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On the Desorption of Ammonia from Silica Gel

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In the investigation on the desorption of ammonia from the surface of silica gel it has been found that a certain amount of irreversibly bound ammonia, decreasing with the increase of the temperature of desorption, always remains in the range between 0° and 70°C. It is independent of the initial amount of adsorbed ammonia. The phenomenon is associated with the existence of different kinds of adsorption centers on the surface of silica gel and is interpreted from a kinetic standpoint.

INTRODUCTION

In studying the adsorption of ammonia on silica gel it was found that the initial properties of the surface of the adsorbent can easily be restored when the specimen is heated in high vacuum at a temperature of 200–250°C (*1, 2*). After such treatment the surface preserves the same number of hydroxyl groups per unit area as before, which is evident from the good reproducibility of the adsorption isotherms and was experimentally confirmed by determining the water content of the specimens by heating up to 1100°C.

It was also established that if evacuation is carried out at low temperatures (for example, at room temperature) a certain amount of irreversibly bound ammonia always remains. It was of interest to study the conditions influencing this latter amount of ammonia in detail.

The data obtained could be associated with the nature of the active surface and the nature of the process of adsorption of the ammonia molecules on the active centers of silica gel.

EXPERIMENTAL

Silica gel with medium size pores (Trade mark "Reanal"), purified by repeated boiling with hydrochloric acid (p.a.), and twice-distilled water, was used for the experiments. The specific surface of the specimens, determined by low-temperature adsorption of nitrogen (BET method) was 366 ± 11 m^2/g. The surface hydroxyl groups ($x = 3.96$ mg eq/g) were determined by the decrease in weight of the specimens, on heating from 200° to 1100°C. It was assumed, as in other similar cases, that the bulk water is exceedingly little. The specimens, placed in a McBain balance, were heated at 200°C in vacuum (10^{-5} mm Hg) to a constant weight (8–10 hr), after which adsorption was carried out, with ammonia purified by resublimation. The temperature of adsorption was maintained by means of an ultrathermostat. After establishing adsorption equilibrium, desorption was carried out.

The kinetic curves of the adsorption and desorption processes show that the first takes place approximately three times more rapidly than does the desorption. This imposes the assumption that slowing down due to diffusion plays a secondary role and that tearing off of adsorbed molecules from the surface of the adsorbent represents the main energy barrier in desorption. The use of an apparatus with a McBain balance and high vacuum hinders heat exchange. For this reason, the temperature of the specimen (when connecting with the vacuum part of the apparatus) was sharply lowered at first (by 10–15°C) due to the heat of desorption and it was

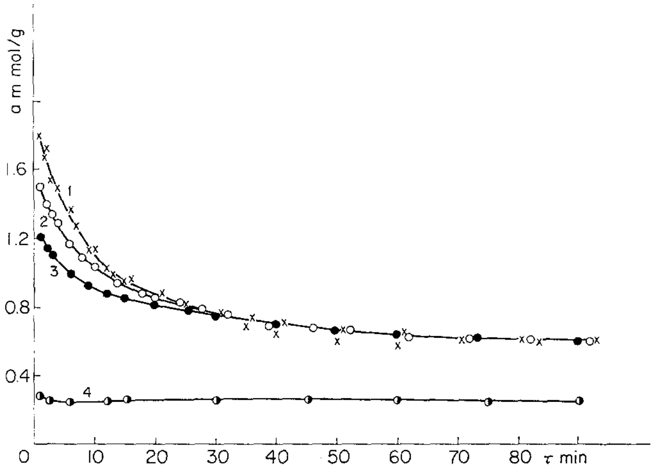

Fig. 1. Desorption of NH_3 from the surface of silica gel at 25°C with various initial amounts of adsorbed ammonia.

