Spectroscopic Studies of Methylamine Adsorption on Gamma-alumina

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In our previous reports¹⁾, the state of formic acid adsorbed on dehydrated silica and on alumina was investigated by means of nuclear magnetic resonance and infrared absorption methods. We thereby concluded that the acid adsorbed on silica was in an undissociated state, but that the free motion of the proton bonded to oxygen was hindered markedly, while a part of the acid dissociated into formate ions on alumina similarly to the way it did on several metal catalysts²⁾.

As the next substance to be studied along these lines and to be reported on in this paper, methylamine, which has a basic character contrary to that of formic acid, was adopted, while gamma-alumina was adopted as the adsorbent. The present research will also be interesting because of the fact that several amines are used so as to estimate the acidities of such oxide-catalysts.

Experimental

Materials. — *Methylamine.* — Methylamine of a chemically pure grade was used after dehydration.

Deuteromethylamine CH_3ND_2. — Methylamine was deuterated by the following exchange reaction.

$$CH_3NH_2 + D_2O \rightarrow CH_3ND_2 + H_2O$$

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1) K. Hirota, K. Fueki, K. Shindo and Y. Nakai, This Bulletin, **31**, 783 (1958); **32**, 1261 (1959).

2) K. Hirota, K. Kuwata and Y. Nakai, This Bulletin, **31**, 861 (1958); J. Fahrenfort and H. F. Hazebrock, *Z. physik. Chem., N. F.*, **20**, 105 (1959).

Alumina.—Aluminum hydroxide, which was prepared from aluminum nitrate, was dried at 130°C for 10 hr. Then, after drying at 450°C for 8 hr., it was further degased at the same temperature for 100 hr. in vacuo (10^{-4} mmHg). The sample thus produced was a porous powder, its apparent density being 0.49 g./cm^3. According to X-ray measurement, it was almost amorphous, and it could be concluded to be gamma-alumina.

Measurement.—The essential measurement procedures were the same as has been reported already[1]. The infrared spectrum of methylamines adsorbed on the alumina powders was obtained on the sample pressed on a NaCl plate placed in a cell with NaCl windows. The infrared apparatus was a Perkin-Elmer Model 221, installed at the Institute of Protein Research, Osaka University. The nuclear magnetic resonance (NMR) spectrum was obtained at a fixed measuring frequency of 60 Mc./sec. with a Varian-V3600 C, installed at the Japan Atomic Energy Research Institute. The chemical shift of the proton resonance spectrum was determined by employing benzene as an external reference substance in a spinning, coaxial-sample tube arrangement (the double-tube method). Other experimental details will be described when necessary.

Results

The Infrared Spectra.—The infrared spectra of the adsorbed state are shown in Fig. 1, where the contribution of gaseous amine to the spectra, if it existed, was eliminated with a compensation cell. The spectra were obtained when the surface coverage, θ, of amines was ca. 0.2. Though the s/n ratio was large, three bands due to adsorption may be clearly identified in Fig. 1. In Table I they are assigned to gaseous amines of strong intensities. A detailed assignment of the bands will be undertaken below. It must be noted that the intensity of the degenerate stretching vibration ($\nu(CH_3)$) of CH_3 is markedly decreased by adsorption as compared with those of the other two bands, $\delta(CH_3)$ and $\delta(NH_2)$.

The NMR Spectra.—Figure 2 shows the NMR spectra of the normal and deuterated amines in liquid and adsorbed states measured at room temperature. It was found that only one signal could be identified over the range up to $\theta=1.2$; i. e., the other signal became too broad. By comparing the spectra of both amines, it is evident that the observed signal corresponds to that of the proton attached to the carbon atom rather than to that attached to the nitrogen atom. As ought to be expected, the half-width of this signal decreased and became sharp with the surface coverage, θ, as is shown in Fig. 3, where θ was determined

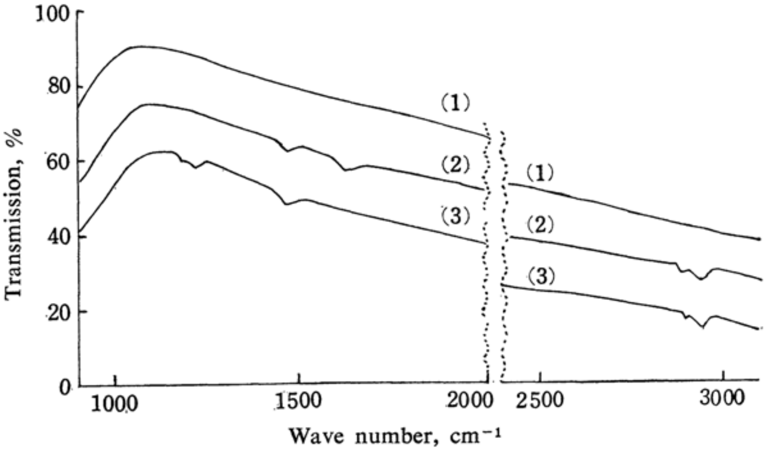

Fig. 1. Infrared spectra of the adsorbed methylamines.
(1) Gamma-alumina, (2) CH_3NH_2 on alumina, (3) CH_3ND_2 on alumina

