JOURNAL OF CATALYSIS 10, 128–133 (1968)

Ethanol Dehydration on Alumina Catalysts

II. The Infrared Study on Adsorption of Diethyl Ether over Alumina

HIROMICHI ARAI, YASUKAZU SAITO, AND YUKIO YONEDA

From the Department of Synthetic Chemistry, Faculty of Engineering,
University of Tokyo, Bunkyo-ku, Tokyo, Japan

Received September 12, 1967; revised November 28, 1967

The structure and thermal decomposition products of diethyl ether adsorbed on alumina have been studied by infrared spectroscopy and mass spectrometry. It was confirmed by infrared spectroscopy that two kinds of surface compounds were formed at different temperature ranges, when dehydrated alumina was exposed to diethyl ether vapor: a coordination complex, $(C_2H_5)_2O\text{-}Al\lt$, below 100°C and a surface ethoxide, $C_2H_5O\text{-}Al\lt$, above 100°C. The coordination complex was thermally decomposed below 130°C, giving a mixture of ethanol, diethyl ether and ethylene, whereas above 130°C more than 97% of the adsorption complex was recovered as ethylene. Correspondingly, the surface ethoxide, which had been made by adsorption at 130°C, was 97% desorbed at 210°C as ethylene. A reaction scheme for the dehydration of ethanol on alumina catalyst is discussed on the ground of these results. For the adsorption of diethyl ether on silica gel, a hydrogen bonding interaction between the oxygen atom of diethyl ether and the surface silanol group was recognized by infrared spectroscopy.

INTRODUCTION

There is a substantial body of literature in which the presence and structure of many active adsorbed intermediates formed through the bonding of the reactants to the catalyst surface have been proposed. Alumina is commonly used as a catalyst or a support. A step toward understanding heterogeneous catalysis is to ascertain the adsorption structure of the reactants and the reaction scheme of the surface compounds. Studies on absorbed molecules by infrared spectroscopy have given much information about the chemical structure and the geometrical arrangement of the adsorbed species (*1*).

It is known that the adsorption of ethers on evacuated silica causes almost complete disappearance of the free hydroxyl band at 3750 cm^{-1}, and that a broad band appears at 3300 cm^{-1} (*2*). This broad band has been assigned as the stretching vibration of the hydroxyl group of the silanol-ether complex in which the OH group was hydrogen-bonded to the oxygen atom of the adsorbed ether (*3*). The structure of adsorbed diethyl ether on alumina has not been studied yet by infrared spectroscopy. Since the desorbed products of the surface ethoxide, formed by ethanol adsorption on alumina (*4*, *5*), include diethyl ether and, moreover, diethyl ether on alumina reacts with the surface hydroxyl group to produce ethanol (*6*), the adsorption sites of diethyl ether and of ethanol may possibly be identical.

It was the purpose of this investigation to determine the adsorption structure of diethyl ether chemisorbed on alumina by infrared spectroscopy and to elucidate the reactivity of the chemisorbed species by the technique of thermal desorption. The reaction scheme of ethanol dehydration over alumina catalyst is discussed in connection with a series of spectroscopic investigations (*4*).

EXPERIMENTAL

Apparatus. A detailed description of the apparatus was reported previously in a paper concerning the chemisorption of ethanol on alumina (*7*). The catalyst in the infrared cell could be heated and exposed to either a vacuum or a variety of gaseous atmospheres *in situ*. The fine powder of alumina or silica gel was pressed at 7000–10 000 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. All infrared spectra were measured by a Model 401G grating type spectrometer (Japan Spectroscopic Co.). The reference beam was attenuated with a specially designed screen in order to compensate the loss of light by scattering, especially at the wave range between 4000 and 2500 cm^{-1}.

Materials. Both alumina and silica gel were the same as reported in the previous paper (*8*). Alumina, prepared by hydrolysis of aluminum isopropoxide and by calcination in air at 550°C for 7 hr, had a BET surface area (N_2 adsorption) of 170 m^2/g. Silica gel, prepared by hydrolysis of ethyl orthosilicate and by calcination in air at 550°C for 7 hr, had a surface area of 600 m^2/g. Diethyl ether (G.R.) was distilled twice over sodium wire 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 cell at first and then slipped down to the light beam part of the cell. After the adsorption equilibrium was attained at room temperature in a diethyl ether atmosphere (10 mm Hg), the vapor and the physisorbed species were removed by evacuation at 30°C. The chemisorbing catalyst thus prepared was slowly heated up to a certain temperature. During the condensation of the desorbed species by a liquid nitrogen trap, the pressure in the infrared cell was always maintained below 2×10^{-3} mm Hg. Therefore, the readsorption of diethyl ether from the vapor phase seems to be negligible. This procedure was repeated at several temperatures till the intensity of the absorption band at 1391 cm^{-1} gave a constant value. The trapped species were analyzed by a mass spectrometer (Consolidated Engineering Corp. Type 21-103C). Since the amounts of ethylene and ethanol were convertible in calculation to that of diethyl ether, the amount of diethyl ether chemisorbed on alumina could be determined.

