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The Infrared Study of the Adsorption of Ethanol on Alumina

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The structure of ethanol adsorbed on alumina has been studied by means of infrared spectroscopy. At room temperature physically-adsorbed ethanol was observed, but it was completely removed by evacuation at 70°C for 2 hr. On the contrary, another adsorbed species remained after long evacuation at 70°C; it was identified as a surface ethoxide ($C_2H_5OAl<$). The concentration of the surface ethoxide on alumina had a linear correlation with the intensity of the CH_3 symmetric deformation band at 1387 cm^{-1}. The molar absorption coefficient of the band at 1387 cm^{-1} decreased parallel with $1/T$ at a higher temperature. The number of adsorption sites was calculated as 2.1×10^{14} sites/cm^2 when the ethanol was exposed at 70°C to an alumina catalyst which had been evacuated at 550°C for 5 hr.

The structure of ethanol adsorbed on alumina has been studied by Naito,[1] Uvarov[2] and Greenler[3] by means of infrared spectroscopy. All these authors identified the surface compound as of the ethoxide type ($C_2H_5OAl<$), comparing its infrared spectra with that of aluminum ethoxide. Naito[1] determined the structure of methanol or ethanol adsorbed on alumina at 20°C by infrared spectroscopy on the ground of the similarity of the spectra to those of the corresponding aluminum alkoxides. Uvarov[2] reported that the surface compound of ethanol adsorbed on alumina was identified as ethoxide, since the surface deuteroxyl group ($\overline{OD}$) of alumina was replaced by OC_2H_5 as the infrared absorption band of the ethyl group appeared with the ethanol adsorption at 300°C. Greenler[3] found three kinds of adsorbed species when either methanol or ethanol was exposed to alumina. He observed a weakly-bound layer of liquid alcohol (physical adsorption) at 35°C which was removed by evacuation. Other species, which remained after prolonged evacuation, were identified as a surface methoxide and ethoxide. When an alumina sample was heated at 170°C in alcohol vapor, a formate-like surface compound was formed from methanol and an acetate-like compound, from ethanol.

Alumina is commonly used as a catalyst or a catalyst support. A step toward understanding its catalytic activities is to ascertain the adsorption mechanisms of the reactants and the number of adsorption sites. Studies of adsorbed molecules by the investigation of their infrared spectra have been shown to give information about the chemical structure and geometrical arrangement of the

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[1] K. Naito, *Bull. Osaka Industr. Res. Inst. (Japan)*, **10**, 160 (1959).
[2] A. V. Uvarov, *Zh. Fiz. Khim. (USSR)*, **37**, 1186 (1963).
[3] R. G. Greenler, *J. Chem. Phys.*, **37**, 2094 (1962).

adsorbed species.[4] It is the intent of this paper to ascertain the ethoxide structure of ethanol chemisorbed on the alumina catalyst and to measure the number of adsorption sites during catalysis by the application of infrared spectroscopy.

Experimental

Apparatus. The experimental apparatus for this investigation, shown in Fig. 1, provides a method to support a catalyst sample in the beam of an infrared spectrometer. The sample cell was similar to that of Peri and Hannan,[5] except that we used sodium chloride windows sealed with glyptal. The catalyst could be heated and exposed to a vacuum or to a variety of gaseous atmospheres *in situ*. 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. Evacuation above 550°C was done at the middle of the cell, around which a furnace was placed high away from the light-beam path. The setting of the 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. All infrared spectra were measured by a Model 401G grating-type spectrometer (Japan Spectroscopic Co.). The instrument was always packed with dried silica gel and fresh soda lime in order to remove any water and carbon dioxide. The reference beam was attenuated with especially-designed screens to compensate for any loss of transmission through the sample by scattering, especially between 4000 and 2500 cm^{-1}. Some preliminary experiments were made; the best compromise of sensitivity and resolution for the highest frequency was obtained at the maximum slit width of 0.9 mm.

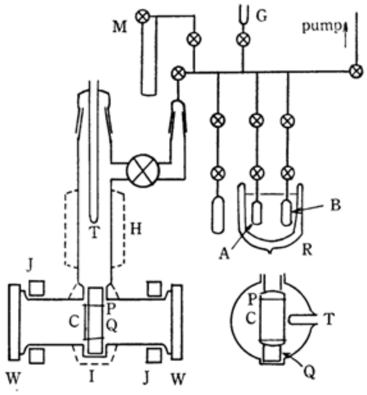

Fig. 1. Cell for infrared study of adsorbed gases.

