibrium was attained at room temperature, the catalyst was heated up to 70°C, the physisorption species and vapor being trapped by liquid nitrogen. The trapped ethanol was then expanded to a vessel of the constant volume and its pressure was measured by a thermocouple gauge. The amount of chemisorption was calculated from the difference between the amount of introduced ethanol and the amount of the trapped ethanol (adsorption method). Then, the catalyst with the chemisorbed species was heated slowly up to a certain temperature. During the condensation of the desorbed species by the liquid nitrogen trap, the pressure in the cell was maintained always below 2×10^{-3} mm Hg. The same procedure was repeated at several predetermined temperatures. The change of the chemisorption amount during the procedure was always monitored by infrared spectroscopy. The desorption treatment by raising the temperature was continued till the intensity of the adsorption band at 1387 cm^{-1} gave a constant value. The trapped species were analyzed by a mass spectrometer (Consolidated Engineering Corp. Type 21-103C). As the amounts of ethylene and diethyl ether were convertible by calculation to that of ethanol, the chemisorption amount could be determined (desorption method). The amount of chemisorption could also be determined by the intensity change of the infrared absorption band at 1387 cm^{-1} (*7*) (IR intensity method). The amounts of chemisorption by these three methods were obtained independently and confirmed to be equal with each other.

RESULTS AND DISCUSSION

The Thermal Desorption of the Surface Compound

In the previous paper (*7*) the structure of ethanol chemisorbed on alumina was identified as a surface ethoxide ($C_2H_5O\text{–}Al<$) by means of infrared spectroscopy, and the number of chemisorption sites was calculated as 2.1×10^{14} sites/cm^2 under such a condition that ethanol was introduced at 70°C to the alumina catalyst which had been evacuated at 550°C for 5 hr.

Since the dehydration products of ethanol are known to be dependent on temperature, the experiments on the thermal desorption of the surface ethoxide were carried out. The desorbed products at a certain temperature were condensed by the liquid

TABLE 1

THERMAL DESORPTION PRODUCTS OF THE SURFACE COMPOUND OF ETHANOL ON ALUMINA IN THE RANGE OF 60° TO 210°C

Temperature range of thermal desorption (°C)	Total adsorbed amount (×10^{-7} mole)	Distribution of desorbed products[a]			Amount of desorption[a] (× 10^{-7} mole)	
		C_2H_5OH	$(C_2H_5)_2O$ (%)	C_2H_4	Total	EtO–[b]
60–80°	160	88	7	5	14	15
80–110°	145	68	28	4	12	15
110–140°	131	30	35	36	15	21
140–170°	110	8	4	88	45	47
170–210°	63	1	3	96	61	63
Total	160	20	9	71	147	161

[a] The analysis of the desorbed products was made by mass spectrometry. The structure of the adsorbed species was ascertained as the ethoxide by infrared spectroscopy during the thermal desorption from 60° to 210°C.

[b] The amount of the ethoxide was calculated by converting the desorption products into the ethoxide, with diethyl ether counted as two ethoxides. A disc of the alumina catalyst of 25 mg was used after the evacuation at 550°C for 5 hr.

nitrogen trap and then analyzed by the mass spectrometer. This procedure was repeated at several temperatures. The distribution of the thermal desorption products is shown in Table 1, indicating a distinct tendency as a function of the desorption temperature. At the low-temperature region, the decomposed products of the surface ethoxide were ethanol and diethyl ether. On the contrary, ethylene was the main desorbed species at the high-temperature region.

During this procedure the amount of ethanol chemisorbed on alumina was obtained at each temperature on the basis of the volumetric mass balance. The previously reported quantitative relationship (7) between the infrared intensity and the chemisorbed amount over the temperature range from 30° to 170°C was confirmed by the present results in good coincidence. The amount of ethanol chemisorbed on alumina as a function of temperature is shown in Fig. 1. Apparently there exists a transition temperature at 135°C. It is of interest to note that this transition temperature is also the turning point of the product distribution of the surface ethoxide decomposition. Nevertheless, there was no difference in the infrared spectra which correlates with the change in product distribution.