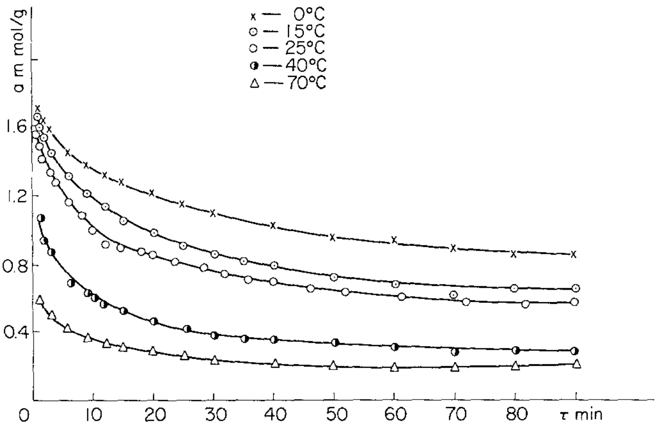

Fig. 2. Desorption of NH_3 from the surface of silica gel at various temperatures.

only after about 20–30 min that its initial value was reached. Under these conditions the kinetic curves obtained are not real isotherms and their quantitative interpretation is very hard, especially in the region where the change of adsorbed amount with time is the greatest. Therefore, in this respect we could only make a qualitative evaluation.

Results and Discussion

Figure 1 contains a number of desorption curves showing the decrease of adsorbed amount with time, at one and the same thermostatic temperature. It is evident that irrespective of the initial amount adsorbed, desorption always leads to one and the same retained amount of ammonia if the temperature has been maintained constant (in our case 25°C, curves 1,2,3). Further, if the amount of adsorbed ammonia has been less than a_∞, practically no desorption takes place (curve 4).

The desorption curves, taken at various temperatures, are shown in Fig. 2. It is clear that in all cases the desorption has not been complete and after some time approaches a definite amount of retained ammonia, a_∞. The latter decreases with the increase of temperature.

Figure 3 illustrates the dependence of a_∞ on the temperature of desorption.

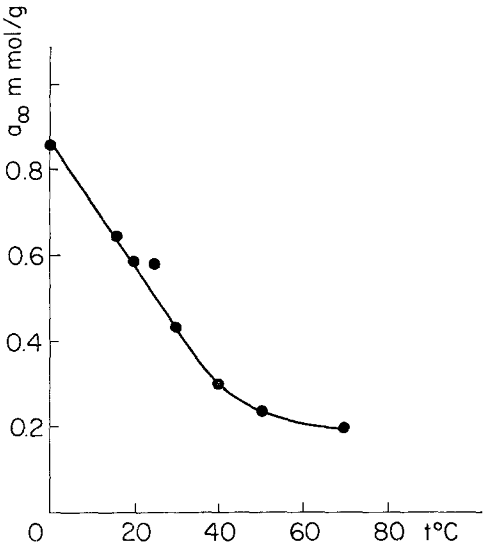

FIG. 3. Dependence of a_∞ on the temperature of desorption.

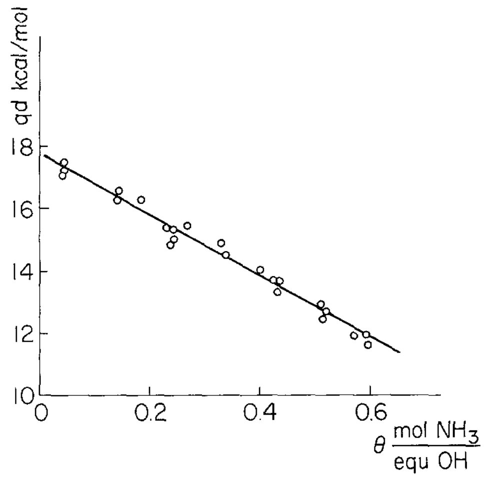

FIG. 4. Differential heat of adsorption of ammonia on silica gel as a function of coverage at 0°C.