A	Water
B	Ethanol
C	Catalyst sample
G	Thermocouple gauge
H	Heater for evacuation at higher temperatures
I	Heater for catalytic reaction below 300°C
J	Jacket for cooling water
M	Manometer
P	0.01 mm platinum wire
Q	Sample holder made by fused quartz
R	Trap of ice (0°C)
T	Thermocouple
W	NaCl window

Materials. The alumina gel and silica gel were the same as used in the previous paper.[6] The alumina gel samples were prepared by the hydrolysis of aluminum isopropoxide and were calcined in air at 550°C for 7 hr. The B. E. T. surface area (N_2 adsorption) was 170 m^2/g. Silica gel samples were prepared by the hydrolysis of ethyl orthosilicate and were calcined in air at 550°C. The B. E. T. surface area (N_2 adsorption) was 600 m^2/g. The ethanol (G. R.) was distilled over magnesium metal twice under diminished pressure in order to remove the water; then it was degassed through several freeze-thaw cycles.

Procedures. The alumina samples were evacuated (*ca.* 10^{-5} mmHg) at 550°C for 5 hr in the upper part of the cell at first, slipped down to the light-beam part of the cell, and then heated at various temperatures before the addition of a given amount of ethanol vapor. After the attainment of the adsorption equilibrium was ascertained at 70°C, the vapor and the physisorbed species were trapped by liquid nitrogen. The trapped ethanol was led into and expanded in a vessel of a constant volume, with the pressure measured by the thermocouple gauge. The amount of chemisorption was calculated first from the difference between the amount of ethanol introduced and the amount trapped. Then, the sample with chemisorbed species was heated slowly up to the predetermined temperatures, with the pressure in the cell maintained below 2×10^{-3} mmHg during the condensation of the desorbed products by the liquid nitrogen trap. The trapped species (ethanol, ethylene, and diethyl ether) were analyzed quantitatively by mass spectrometry. As the amounts of ethylene and diethyl ether could be converted to that of ethanol, the chemisorption amount of the introduced ethanol had to be determined independently. The amount of chemisorption thus obtained was confirmed to be equal to the amount of chemisorption obtained by the first method. Correction curves of the thermocouple gauge between pressure and voltage were obtained with regard to air, ethanol, water and ethylene.

Results and Discussion

The accumulation of knowledge on the molecular structure of chemisorbed species on the active sites is necessary in order to study the properties of heterogeneous catalysts. In order to separate the physisorption effect on active sites of the alumina surface from the chemisorption effect, adsorption on silica gel was attempted, since silica gel is inactive for the dehydration reaction of ethanol and is considered to have no chemisorption sites. At room temperature, ethanol vapor was adsorbed on the surface of a silica plate which had been evacuated at 550°C for 5 hr *in situ*,

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4) R. P. Eischens and W. A. Pliskin, "Advances in Catalysis," Vol. 10, Academic Press Inc., New York (1958), p. 1.

5) J. B. Peri and R. B. Hannan, *J. Phys. Chem.*, **64**, 1526 (1960).

immediately after its introduction into the cell. The infrared spectrum of ethanol adsorbed on silica at room temperature was similar to that of ethanol in a carbon tetrachloride solution from 4000 cm^{-1} to 1250 cm^{-1}. The intensity of the band at 2965 cm^{-1} representing the CH_3 stretching vibration and the pressure in the cell gave the amount of ethanol adsorbed on silica, and the amount decreased gradually as the temperature became higher. The adsorbed species was desorbed by evacuation at 70°C for 2 hr. The sharp absorption band representing the free hydroxyl group of silica at 3745 cm^{-1} decreased in intensity and shifted to a lower frequency upon ethanol adsorption, whereas the evacuation treatment restored the original band of the silanol group. Blyholder *et al.*[7] reported that the ethanol physically adsorbed on pure silica gel disappeared upon evacuation at 20°C for one-half hour. Therefore, it may be concluded that the ethanol adsorbed on alumina must be composed of a physisorbed species which would be removed by evacuation at 70°C for 2 hr and of a chemisorbed species not removed by the same treatment.

The infrared spectra of ethanol chemisorbed on alumina from 4000 cm^{-1} to 1000 cm^{-1}, as well as that of aluminum ethoxide, are shown in Fig. 2. These spectra strongly suggest that the compound formed on the alumina surface has an ethoxide structure, as has been proposed by Naito,[1] Uvarov,[2] and Greenler.[3] A broad band at 1650 cm^{-1}, representing the mode of H_2O bending vibration due to physically-adsorbed water,[6] disappeared upon evacuation at 100°C, as is shown in Fig. 3. Another broad band, between 3700 cm^{-1} and 3450 cm^{-1}, remained after evacuation at 100°C and was identified as the hydrogen-bonded hydroxyl group on the alumina surface, since the hydrogen-bonded hydroxyl group on the surface of amorphous silica was identified by McDonald.[8] The removal of a water molecule from the surface of alumina gel at a higher temperature would create an exposed oxide ion and a bare aluminum ion.