The heterogeneity of the adsorption sites for ethanol on the alumina catalyst is deduced either from the results of the thermal desorption in Table 1 or from the temperature dependence of the chemisorption amount shown in Fig. 1. Moreover, the adsorption rate was changed as a function of the surface coverage. Various strengths of the aluminum–oxygen bond should exist among the surface ethoxide on the alumina catalyst. The surface

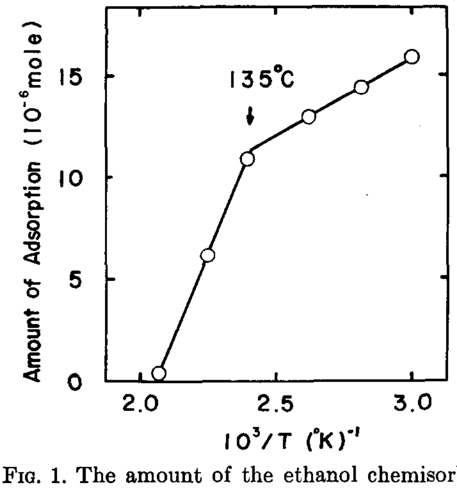

FIG. 1. The amount of the ethanol chemisorbed on alumina as a function of temperature. The alumina sample of 25 mg was used.

ethoxide with the weakest aluminum–oxygen bond may react with the proton to form ethanol. In fact, at the temperature range between 60° to 110°C, the sole desorbed species was ethanol. The surface ethoxide with the medium bond strength may produce ethanol or diethyl ether at the intermediate temperature range between 110° and 135°C. In order to form diethyl ether two nearest ethoxides should react, one of the ethoxides being split off at the aluminum–oxygen bond and the other at the carbon–oxygen bond. The surface ethoxide with the strongest aluminum–oxygen bond may be stable below 135°C, and give ethylene as the main product at the temperature range above 135°C, by splitting off the carbon–oxygen bond of the surface ethoxide instead of the aluminum–oxygen bond.

The Effect of Surface Concentration on the Product Distribution

The effect of the surface ethoxide concentration on the product distribution was studied in detail in the low-temperature region. The maximum amount of ethanol chemisorption at 70°C was obtained as 15.8×10^{-6} mole for 25 mg of the alumina catalyst which had been evacuated at 550°C for 5 hr. However, the maximum amount of ethanol chemisorbed at 135°C decreased to 11.8×10^{-6} mole on the same catalyst. When 5.4×10^{-6} mole of ethanol was introduced at 70°C, all ethanol molecules were retained on the catalyst, giving 34% of the surface coverage found at maximum chemisorption at 70°C. With the catalyst heated at 135°C, the surface ethoxide was decomposed, yielding 66% ethylene, 28% ethanol, and 6% diethyl ether.

Out of 10.8×10^{-6} mole of ethanol introduced at 70°C, 10.4×10^{-6} mole of ethanol (the surface coverage: 65%) was chemisorbed, from which 37% ethylene, 43% ethanol, and 20% diethyl ether were produced. At the introduction of 16.2×10^{-6} mole of ethanol at 70°C, 14.8×10^{-6} mole of ethanol (the surface coverage: 93%) was retained and the ethylene formation was suppressed down to 25%, whereas ethanol and diethyl ether became prevailing, at yields of 49% and 26%, respectively. The arrows along the abscissa axis of Fig. 2 show the adsorption amounts at 70°C and the decrements of the adsorbed ethanol as the results of heat treatment at 135°C. These amounts were calculated on the mass balance basis. The decrease of adsorbed ethanol between 70° and 135°C was 0.87×10^{-6}, 2.90×10^{-6}, and 4.51×10^{-6} mole for these three coverages.

