JOURNAL OF CATALYSIS 13, 255–260 (1969)

On the State of Ammonia in the Adsorbed Phase

V. I. KVLIVIDZE,* R. A. BRANTS,† V. F. KISSELEV,*
AND G. M. BLIZNAKOV†

*From the *State University of Moscow, Faculty of Physics, Moscow, U.S.S.R., and the †Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria*

Received March 19, 1968; revised September 10, 1968

The NMR spectra of ammonia adsorbed on silica gel treated at 200° and 700°C and on zeolite (NaX) heated at 77–300°K have been studied. The dependence of the line width and the second moment on coverage has been measured. It has been shown that the surface of silica gel is inhomogeneous and ammonia adsorption proceeds on different types of centers. The phase transition with melting has been observed on NH_3 adsorbed on zeolite at $T \approx 145°K$ (i.e., below the melting point of ammonia). The causes for the decrease in the melting point are considered.

INTRODUCTION

In order to elucidate the mechanism of the elementary act of adsorption and catalysis, it is necessary to investigate the nature of the adsorption centers and the state of adsorbed substances in the adsorbed phase. In an earlier paper we investigated in detail the silica gel–water system. The data from NMR (*1, 2*) and IR (*3, 4*) studies as well as the isotherms and the differential heats of adsorption (*1*) have shown that within the range of lower coverages water adsorption takes place not on the OH groups but on more active centers. It has been shown (*1, 4*) that the Si atoms on the surface which are coordinatively unsaturated can be such centers. This explanation has been given by Weyl (*5*).

The problem has been discussed in ref. (*1*), where it was pointed out that the larger is the number of OH groups connected with a given Si atom, the higher is its coordinative unsaturation. Dehydration of the sample produces a decrease in the coordinative unsaturation of the Si atoms on the surface, thus leading to a decrease in the adsorptive capacity of the specimen. At higher coverages, adsorption is for the most part due to the formation of hydrogen bonds. The mechanism of filling the zeolite (NaX) pores with water has also been studied (*6, 12*). Investigations of the zeolite–water and silica gel–water systems within a wide temperature range (*6, 7*) have shown that the phase transition occurs at temperatures far below 0°C and has some peculiarities associated with the large adsorbate–vapor interface and the defects of the crystalline phase of the adsorbate. It was of interest to study the extent to which these peculiarities are preserved with adsorption of other kinds of molecules.

In the present work, ammonia was chosen as a suitable adsorbate since its molecules have an electronic structure which is close to that of water. In refs. (*8–10*), the heats of adsorption of ammonia on silica gel specimens differing in the hydration extent of their surfaces have been studied. According to ref. (*10*), the values of the differential heats of adsorption (q_0) in the initial range of coverage are within the interval between 18 and 15 kcal/mole depending on the temperature of the preliminary heating of the samples. These high values cannot be explained by the formation of hydrogen bonds between the NH_3 molecules and the surface OH groups as had been assumed previously (*14, 15*). Studies of the IR spectra (*3*) have shown the existence of more strongly bound ammonia molecules on the surface. The formation of a

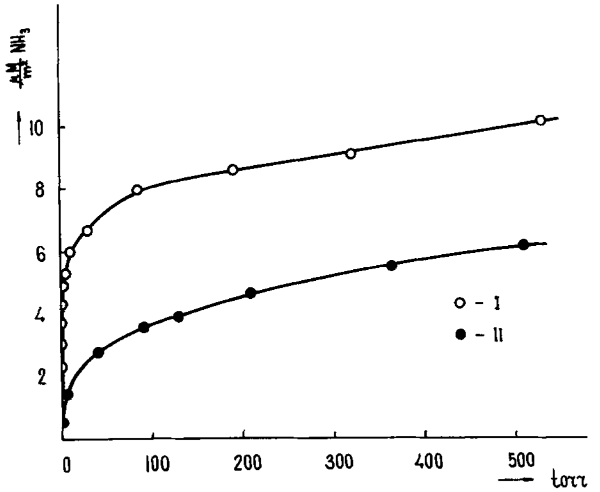

FIG. 1. Isotherms obtained at 25°C for ammonia adsorption on silica gel (samples of series I and II).

donor–acceptor bond between the nitrogen atom in the NH_3 molecule and the free *d*- orbits of Si on the surface with the aid of a free electron couple is quite possible, as it is with water adsorption (*1*, *4*). We studied the NMR spectra of ammonia adsorbed on silica gel treated at 200° and 700°C and on zeolite (NaX) heated at 77–300°K.