RESULTS AND DISCUSSION

Diethyl Ether Adsorbed on Silica Gel

As for the diethyl ether adsorbed on silica gel which had been evacuated at 550°C, its infrared spectrum was very similar to that of a carbon tetrachloride solution between 3000 and 1250 cm^{-1}, as is shown in Fig. 1. These absorption bands due to the adsorbed ether disappeared completely by the evacuation at 30°C for 30 min. A sharp band at 3745 cm^{-1} due to the silanol group of the surface was changed

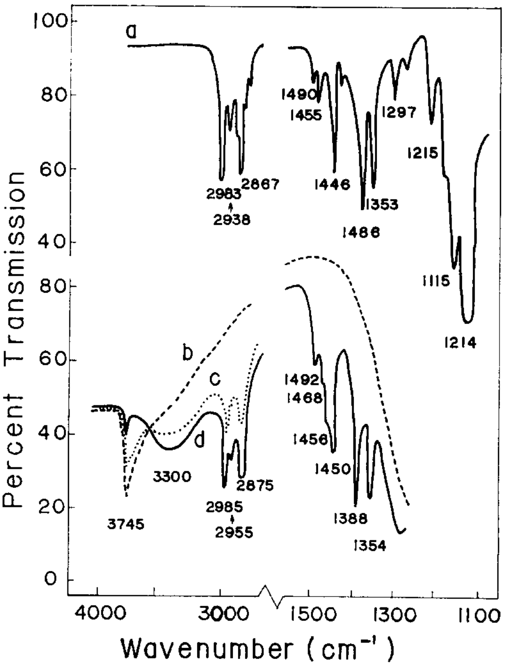

FIG. 1. The infrared spectra of diethyl ether adsorbed on silica gel. (a) The spectrum of diethyl ether in carbon tetrachloride solution. (b) The spectrum of silica gel after the evacuation at 550°C for 5 hr. (c) The spectrum of diethyl ether adsorbed on silica gel at 30°C (0.5 mm Hg). (d) The spectrum of diethyl ether adsorbed on silica gel at 30°C (1.0 mm Hg).

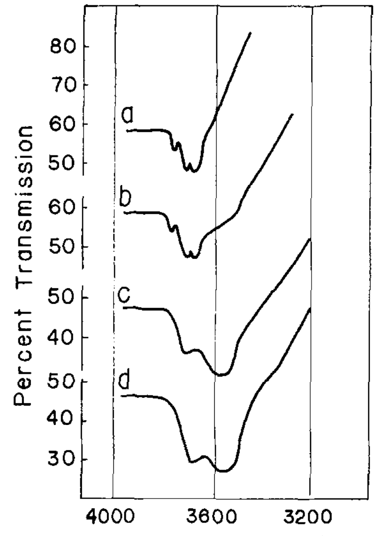

FIG. 2. The infrared spectra of the surface hydroxyl of alumina after the adsorption of diethyl ether, ethanol, and water recorded between 4000 and 3200 cm^{-1} at 30°C. (a) The background spectrum of alumina which had been evacuated at 550°C for 5 hr. (b) The spectrum of the surface hydroxyl of alumina after the diethyl ether adsorption at 30°C and evacuation at 30°C. (c) The spectrum of the surface hydroxyl of alumina after the ethanol adsorption at 70° and evacuation at 70°C. (d) The spectrum of the surface hydroxyl of alumina after the water adsorption at 100° and evacuation at 100°C.

into a broad band at 3300 cm^{-1} by the introduction of diethyl ether, which was restored to the original sharp band upon evacuation. Since the broad band at 3300 cm^{-1} was assigned as the hydrogen-bonded hydroxyl group (*2*, *3*), the adsorption of diethyl ether on silica gel seems to take place by hydrogen bonding between the oxygen atom of diethyl ether and the hydrogen atom of the surface silanol group.