TABLE I. THE IR ADSORPTION BANDS OF METHYLAMINES

Modes of vibration	Gaseous state* CH_3NH_2 cm^{-1}	Gaseous state* CH_3ND_2 cm^{-1}	Adsorbed state CH_3NH_2 cm^{-1}	Adsorbed state CH_3ND_2 cm^{-1}
(a) ν (CH_3), Degenerated stretching vibration of CH_3	2961	2961	2927	2927
(b) δ (CH_3), Degenerated deformation vibration of CH_3	1473	1468	1470	1465
(c) δ (NH_2), Scissoring vibration of NH_2	1623	1234	1603	1214

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* The bands determined were practically the same as those of the literature (A. P. Gray and R. C. Lard, *J. Chem. Phys.*, **26**, 690 (1957)).

under the assumption that the molecular cross section of methylamine was 18 Å^2. Another interesting point is the chemical shift to the adsorbed state from the liquid state. Since the so-called "bulk effect" is superposed on this effect, a quantitative discussion, besides the relation shown in Fig. 3, will be postponed to later paragraphs.

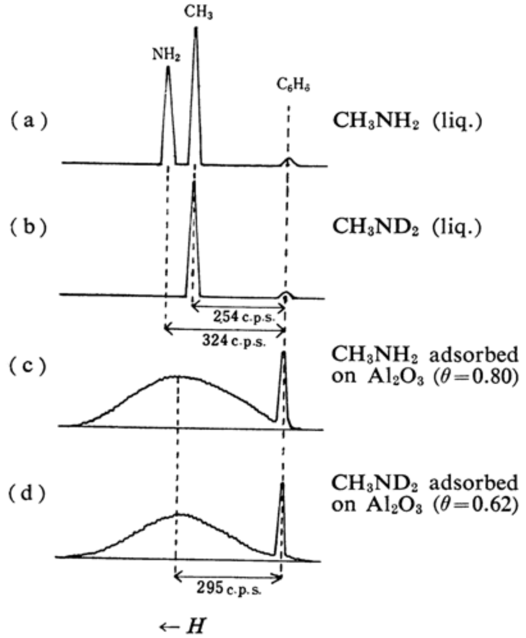

Fig. 2. NMR spectra of the methylamines adsorbed on alumina (schematic).

Discussion

Adsorbed States of Amines.—In the region between 1100∼3300 cm^{-1}, three strong bands are observed on gaseous methylamine, e. g., 2961, 1473 and 1623 cm^{-1}; these are assigned to be $\nu(CH_3)$, $\delta(CH_3)$ and $\delta(NH_2)$ respectively, while the corresponding ones are observed on deuterated methylamine, CH_3ND_2, at 2961 cm^{-1} ($\nu(CH_3)$), 1468 cm^{-1} ($\delta(CH_3)$) and 1234 cm^{-1} ($\delta(ND_2)$) respectively. It is natural, therefore, to correlate them, as has been done in Table I, to the three bands observed when both amines were adsorbed. However, there were some shifts to a lower frequency in $\nu(CH_3)$, $\delta(NH_2)$ and $\delta(ND_2)$. These shifts seem to suggest the occurrence of some structural change of methylamines due to adsorption. The same conclusion will be derived from the data of the NMR spectra below.

As has already been mentioned, two marked changes were observed in the NMR spectra when either of the two methylamines was adsorbed on alumina: a disappearance of the signal of the aminyl-proton and a broadening of that of the methyl-proton.

Judging from these results, methylamine seems to be adsorbed in such a state that the hydrogen of the aminyl group is more resticted than that of the methyl group; i. e., amine is bonded to alumina via the nitrogen atom. Such a model is convenient to explain the change of the δ (NH_2) absorption band, because the bond angle between the N–H groups would be deformed due to adsorption, even though the three bonds of nitrogen atom orient one another so as to take a pyramidal structure, according to microwave-spectroscopic research$^{3)}$.

The Nature of the Bond between Amines and Alumina.—It is, therefore, highly probable that both methylamines are adsorbed on alumina, making the nitrogen atom nearer to the surface than the carbon atom. Let us investigate the nature of the interaction of both atoms from the viewpoint of the adsorbent.

According to recent research$^{4)}$, extremely dehydrated alumina acts as a Lewis acid; e. g., the aluminum atom of such alumina can accept a pair of electrons in its vacant *p*-orbitals, making a kind of bond with the adsorbate molecule. On the present drastically dehydrated alumina, it is natural to assume, therefore, that part of the unpaired electrons of the nitrogen atom will move to the aluminum atom. However, considering the fact that the adsorption heat is not very high, the degree of electron transfer may not be very high*.