EXPERIMENTAL

Silica gel with large pores (Trade mark "Reanal"), purified by boiling with HCl and repeated treatment with twice-distilled water, was used for the experiments. The specific surface area of the samples, determined by low-temperature adsorption of nitrogen, was 370 ± 10 m²/g. Ammonia was purified by resublimation and carefully dried. The dosage of ammonia in the ampoules containing silica gel was carried out at 25°C using a McBain balance. Simultaneously, the adsorption isotherms were obtained. Two series of specimens were prepared. Series I contained silica gel samples heat-treated at 200°C in vacuum (10^{-5} mm Hg) to a constant weight. Series II consisted of specimens of silica gel dehydrated in air at 700°C, then at 200°C in vacuum (10^{-5} mm Hg) for 12 hr. The water content determined [according to (*20*)] by the decrease in weight of the specimens was 5.4 μmole/m² H_2O (or 10.9 μmole/m² OH) for series I and 0.72 μmole/m² H_2O (or 1.44 μmole/m² OH) for series II. After the dosage of ammonia at the given pressure had finished, the ampoules containing silica gel were filled with helium for ensuring a good heat exchange (*6*). We also investigated zeolite (NaX), whose adsorption properties had been studied earlier (*12*). The zeolite was dehydrated at 350°C in vacuum. The amount of adsorbed ammonia was determined by means of a gas burette.

The NMR spectra were taken using a spectrometer with low resolution (*2*). The low-temperature thermostat where the sample was placed enabled us to reach temperatures in the range between 77° and 300°K with an accuracy of ±0.5°. On the basis of the spectra obtained, the line width, ΔH (the distance between the maxima of the derivative) and the second moment, S^2, were determined.

RESULTS AND DISCUSSION

Figure 1 contains the adsorption isotherms of ammonia for the two series of specimens. On the basis of data from low-temperature physical adsorption of ammonia on graphitized soot (*13*), the area which corresponds to 1 molecule in the Brunauer monolayer was assumed to be $\omega = 13.1$ Å². Hence, the capacity of the monolayer will be $a_m = 12.8$ μmole/m². This quantity will be different for the heterogeneous silica gel surface and will increase with dehydration of the surface (*1*), but qualitatively it can be established that all of our adsorption measurements at 25°C correspond to coverages lower than 0.8. As was to be expected, the adsorption of ammonia decreased sharply with dehydration of the surface.

Figure 2 shows the dependence of the linewidth, ΔH, of the NMR signal on coverage for both series of silica gel samples at 25°C. ΔH decreases sharply in the adsorption region around 0.8 μmole/m^2 for the samples of series II. In series I, ΔH changes smoothly, but in the range of coverages of $\sim$1 μmole/m^2, the rate of changing of ΔH again decreases sharply with increasing coverage. At coverages above 4.0 μmole/m^2, ΔH for series I is higher than ΔH for series II, due perhaps to the greater mobility of molecules on the dehydrated surface and their weaker interaction with the surface. This is in agreement with the decrease in the heats of adsorption with dehydration of the surface (*10*).