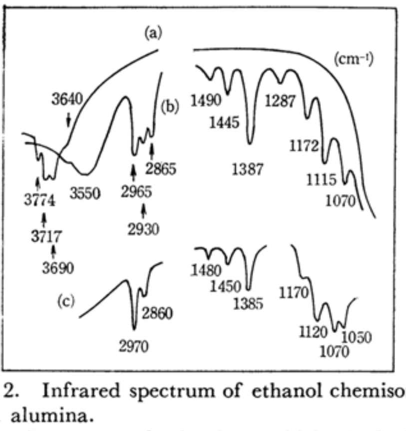

Fig. 2. Infrared spectrum of ethanol chemisorbed on alumina.
(a) Spectrum of alumina which had been evacuated at 550°C for 5 hr. (b) Spectrum of ethanol on alumina at 70°C after evacuation of sample cell at 70°C. (c) For comparison the spectrum of $Al(C_2H_5O)_3$ is also shown by Greenler (Ref. 3).

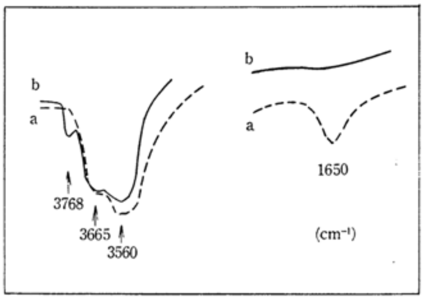

Fig. 3. Infrared spectra of alumina at 100°C.
(a) With water vapor of 4.6 mmHg at 100°C
(b) After evacuation at 100°C for 1 hr

The quantity of the chemisorption of water, 1.9×10^{14} sites/cm^2, was almost the same as that of ethanol, 2.1×10^{14} sites/cm^2, for alumina gel which had been evacuated at 550°C for 5 hr. These values were obtained from the adsorption amount by measuring volumetrically the difference between the total amount of water or ethanol added to the system and the amount remaining in the vapor phase. The amount of surface ethoxide decomposed completely by heating corresponded to the adsorption amount obtained above. Therefore, water would be decomposed on the dehydrated alumina surface, with the hydroxyl ion attached to the exposed aluminum ion and the proton to the oxide ion, to give a hydroxyl monolayer over the alumina surface until all the adsorption sites were covered. The same mechanism would be applied to ethanol adsorption at 30°C on the dehydrated alumina surface, where surface ethoxide would be produced on the exposed aluminum ion, accompanied by the formation of a hydroxyl group. The existence of both the hydrogen-bonded hydroxyl group and ethoxide (C_2H_5O–Al<) was ascertained on the alumina surface at 70°C by infrared spectroscopy, as is shown in Fig. 2. The number of adsorption sites for alumina which had been evacuated at 550°C for 5 hr was calculated to be 2.0×10^{14} sites/cm^2 by the amount of the saturated chemisorption of ethanol or water, which corresponds to that of either exposed aluminum ions or oxide ions on the surface. The number of exposed aluminum ions was also reported by Peri[9]

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6) H. Arai, Y. Saito and Y. Yoneda, This Bulletin, **40**, 312 (1967).
7) G. Blyholder and L. P. Neff, *J. Catalysis*, **2**, 138 (1963).
8) R. S. McDonald, *J. Phys. Chem.*, **62**, 1168 (1958).
9) J. B. Peri, *ibid.*, **69**, 220 (1965).

to be dependent on the dehydration temperature. Adsorption sites for ethanol on alumina appeared at a higher temperature than 100°C upon dehydration. It was observed in infrared spectroscopy that the following reaction took place slightly on alumina at 70°C:

$$C_2H_5OH \text{ (gas)} + \text{HO–Al}< \; = \; C_2H_5O\text{–Al}< + H_2O \text{ (gas)}$$

A lot of absorption bands due to stretching or bending vibrations of the CH_3, the CH_2, or the CO group were observed for chemisorbed ethanol on alumina. The number of adsorption sites would be obtained by the use of the intensity of the absorption band which might be least influenced by surface bondage.

The selection of the band least influenced by surface bondage must be made according to the following criteria:

(1) The absorption band must not be superposed upon by background bands of the catalyst.