Diethyl Ether Adsorbed on Alumina

The infrared spectra of water, ethanol, and diethyl ether adsorbed on alumina which had been evacuated at 550°C are shown for the region from 4000 to 3200 cm^{-1} in Fig. 2. A broad band at 3550 cm^{-1} appeared immediately after water or ethanol was introduced, whereas no broad band was observed in the same range for the diethyl ether adsorption. The appearance of the broad band at 3550 cm^{-1} owing to water adsorption on alumina is demonstrated in more detail in Fig. 3. This broad band at 3550 cm^{-1} was also attributed to the hydrogen-bonded hydroxyl group. Therefore, it can be deduced that diethyl ether was not adsorbed on the hydroxyl group of the evacuated alumina surface at 30°C in contrast to water or ethanol, while diethyl ether was adsorbed on silica gel by hydrogen bonding as stated above.

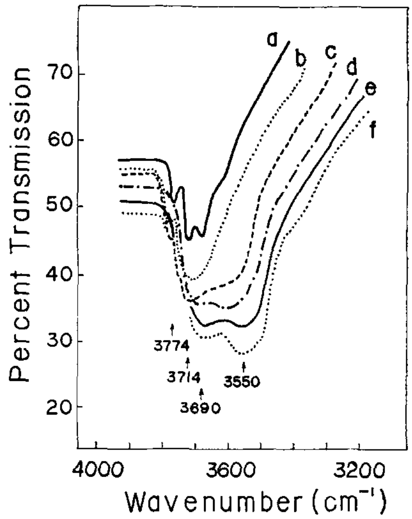

FIG. 3. The infrared spectra of the surface hydroxyl of alumina as a function of the amount of water adsorption on alumina which had been evacuated at 550°C for 5 hr. The alumina sample of 25 mg was used. (a) The background spectrum of alumina evacuated at 550°C for 5 hr. (b) The spectrum of the surface hydroxyl of alumina after the water chemisorption of 2.8×10^{-6} mole. (c) 5.6×10^{-6} mole. (d) 8.4×10^{-6} mole. (e) 11.2×10^{-6} mole. (f) 14.0×10^{-6} mole.

The NMR spectrum of a mixture of diethyl ether and aluminum chloride in a carbon tetrachloride solution consisted of a methyl triplet and a methylene quartet. The chemical shifts to down field of 0.385 and 1.04 ppm for the methyl and methylene protons, respectively, were observed for the mixture from pure diethyl ether in the carbon tetrachloride solution in reference to the internal tetramethylsilane. In other words, the methylene protons of diethyl ether were unshielded by electrons to a greater extent than the methyl protons by being mixed with aluminum chloride in the carbon tetrachloride solvent. This strongly suggests that a coordinated bond is formed between the oxygen atom of diethyl ether and the aluminum atom of aluminum chloride in the solution of carbon tetrachloride.

The coordination compound, $(C_2H_5)_2O$-$AlCl_3$ (m.p. 35°C) (*9*), in the carbon tetrachloride solution gave a very similar infrared spectrum to the diethyl ether adsorbed on alumina at 30° or 70°C in the range from 3000 to 1000 cm^{-1}, as is shown in Fig. 4. This similarity will assure the assignment that the adsorption structure of diethyl ether on alumina at 30° or 70°C is of the coordination type, such as $(C_2H_5)_2O$-$Al<$.

The infrared spectrum taken at 130°C after heating alumina at 130°C in diethyl ether (10 mm Hg), followed by the evacuation at 130°C for 2 hr, is given in Fig. 5. The infrared spectra of the adsorbed ethanol on alumina [introduced at 70°C and evacuated at 70°C for 2 hr (*4*)] and of aluminum ethoxide are shown for comparison in the same figure. They are apparently similar to each other and are certainly different from those of the coordination type shown in Fig. 4. It is, therefore, concluded that the adsorption structure of diethyl ether on alumina at high temperature is dissociative, the surface ethoxide being formed.