Study of the NMR spectra at low temperatures may give additional information concerning the state of the adsorbed substance. Figure 3 shows the dependence of the second moment, S^2, of NH_3 adsorbed on silica gel at 25°C (various degrees of coverage) after a successive quick freezing of the ampoules at 90°K. As has been shown earlier (*6*, *7*), when there is helium in the ampoules, the freezing of ammonia on the ampoule walls can be neglected. It is evident from Fig. 3 that S^2 for both samples changes with increasing concentration of the adsorbed molecules, these changes being most pronounced in series I. For strongly bound NH_3 molecules, S^2 is 38 Oe^2, when the H–N–H angle is 107° and the H–N distance, 1.01 A. Rotation around a threefold axis causes a decrease of S^2 down to 9.3 Oe^2. As follows from ref. (*18*), at 90°K the molecules of solid ammonia rotate around a threefold axis. The samples of series II (Fig. 3, curve 2) show that in the range of low coverages the S^2 value is considerably lower than 9.3 Oe^2. This means, probably, that the axis of rotation of the NH_3 molecules performs a precession. With increasing coverage, the importance of the intermolecular interaction, i.e., of the hydrogen bonds between the adsorbed NH_3 molecules, increases, this producing (as in the case of solid ammonia) a decrease in the angle of precession and an increase in S^2.

When studying the data from the NMR spectra of the silica gel in series I, it must be taken into account that the signal is partially determined by the protons of the surface OH groups whose effect is especially strong with lower coverages. The character of the curve is determined by serveral factors: the type of mobility of the ammonia molecules, the magnetic dipole-dipole interaction of the adsorbed molecules with the protons of the surface OH groups, and the relative amount of protons of the NH_3 molecules. It is impossible, however, to take into

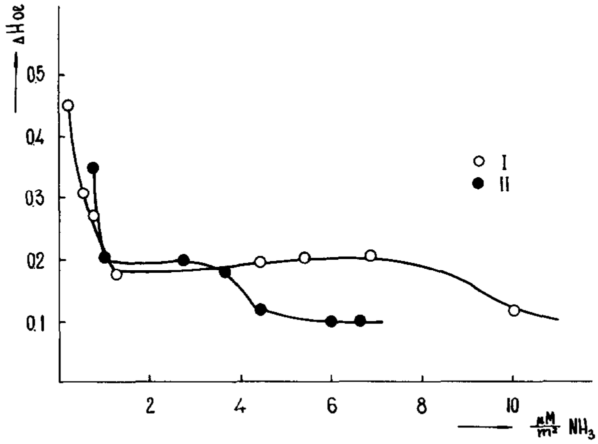

FIG. 2. Dependence of the linewidth (ΔH) of the NMR signals of ammonia adsorbed on silica gel (series I and II) at 25°C, upon the concentration of the molecules.

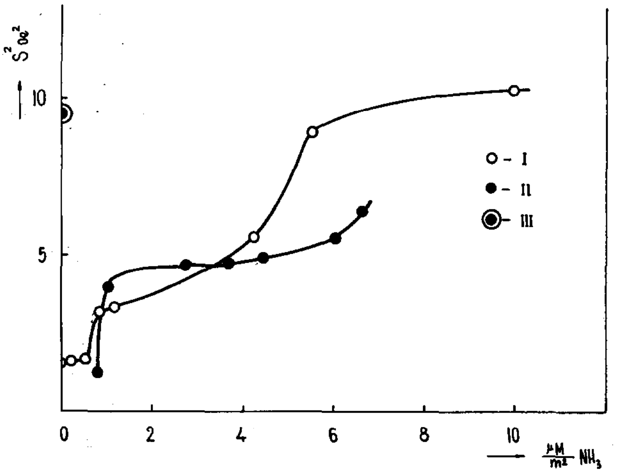

FIG. 3. Dependence of the second moment (S^2) of NMR signals on the concentration of adsorbed ammonia molecules at 90°K (series I and II); III, S^2 values for solid ammonia.

account all these factors (except the latter one). On the basis of the data concerning the relative amount of protons in the adsorbed phase and the values for S^2 of the OH groups and the NH_3 molecules rotating around a threefold axis, the following conclusions can be made. When the effect of the dipole–dipole interaction (which can only cause an increase in S^2) is not taken into consideration and when assuming that the adsorbed molecules rotate around a threefold axis, the S^2 values at low coverages are 1.8 Oe^2 and 2.2 Oe^2, i.e., they are higher than the experimental values (1.6 and 1.65, respectively). Hence, it may be concluded that in the initial region of coverages at 90°K, the mobility of the NH_3 molecules in the samples of series I is also higher than it is in solid ammonia at the same temperature. With increasing coverage, the mobility of the molecules decreases due to the formation of intermolecular hydrogen bonds, while the dipole–dipole interaction increases. Both causes lead to an increase in S^2.