The amounts of ethylene, ethanol, and diethyl ether produced at different surface concentrations are shown in Fig. 2. At the high concentration of the surface ethoxide the figure clearly shows that the formation of ethylene is suppressed, whereas the formation of ethanol or diethyl ether is favored. The ratios of the desorption amount to the adsorption amount were 0.16, 0.28, and 0.31 for the three cases mentioned above. The amounts of desorption as well as the desorption/adsorption

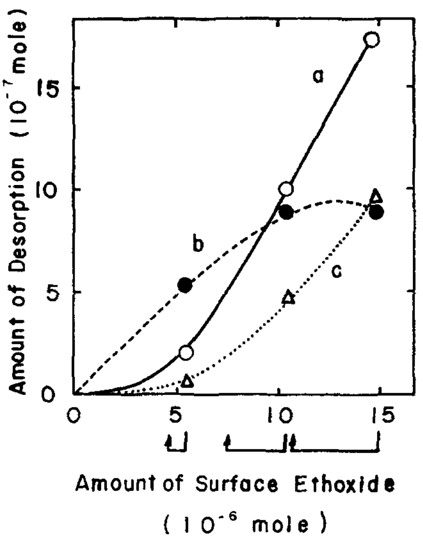

FIG. 2. The product distribution of the thermal desorption from 70° to 135°C as a function of the surface ethoxide concentration. (a) The amount of ethanol. (b) The amount of ethylene. (c) The amount of diethyl ether. The arrows indicate the total amount of the thermal desorption from 70° to 135°C. An alumina sample of 25 mg was used.

ratio were larger for the catalyst on which more ethanol was adsorbed.

The amount of the remaining adsorbed ethanol at 135°C was calculated as 4.5×10^{-6}, 7.5×10^{-6}, and 10.3×10^{-6} mole for the three coverages, which are shown as the arrowheads of Fig. 2. These values are in good accord with the values obtained from the infrared intensity measurements, i.e., 4.8×10^{-6}, 7.9×10^{-6}, and 10.0×10^{-6} mole, respectively (*7*).

As far as the mechanism of the diethyl ether formation on alumina is concerned, the Langmuir-Hinshelwood mechanism is more favorable than the Rideal mechanism by reason that the diethyl ether formation was favored by increasing the concentration of surface ethoxide and that diethyl ether was produced in the cell with the total pressure maintained always below 2×10^{-3} mm Hg during the thermal desorption.

The remaining surface ethoxide of 6.0×10^{-6} mole at 135°C gave the desorbed products at 210°C of ethylene 94%, diethyl ether 2%, and ethanol 4%. In another example, the desorption products at 210°C from 11.4×10^{-6} mole ethoxide remaining at 135°C were ethylene 91%, diethyl ether 6%, and ethanol 3%. Therefore, in the high-temperature region almost all the products were ethylene without regard to the surface ethoxide concentration.

The effect of the surface hydroxyl concentration on the product distribution was then investigated in the low-temperature region. A certain amount of water was previously adsorbed on the alumina catalyst at 100°C. Ethanol was introduced at 70°C and the catalyst was evacuated for an hour. After this evacuation at 70°C, the catalyst was heated at 135°C and the desorbed products were trapped and analyzed. In Fig. 3 both the total and the component amounts of the desorbed species were plotted as a function of the amount of preadsorbed water. It is clearly shown that the formation of diethyl ether and especially of ethylene was poisoned with the increase of the preadsorbed water. At the high-temperature region almost all the products were ethylene without regard to the amount of the preadsorbed water.

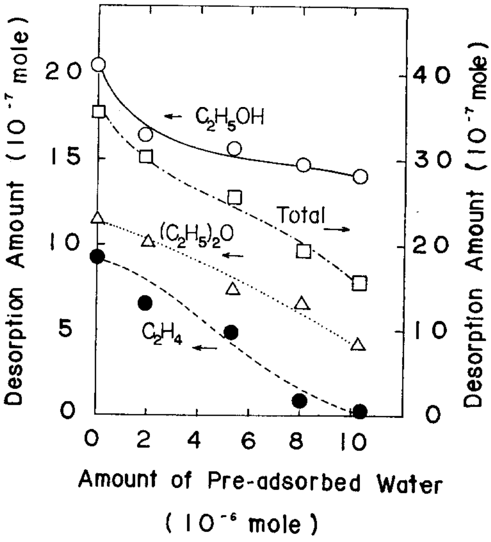

FIG. 3. The effect of the preadsorbed water on alumina on the product distribution of the thermal desorption from 70° to 135°C.