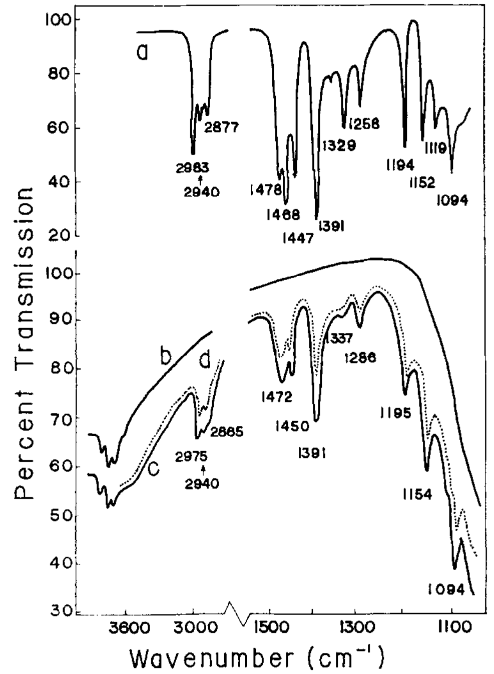

FIG. 4. The infrared spectra of diethyl ether on alumina at low temperature. (a) The spectrum of $(C_2H_5)_2O$-$AlCl_3$ complex in carbon tetrachloride solution. (b) The spectrum of alumina evacuated at 550°C for 5 hr. (c) The spectrum of diethyl ether adsorbed on alumina at 30°C, after the evacuation at 30°C for 2 hr. (d) The spectrum of diethyl ether adsorbed on alumina at 70°C, after the evacuation at 70°C for 2 hr.

The thermal desorption products of the surface compound of diethyl ether on 25 mg of alumina which had been evacuated at 550°C for 5 hr prior to the introduction of diethyl ether at 30°C, were analyzed by mass spectrometry. The distribution of desorbed products in the range of 30° to 210°C is shown in Table 1. The amount of ethyl group (C_2H_5–) in this table was given

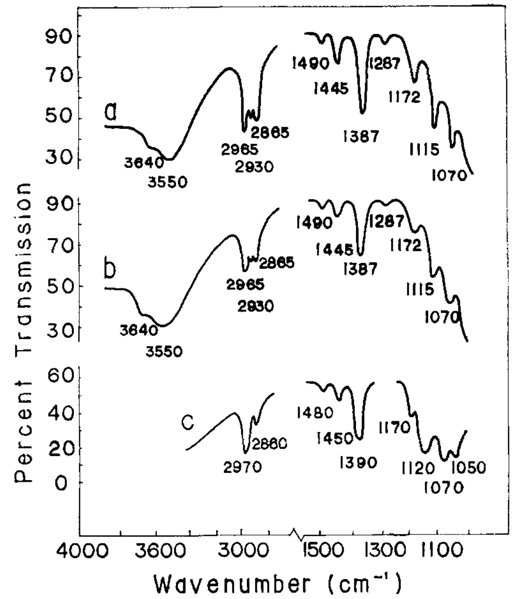

FIG. 5. The infrared spectra of diethyl ether on alumina at high temperature. (a) The spectrum of the ethanol adsorbed on alumina at 70°C after the evacuation at 70°C for 2 hr (ref. *7*). (b) The spectrum taken at 130°C after heating the alumina catalyst at 130°C in diethyl ether (10 mm Hg), followed by the evacuation at 130°C for 2 hr. (c) The reference of aluminum ethoxide given by Greenler (ref. *5*).

TABLE 1
THE THERMAL DESORPTION PRODUCTS OF THE SURFACE COMPOUND OF DIETHYL ETHER ON ALUMINA AT THE RANGE OF 30° TO 210°C

Temperature range of thermal desorption (°C)	Total adsorbed amount (× 10^{-7} mole)	Distribution of desorbed products (%)			Amount of desorption (× 10^{-7} mole)	
		C_2H_5OH	$(C_2H_5)_2O$	C_2H_4	Total	C_2H_5[a]
30–70°	59	14	83	3	26	47
70–90°	35	19	74	7	10	17
90–140°	27	14	36	50	13	18
140–170°	18	1	1	98	27	27
170–210°	4	1	2	97	8	9
Total	59	9	40	51	84	118

[a] See text.

by counting ethanol or ethylene as one ethyl group and diethyl ether as two. At low temperature, the main desorption product of diethyl ether adsorbed on alumina was diethyl ether itself. The assignment of an adsorption structure of the coordination type, $(C_2H_5)_2O\text{-}Al<$, at 30° or 70°C by infrared spectroscopy is thus supported by the thermal desorption experiments. This fact also affords evidence that the adsorption sites on the alumina surface for diethyl ether are the exposed aluminum ions, which are acting the role of Lewis acid.