The data concerning the dependence of the linewidth (Fig. 2) and the second moment (Fig. 3) on coverage show that the character of the adsorption interaction changes upon increasing the amount of adsorbed ammonia up to 1 μmole/m². On this basis it may be maintained that the number of primary adsorption centers of ammonia on silica gel does not exceed 6×10^{13} cm². This value is in good agreement with the data (*2, 11*) for the number of the primary centers of water adsorption on silica gel. The stepwise change of the second moment and the linewidth (especially with samples of series II) shows that with increasing adsorption, the ammonia molecules form groups around the primary centers. Comparison with the previously obtained data (*1, 2*) shows the existence of a great similarity between the mechanisms of water and ammonia adsorption. Recently, it has been shown (*16*) that in the range of very low coverages, ammonia is adsorbed on silica gel according to a coordination mechanism. The data concerning the positive charge of the surface of oxidized Si during ammonia adsorption indicate a coordination mechanism. According to the proposed mechanism (*17*), the positive charge corresponds to the formation of donor–acceptor bonds on the surface. At higher coverages, adsorption follows a hydrogen bond mechanism (*3, 14–16*). Thus on the heterogeneous silica gel surface there are several adsorption centers, which is in agreement with the results from investigations on ammonia desorption (*9*).

Zeolite NaX was used for investigations of the phase transitions in adsorbed ammonia. The ampoules with zeolite containing 6 mmole/g and 8 mmole/g of ammonia (which corresponds to 10 or 14 ammonia molecules per large cavity of zeolite) were

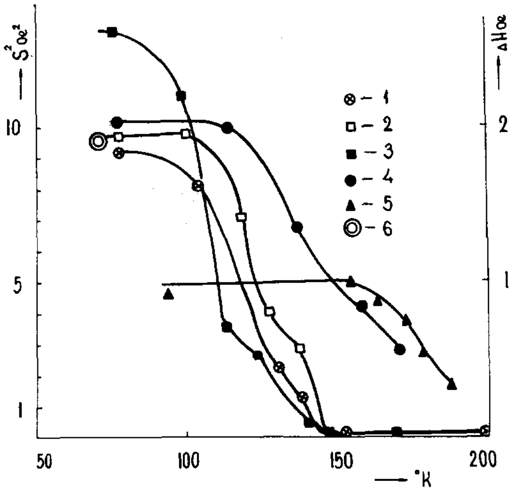

FIG. 4. Dependence of the linewidth (ΔH) and the second moment (S^2) of the NMR signals of adsorbed ammonia on temperature. For zeolite (NaX): 1, S^2 for ammonia adsorption $a = 6$ mmole/g; 2, S^2 for $a = 8$ mmole; 3, ΔH, $a = 8$ mmole/g. For silica gel, series I: 4, S^2, $a = 10.3$ μmole/m²; 5, ΔH, $a = 10.3$ μmole/m²; 6, S^2 for solid ammonia.

cooled down to 77°K. Figure 4 shows the dependencies of ΔH and S^2 on temperature for various samples. The character of the change in the linewidth for adsorbed ammonia essentially differs from the corresponding curve for solid ammonia obtained by us in preliminary experiments. Within the range of 77–90°K, S^2 for adsorbed ammonia is close to the value for solid ammonia (*18*). The rise in temperature from 90° to 130°K produces a considerable decrease in ΔH and S^2 for ammonia adsorbed on zeolite due to the appearance of an additional degree of freedom in rotation. At ~145°K, a sharp decrease in S^2 occurs which indicates the appearance of a diffusion movement, i.e., the transition of ammonia into the liquid state. The region of sharp decrease of ΔH and S^2 depends on the extent of filling of the zeolite pores with ammonia. When adsorption increases up to 8 mmole/g, this temperature range is shifted to the region of higher temperatures.