As regards the scheme of ethylene formation, Schwab found that the dehydrated ethylene from CH_3CD_2OH and CH_3CH_2-OD on alumina was $CH_2{=}CD_2$ and $CH_2{=}CH_2$, respectively (*13*). Topchieva *et al.* proposed that the surface ethoxide is the

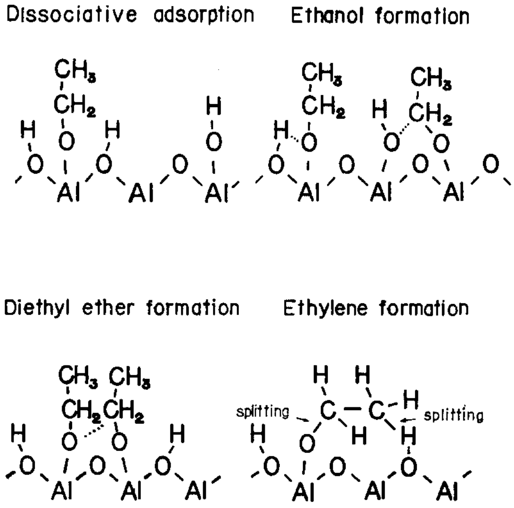

FIG. 4. The structure of the ethanol adsorbed on the alumina catalyst and the desorption scheme of the surface ethoxide over the alumina catalyst.

reaction intermediate of the ethylene formation (*3*). Pines *et al.* described the ethylene formation in a concerted way (*2*). In order to explain the decreasing tendency to ethylene formation with increased amounts of surface ethoxide and surface hydroxyl on alumina stated above, the hypothesis of the carbonium ion mechanism is unfavorable. However, the concerted mechanism seems to be reasonable. The methyl hydrogen of the surface ethoxide is abstracted by the exposed oxide ion adjacent to it and, at the same time, the carbon–oxygen bond of the surface ethoxide is split.

The reaction scheme of the surface ethoxide decomposition proposed for the alumina catalyst is summarized in Fig. 4.

TABLE 2

PRODUCT DISTRIBUTION OF THE THERMAL DESORPTION OVER VARIOUS CATALYSTS AT THE RANGE OF 25° TO 400°C

Catalyst	Alumina		SA-1		SA-1-Na3		SA-2	
Composition	pure Al_2O_3		Al_2O_3 13%		Al_2O_3 13% 0.186Na meq/g		Al_2O_3 27%	
Surface area (m^2/g)	170		540		480		310	
	(%)	($\times 10^{-8}$ mole/m^2)	(%)	($\times 10^{-8}$ mole/m^2)	(%)	($\times 10^{-8}$ mole/m^2)	(%)	($\times 10^{-8}$ mole/m^2)
25 - 70°C								
C_2H_5OH	100.0	55.6	98.6	2.78	94.0	0.75	99.8	20.08
$(C_2H_5)_2O$	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.10
C_2H_4	0.0	0.0	1.4	0.03	6.0	0.05	0.0	0.0
total		55.6		2.81		0.80		20.18
EtO- [a]		55.6		2.81		0.80		20.28
70 - 135°C								
C_2H_5OH	75.8	38.9	81.7	3.53	96.9	2.30	91.3	10.87
$(C_2H_5)_2O$	18.8	9.62	0.8	0.03	0.2	0.003	2.8	0.45
C_2H_4	5.4	2.80	17.5	0.75	2.9	0.06	5.8	0.72
total		51.3		4.31		2.36		12.04
EtO- [a]		60.9		4.34		2.36		12.49
135 - 210°C								
C_2H_5OH	4.1	2.20	4.6	0.15	41.1	0.03	8.4	1.48
$(C_2H_5)_2O$	7.4	3.98	1.1	0.63	1.5	1.07	4.8	0.86
C_2H_4	88.4	46.1	94.3	13.0	57.3	1.47	86.8	15.64
total		52.3		13.8		2.57		17.98
EtO- [a]		56.2		13.9		2.60		18.84

TABLE 2 (*Continued*)