(2) The molar extinction coefficient of the absorption band must be far larger than the level of detection.

(3) The absorption band must be assigned to the vibration mode of the group farthest away from surface bondage.

Although the CH_3 asymmetric or symmetric stretching vibration was superposed upon by absorption bands of both the alumina and the CH_2 asymmetric and symmetric stretching vibration, the band of the CH_3 symmetric bending vibration at 1387 cm^{-1} satisfied the above three criteria. The intensity of the absorption band at 1387 cm^{-1} was plotted against the amount of adsorption as is shown in Fig. 4. It was revealed that the amount of ethanol chemisorbed was 1.6×10^{-5} mol at 70°C for an alumina sample of 25 mg which had been evacuated at 550°C for 5 hr. The bonding strength of the CO of ethoxide adsorbed on the aluminum ion would be easily affected by the heterogeneity of the alumina surface. The heterogeneity ought to be clarified by measuring the amount of desorption at different temperatures. Some results concerning the surface heterogeneity and the reaction selectivity of the alumina catalyst for the dehydration of ethanol will be published later.

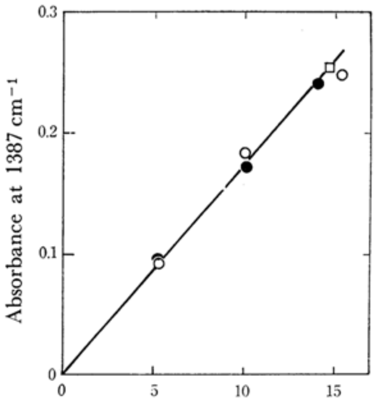

Fig. 4. Relation between surface concentration and absorbance at 1387 cm^{-1} of ethanol chemisorbed on alumina, which had been evacuated at 550°C for 5 hr. Infrared spectra were measured at 70°C. Sample weight of alumina was 25 mg.
● In case of addition of ethanol at once
○ In case of addition of ethanol succesively
□ Evacuation for 1 hr at 70°C after adsorption equilibrium of ethanol vapor of 12 mmHg at 70°C

Infrared radiation from a heated sample or a cell directly to the detector of the spectrometer must be taken into account when infrared spectra are measured at higher temperatures. Suppose that two samples of the same transparency were easily obtained, then it would be far better to compensate by the reference beam in the double-beam spectrometer. However this is very difficult, since the sample plates must be thick to secure a large surface area, while the same transparency is demanded for both of them. In order to compensate for the radiation from the sample and the cell, the following relationships were used to offset the radiation effects:

$$T_\nu = \frac{X_\nu - Z_\nu}{Y_\nu - Z_\nu}, \tag{1}$$

$$A_\nu = -\log_{10} T_\nu, \tag{2}$$

$$\varepsilon_\nu = \frac{A_\nu}{cl} = \frac{A_\nu}{\dfrac{M}{hkl}\, l} = \frac{A_\nu hk}{M}, \tag{3}$$

where T_ν is the true transmittance at the wave number, ν cm^{-1}; X_ν, the transmittance after the addition of ethanol; Y_ν, the transmittance before the addition of ethanol; Z_ν, the radiation from the sample and the cell; A_ν, the absorbance; ε_ν, the molar extinction coefficient of the adsorbing species ($mol^{-1}\, l\, cm^{-1}$); h, k and l, the geometrical dimensions of the sample pellet, the height, the width, and the thickness (cm) respectively; c, the concentration of adsorbing species in the sample pellet (mol/l), and M, the mol of the added ethanol. Since Z_ν is the function of both the temperature of the sample pellet and the wave number of monochromatic infrared light, Z_ν increases as the temperature becomes higher and as the wave number decreases, as is shown in Fig. 5.

As the measurement temperature increased, the intensity of each absorption band of the adsorbed ethoxide decreased. The molar extinction coefficient of the adsorbing species (ε_ν) was found to be decreasing in inverse proportion to the temperature of the measurement in Kelvin degrees. The temperature effect for the CH_3 symmetric

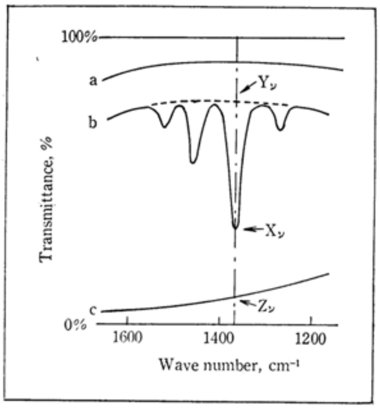

Fig. 5. Interpretation of X_ν, Y_ν and Z_ν.