Such an electron transfer due to adsorption may also be shown to be possible by the NMR spectra, which give the direction of the transfer by the chemical shift. As is shown by Fig. 2, the signal of the methyl proton shifts to a higher field, apparently suggesting the increase of electrons at the carbon atom, though the reverse result would be expected. The above discrepancy will disappear if the bulk-susceptibility correction is taken into consideration.

When the double-tube method was adopted, the net shift, δ, may be given from the observed shift, δ_{obs}, by the following formula$^{6)}$:

$$\delta=\delta_{\text{obs}}+\frac{2\pi}{3}(\chi_{\text{ref}}-\chi) \tag{1}$$

where χ_{ref} and χ denote the volume magnetic

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3) K. Shimoda, T. Nishikawa and T. Itoh, *J. Phys. Soc. Japan*, **9**, 974 (1954); T. Itoh, ibid., **11**, 264 (1956); T. Nishikawa, ibid., **12**, 668 (1957).

4) Cf., Actes du II Congrès International de Catalyse, Technip, Paris (1960).

* According to the results of Sakai$^{5)}$, the heat of the adsorption of methylamine on alumina is 7.9 kcal./mol. at room temperature.

5) T. Sakai, K. Fueki and K. Hirota, 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961, No. 3360.

6) Cf., J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance", McGraw-Hill Book Co., New York (1959), p. 81.

susceptibilities of the reference substance and of the adsorbate respectively. The chemical shift observed, Δ, corresponds to the difference in δ's between the liquid and the adsorbed state of methylamine, irrespective of the reference substance, benzene. Thus, Δ is given from Eq. 1 by

$$\Delta = (\delta_{\mathrm{liq}} - \delta_{\mathrm{ads}})_{\mathrm{obs}} + \frac{2\pi}{3}(\chi_{\mathrm{ads}} - \chi_{\mathrm{liq}}) \qquad (2)$$

where the volume susceptibility of methylamine χ_{liq} is calculated to be -0.67×10^{-6} from the specific susceptibility⁷⁾ and its density, (0.767 g./cc.). Thus, Δ may be calculated to be 0.35 p. p. m., if the specific susceptibility of alumina is assumed to be that of a dehydrated alumina, i. e., -0.350×10^{-6} ⁸⁾. Therefore, it can be said that the net shift was to the lower field, suggesting an electron transfer from the carbon atom. Such a result will be noteworthy if compared with formic acid/silica system¹⁾, where such a chemical shift due to adsorption may be practically neglected (+0.01 p. p. m.).

On the other hand the conclusion already mentioned is supported by the fact that electron density decreased at the carbon atom as a result of adsorption ; the decrease of ν (CH_3) in wavelength can be explained by this model. However, it is difficult at the present stage of study to estimate quantitatively either the increase in electron density at the aluminum atom or the exact nature of the bond between the amine and alumina.

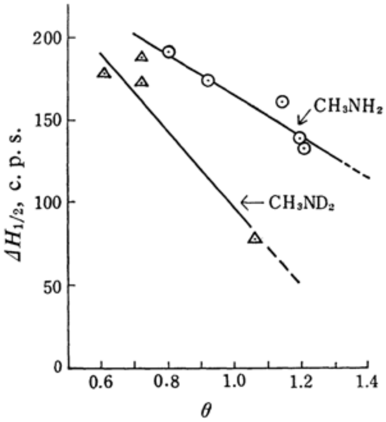

Fig. 3. Change of the half-width of NMR signal of the adsorbed methylamines.

If the amine molecule is chemisorbed on alumina via the nitrogen atom, as has been suggested above, it is not strange that the motion of the aminyl group will be hindered so much more than that of the methyl group that the proton signal of the former may become very broad. For the same reason, it is possible that the signal of the latter may become sharp as the amount of adsorption increases. Thus, the results shown in Fig. 3 may be explained qualitatively.

Finally, it may be added that, according to our recent spectroscopic research, an aromatic amine, aniline, seems to be adsorbed also via its nitrogen atom on alumina⁹⁾, though it takes not a pyramidal but a planar structure. On the other hand, such an adsorbed model will provide other evidence on the role of the Lewis acid sites of alumina, recently proposed by Peri¹⁰⁾, on the isomerization catalyst.

Summary

It can be confirmed directly by means of NMR and infrared spectra that methylamine is chemisorbed on dehydrated gamma-alumina at room temperature, making a bond probably with the aluminum atom via the nitrogen atom ; this conclusion is supported by the fact that the proton signal of the aminyl group cannot be observed at such a surface coverage when that of the methyl group is observed, and the fact that the deformation band of the NH_2 group and the stretching band of CH_3 group change as a result of adsorption.

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7) "Kagaku-Benran", Maruzen, Tokyo (1958), p. 642.

8) P. Pascal, *Compt. rend.*, **178**, 481 (1924).

9) K. Fueki, K. Hirota and H. Otouma, 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962, No. 21 303.

10) J. B. Peri, Actes du II Congrès International de Catalyse, Technip, Paris (1960), p. 1333.