Catalyst	Alumina		SA-1		SA-1-Na3		SA-2	
	(%)	$\left(\frac{\times 10^{-8}}{\text{mole/m}^2}\right)$	(%)	$\left(\frac{\times 10^{-8}}{\text{mole/m}^2}\right)$	(%)	$\left(\frac{\times 10^{-8}}{\text{mole/m}^2}\right)$	(%)	$\left(\frac{\times 10^{-8}}{\text{mole/m}^2}\right)$
210 - 300°C								
C_2H_5OH	0.9	0.05	0.6	0.10	1.0	0.08	0.6	0.13
$(C_2H_5)_2O$	0.0	0.0	0.0	0.0	0.4	0.03	0.3	0.07
C_2H_4	99.1	3.92	99.4	12.7	98.6	8.18	99.1	20.07
total		3.97		12.8		8.28		20.27
EtO- [a]		3.97		12.8		8.31		20.34
300 - 400°C								
C_2H_5OH	4.5	0.13	0.8	0.01	3.5	0.05	1.3	0.03
$(C_2H_5)_2O$	0.0	0.0	0.2	0.003	2.5	0.03	0.0	0.0
C_2H_4	95.5	2.89	99.0	2.90	94.0	0.82	98.7	3.34
total		3.02		2.91		0.90		3.37
EtO- [a]		3.02		2.91		0.93		3.37
25 - 400°C								
C_2H_5OH	57.8	96.9	19.2	7.0	28.4	4.25	44.0	32.4
$(C_2H_5)_2O$	8.2	13.6	0.5	0.18	0.6	0.08	2.0	1.48
C_2H_4	34.0	55.7	80.3	29.3	71.0	10.61	54.0	39.8
total		166.2		36.4		14.94		73.8
EtO- [a]		179.8		36.6		15.0		75.8

[a] The amount of ethoxide was calculated by converting the desorption products into the ethoxide, with diethyl ether counted as two ethoxides. All the catalysts were evacuated at 450°C for 5 hr after the calcination in air at 550°C for 7 hr.

The Ethanol Adsorbed on Silica-Alumina or Silica Gel

The adsorption and the thermal desorption of ethanol on silica-alumina or silica gel were studied in comparison with alumina.

Alumina, silica-alumina with 13% Al_2O_3 (designated as SA-1) and the same silica-alumina, Na^+-exchanged (SA-1-Na3), silica-alumina with 27% Al_2O_3 (SA-2), and silica gel were all calcined at 550°C for 7 hr and then evacuated at 450°C for 5 hr before the ethanol adsorption. Some specifications concerning these catalysts as well as the results on the adsorption amount and the thermal desorption are summarized in Table 2. As for silica gel (the surface area: 600 m^2/g), the total amount of desorption was 13.0×10^{-8} mole/m^2, most of which was ethanol. As is indicated in the fourth row, the total amount of the desorbable ethoxide for SA-

1, SA-2, and alumina increases with the content of alumina. This fact may suggest that the adsorption sites of ethanol on silica-alumina are the surface aluminum ions. Unfortunately, however, its ascertainment by infrared spectroscopy is impossible, because the transmitting allowance of the infrared light for silica-alumina is only up to 1250 cm^{-1}.

The transition temperature concerning the distribution of the desorbed species was recognized also at about 135°C for silica-alumina. However, the formation of diethyl ether was strongly suppressed for silica-alumina throughout the temperature range. The Na^+-exchanged silica-alumina gave the decreased amount of the ethanol adsorption and the decreased reactivity of the adsorbed ethanol.

The difference between silica-alumina and alumina in the characteristics of ethanol dehydration, i.e., the decrease of the amount of ethanol adsorbed and the suppression of diethyl ether formation, may be explained either by the dilution effect of aluminum with silicon, or by the different acidic natures of these two kinds of solids (*12*).

SUMMARY

The main components of the desorbed products of the surface ethoxide on alumina below 135°C were ethanol and diethyl ether, whereas ethylene was obtained above 135°C. The diethyl ether formation was favored with increased surface concentration of the ethoxide, suggesting the Langmuir-Hinshelwood mechanism due to ethoxide pairs on the surface. Ethylene may be formed by methyl hydrogen abstraction by the adjacent exposed oxide ion in a concerted mechanism.

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