The amount of retained ammonia, bound to the surface more firmly, could be explained if we assume the existence of at least two kinds of adsorption centers on the surface of silica gel, on which ammonia is adsorbed with different strength. There arises now the question about the nature of these centers. There is no unique opinion in the literature at present about the nature of adsorption of ammonia on silica gel. In one of the first works on this subject Bastick assumed that at low coverages the adsorption is a chemical process, resulting in the formation of NH_4^+, passing gradually into a physical process (*3*). He made this conclusion on the basis of the heat of adsorption, which at low coverages is very high. A direct measurement of the differential heat of adsorption, carried out in our laboratory, confirmed the results of Bastick: The differential heat of adsorption has in general a considerable value and represents a decreasing function of coverage; the value of $q_d^0 \approx 17\,800$ cal/mole was obtained for specimens heated at 200°C [(Fig. 4; measurements were carried out at 0°C by Mr. I. Markov, using an ice calorimeter (*10*)]. Studies on some of the infrared adsorption spectra, nevertheless, lead some authors to the conclusion that adsorption of ammonia on the surface of silica gel takes place without formation of complexes of ammonia (*4*, *5*). The high value of the differential heat of adsorption could be associated with the fixation of ammonia by means of more than one hydrogen bond (for example, with three hydrogen bonds). Further, as was shown by West, Whatley, and J. Kane (*7*), participation of oxygen from the siloxane chains must be rejected. Sidorov (*8*) assumed the formation of donor-acceptor bonds between ammonia (N donor) and the atoms of silicon, possessing free orbits and strength of the order of 20 000 cal/mole.

On the other hand, the gradual decrease of the differential heat of adsorption with coverage could be associated with the results of investigations of Kvlividze (*9*), which showed that at least three kinds of adsorption centers are available on the surface of silica gel: single hydroxyl groups, double, and more complex formations, having different adsorption abilities.

The results of all these investigations show that the surface of silica gel is highly heterogeneous with respect to adsorption centers. The amounts of retained ammonia could be considered as the result of adsorption on such kinds of centers, from which the desorption of the ammonia molecules at a definite temperature would be less probable. Hence, irrespective of the kind and the distribution of the adsorption centers on silica gel and the interaction of the adsorbed molecules in the adsorbate, the interpretation of the phenomenon could be made from a purely formal kinetic standpoint. It was experimentally found, as has already been mentioned, that the differential heat of adsorption decreases linearly with coverage (Fig. 4). Because at high coverages the energy of activation of desorption is relatively small, the removal of the adsorbed ammonia takes place more easily. With the progress of the adsorption process, the removal of each successive portion of ammonia becomes harder, due to the increase of the energy barrier, till a value is reached of the energy of desorption at which the rate of the process becomes practically zero, which will also determine the retained amount of chemisorbed ammonia, corresponding to a definite coverage θ.

Using the simplest scheme possible for the desorption process, the following equation could be written for the rate of desorption:

$$-d\theta/dt = \kappa\theta \exp\left[-q_d(\theta)/RT\right] \qquad (1)$$

where $q_d(\theta)$ is the energy of activation of desorption, which with a certain approximation could be assumed as being equal to the differential heat of adsorption at a given degree of coverage.

Evidently, the retained amount of bound ammonia is determined by the condition

$$-(d\theta/dt)_{\theta_i^\infty, T_i} = \kappa\theta_i^\infty \exp\left[-q_d(\theta_i^\infty)/RT\right] \approx 0 \qquad (2)$$

from which it follows that

$$[q_d(\theta_1^\infty)/T_1] - R\ln(\theta_1^\infty) = [q_d(\theta_2^\infty)/T_2] - R\ln(\theta_2^\infty) = \ldots = [q_d(\theta_i^\infty)/T_i] - R\ln(\theta_i^\infty) = \text{const.} \qquad (3)$$

The values for the various $q_d(\theta_i^\infty)$ can be determined from the curve, showing the dependence of the differential heat of adsorption on θ, which for 0°C and the specimen heated out at 200°C is given in Fig. 4. The ratios, calculated for various temperatures, are presented in Table 1.

TABLE 1
RATIO BETWEEN THE DIFFERENTIAL HEAT OF ADSORPTION AND THE ABSOLUTE TEMPERATURE

T_i(°K)	θ_i^∞	$q_d(\theta_i^\infty)$ (cal/mole)	$q_d(\theta_i^\infty)/T_i - R\ln(\theta_i^\infty)$
343	0.049	17.450	56.8
313	0.075	17.200	60.0
298	0.148	16.550	59.3
288	0.161	16.450	60.7
273	0.216	16.000	61.6

It is evident that the calculated ratios between the differential heats of adsorption and the corresponding absolute temperatures have approximately the same value, which is in agreement with the assumption already made, in spite of the tendency toward gradual increase of this ratio, giving a difference of about 9%. The latter could be assigned partly to inaccuracy of the experiment and partly to the approximation already made.

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