Figure 4 shows that for ammonia adsorbed on silica gel, S^2 depends very little on temperature up to 130°K, then begins to decrease. The decrease of ΔH is observed above 150°K. The lower temperature of the ammonia phase transition on zeolite and silica gel with respect to that of normal ammonia (melting point, 195°K) may be due to the structure change of the adsorbed substance. On account of the large adsorbate–vapor interface, a large number of molecules will be more weakly bound to each other than in the bulk of the adsorbate (*19*). On the other hand, the crystalline phase will have a great number of defects due to the crystallization taking place in a limited pore volume and in the presence of an active surface. Both factors will further melting at lower temperatures. According to Volmer-Tamman, the phase transition temperature depends on the size of the particles, i.e., in our care, on the highly dispersed crystalline phase of adsorbate. Note that the molecules of solid ammonia form two hydrogen bonds while the water molecules in the solid state form four bonds. The stretching of hydrogen bonds in adsorbed water should reach a higher extent than in ammonia. The decrease in temperature of the phase transition of ammonia is really smaller ($T \approx 50°$) than that of water ($T \approx 90$–$100°$) (*7*).

REFERENCES

1. EGOROV, M. M., KVLIVIDZE, V. I., KISSELEV, V. F., AND KRASSILNIKOV, K. G., *Kolloid. Z.* **212,** 126 (1966).

2. KVLIVIDZE, V. I., *Dokl. Akad. Nauk SSSR* **157,** 158 (1964).

3. SIDOROV, A. N., *Zh. Fiz. Khim.* **30,** 995 (1956).

4. IGNAT'EVA, L. A., KISSELEV, V. F., AND CHOUKIN, G. D., *Dokl. Akad. Nauk SSSR* **179** (1968).

5. WEYL, W. A., AND HAUSER, E. A., *Kolloid. Z.* **104,** 72 (1954).

6. KVLIVIDZE, V. I., KISSELEV, V. F., AND SERPINSKI, V. V., *Dokl. Akad. Nauk SSSR* **165,** 111 (1965).

7. KVLIVIDZE, V. I., AND KISSELEV, V. F., *Zh. Strukt. Khim. (USSR),* **8,** 221 (1967).

8. BASTICK, J., *Compt. Rend.* **234,** 1279 (1952).

9. BLIZNAKOV, G., AND POLIKAROVA, R., *J. Catalysis* **5,** 18 (1966).

10. BLIZNAKOV, G., MARKOV, I., AND BAKARDJIEW, I., *Commun. Dept. Chem., Bulgarian Acad. Sci.* **1,** No. 2. (1968), in press.

11. MICHEL, D., *Z. Naturforsch.* **B22a,** 1751 (1967).

12. Dubinin, M. M., Shukovskaya, E. G., and Murdmaah, K. O., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk.* p. 960 (1962).
13. Voskresenski, A. A., *Dokl. Akad. Nauk SSSR* **119**, 724 (1958).
14. Kisselev, A. V., Lygin, V. I., and Titova, T. I., *Zh. Fiz. Khim.* **38**, 2730 (1964).
15. Cant, N. W., and Little, L. H., *Can. J. Chem.* **43**, 1252 (1965).
16. Camaro, B., Dunken, H., and Fink, P., *Z. Chem.* **8**, 155 (1968).
17. Kisselev, V. F., *Dokl. Akad. Nauk SSSR* **176**, 124 (1967).
18. Gutowsky, H. S., and Pake, G. E., *J. Chem. Phys.* **18**, 162 (1950).
19. Fletsher, N. H., *Phil. Mag.* **7**, 255 (1962).
20. Egorov, M. M., Krassilnikov, K. G., and Kisselev, V. F., *Zh. Fiz. Khim.* **32**, 2448 (1958).