(a) Infrared spectrum of alumina (background)
(b) Infrared spectrum of ethanol adsorbed on alumina
(c) Radiation from sample pellet and cell

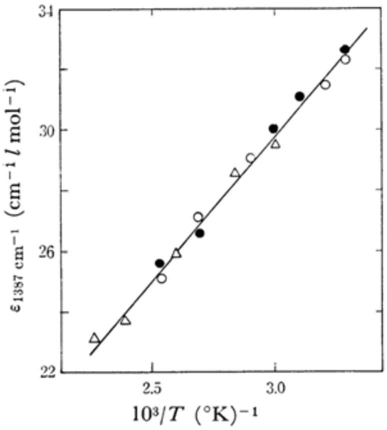

Fig. 6. Relationship between molar absorption coefficient at 1387 cm⁻¹ and temperature.

△ ε_ν was calculated from the amount of desorption at each temperature.
● Infrared spectra were measured from 120°C down to 30°C where the amount of adsorption was constant after evacuation at 140°C for 2 hr.
○ Infrared spectra were measured from 30°C up to 120°C where the amount of adsorption was constant after evacuation at 140°C for 2 hr.

bending vibration at 1387 cm⁻¹ is shown in Fig. 6. This relationship satisfies the equation proposed by Lisitsa *et al.*[10]:

$$\varepsilon_\nu = \frac{\dfrac{a}{\nu}T}{(\nu_0-\nu)^2+bT^2}, \tag{4}$$

where a and b are parameters; ν_0, the frequency corresponding to ε_{max}; and T, the temperature of the measurement in °K. If $\nu=\nu_0$ is put into Eq. (4);

$$\varepsilon_{max} = \frac{B}{T}, \tag{5}$$

is obtained, where B is an experimental parameter. When we want to obtain the true amount of species adsorbed at a given temperature during catalysis, proper attention should be paid to Eq. (4) or (5).

The absorbance derived above can be converted into the value of the surface concentration of the adsorbing species by using Eq. (6):

$$\sigma = \frac{10^{-3}A_\nu D\boldsymbol{N}}{W\varepsilon_\nu S}, \tag{6}$$

where σ is the surface concentration of adsorbing species (cm⁻²); $D=hk$, the geometrical area of the sample pellet (cm²); $\boldsymbol{N}$, Avogadro's number; S, the internal surface area of the pellet (cm²/g), and W, the weight of the pellet (g). According to Eqs. (5) and (6), the following equation is derived to give the amount of adsorption at any temperature:

$$\sigma_{\mathrm{T}} = \frac{10^{-3}A_\nu D\boldsymbol{N}T}{WBS}, \tag{7}$$

where B is 9.9×10^3 (cm⁻¹ l mol⁻¹ °K) in the case of the absorption band at 1387 cm⁻¹ of the adsorbed ethoxide. Finally, using these equations,

$$\sigma_{\mathrm{T}} = 6.1\times10^{19}\frac{DA_\nu T}{WS} \tag{8}$$

Substituting $W=0.025$ g, $D=1.7$ cm², and $S=1.7\times10^6$ cm²/g for the experimental values, the following equation is derived:

$$\sigma_{\mathrm{T}} = 2.4\times10^{12}A_\nu T \tag{9}$$

Thus the amount of adsorbing species can be calculated by using the absorbance at 1387 cm⁻¹ at a certain temperature of the system.

Conclusion

The amount of adsorption of the ethanol chemisorbed on the alumina catalyst should be directly proportional to the absorbance of the CH_3 symmetric deformation band at 1387 cm⁻¹, since the methyl group occupies a position far away from the bond of adsorption between the adsorbed compound and the alumina catalyst. The fact that the wave number of this absorption band, 1387 cm⁻¹, was the same as that of free ethanol might be evidence of no influence by the different strength of the aluminum-oxygen bond due to the heterogeneity of the alumina surface. The number of adsorption sites was calculated as 2.1×10^{14} sites/cm² when ethanol was exposed at 70°C to an alumina catalyst which had been evacuated at 550°C for 5 hr.

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[10] M. P. Lisitsa and I. N. Khalimonova, *Optika Spektrosk. (USSR)*, **11**, 332 (1961).

The relationship between the molar absorption coefficient and the temperature is applicable from 25°C to 300°C. Therefore, after the influence of the temperature is taken into account and after all of the absorption bands are identified as belonging to vapor, physisorbed or chemisorbed species, it is possible to ascertain the amount of adsorption at the working state of catalysis by measuring the intensity of the infrared absorbance at the reaction temperature.

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