When 25 mg of alumina was heated at 130°C in diethyl ether (10 mm Hg) and was evacuated at the same temperature for 2 hr, all the surface ethoxide was desorbed at 210°C as the mixture of ethanol 1%, diethyl ether 2%, and ethylene 97%. The amount of the surface ethoxide was obtained as 4.2×10^{-6} mole. This will confirm the assignment of the dissociative adsorption structure of diethyl ether on alumina at high temperature. The transition temperature of the adsorption structure of diethyl ether on alumina from the coordination type to this ethoxide type seems to be 100°C.

The chemisorption of ethanol on alumina was previously confirmed to take place in a dissociative way (*4*). Moreover, the thermal desorption products from the dissociatively adsorbed ethanol were ethanol and diethyl ether below 135°C and ethylene above 135°C (*4*).

As far as both the chemisorption of ethanol and the high temperature adsorption of diethyl ether on alumina are concerned, the surface aluminum ethoxide is the common adsorption species. As for the thermal desorption products, the chemisorption of ethanol and diethyl ether on alumina also correspond at low and high temperatures, respectively. All these results are interpreted without contradiction in the following reaction sequences.

$$
\begin{aligned}
&(C_2H_5)_2O(g) + Al<(cat) + O\text{-}Al<(cat) \\
&\rightleftarrows (C_2H_5)_2O\text{-}Al<(cat) + O\text{-}Al<(cat) && (1) \\
&\rightleftarrows C_2H_5O\text{-}Al<(cat) + C_2H_5\text{-}O\text{-}Al<(cat) && (2) \\
&\rightarrow 2C_2H_4(g) + Al<(cat) + O\text{-}Al<(cat) \\
&\qquad + H_2O(g) && (3)
\end{aligned}
$$

Reaction (1) is mainly observed at low temperature. Reactions (2) and (3) occur at high temperature. Since reaction (3) is a step of the dehydration reaction of ethanol, it is strongly suggested that the surface ethoxide is the common reaction intermediate of ethylene formation on alumina catalyst from either ethanol or diethyl ether.

SUMMARY

According to the results of infrared spectroscopy, the structure of adsorbed diethyl ether on alumina is of the coordination type, $(C_2H_5)_2O\text{-}Al<$, below 100°C and the ethoxide type, $C_2H_5O\text{-}Al<$, above 100°C, whereas only the hydrogen-bonding type is observed on silica gel. The thermal desorption products of diethyl ether adsorbed on alumina were mainly diethyl

ether itself at low temperature and ethylene at high temperature. The adsorption sites on the alumina surface for diethyl ether are concluded to be the exposed aluminum ions, which are acting the role of Lewis acid. The adsorption of ethanol on alumina was previously confirmed to take place in a dissociative way, the surface ethoxide being formed, and the thermal desorption products were ethanol and diethyl ether at low temperature and mainly ethylene at high temperature. Therefore, it is strongly suggested that the surface ethoxide is the common reaction intermediate of the ethylene formation on alumina catalyst from either ethanol or diethyl ether.

REFERENCES

1. EISCHENS, R. P., AND PLISKIN, W. A., *Advan. Catalysis* **10,** 1 (1958); SHEPPARD, N., *Spectrochim. Acta* **14,** 249 (1958); CRAWFORD, N., *Quart. Revs.* **14,** 378 (1960); LITTLE, L. H., *in* "Infrared Spectra of Adsorbed Species," p. 8. Academic Press London, New York, 1966.
2. DAVYDOV, V. YA., KISELEV, A. V., AND LYGIN, V. I., *Kolloid. Zh.* **25,** 152 (1963).
3. MCDONALD, R. S., *J. Phys. Chem.* **62,** 1168 (1958); MCDONALD, R. S., *J. Am. Chem. Soc.* **79,** 850 (1957); BASILA, M. R., *J. Chem. Phys.* **35,** 1151 (1961).
4. ARAI, H., TAKE, J., SAITO, Y., AND YONEDA, Y., *J. Catalysis* **9,** 146 (1967).
5. GREENLER, R. G., *J. Chem. Phys.* **37,** 2094 (1962).
6. WINFIELD, M. E., *in* "Catalysis" (P. H. Emmett, ed.), Vol. VII, p. 93. Reinhold, New York, 1960.
7. ARAI, H., SAITO, Y., AND YONEDA, Y., *Bull. Chem. Soc. Japan* **40,** 731 (1967).
8. ARAI, H., SAITO, Y., AND YONEDA, Y., *Bull. Chem. Soc. Japan* **40,** 312 (1967).
9. OLAH, G. A., in "Friedel-Crafts and Relative Reactions," Vol. 1 p. 700. Interscience, New York and London, 1963.