37. *The Sorption of Ammonia on Silica Xerogel Surfaces.*

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The nature of the adsorption of ammonia on silica xerogel and modified silica xerogels has been investigated. Two approaches were used, (*a*) kinetic studies of the desorption process from 100 to 180° and (*b*) measurement of isosteric heats of adsorption, from adsorption isotherms determined from −30 to 38°. Xerogels were modified by thermal dehydration and by impregnation with cobalt chloride and other transition metal compounds. Figures for ultraviolet reflectance spectra of impregnated xerogels are included. The absorption pattern is complex and appears to indicate that the effect is partly physical and partly chemical in nature.

In recent years, much attention has been given to the physical adsorption on silica of gases, such as nitrogen, its object of investigating important surface properties including capillary shapes, surface areas, etc.[1] At the same time, Kiselev [2] has focused attention less on the purely statistical nature of the adsorption process and more on the chemical interplay between the adsorbate and xerogel surface; the field has thus been extended to include studies of the nature of the adsorbed complex. Mainly infrared and static adsorption techniques have been used in these investigations, and have yielded valuable information, particularly about the nature of the adsorbed species formed by water, benzene, and methanol vapours.

In our experiments, the gas–solid interaction has been examined by kinetic studies of the desorption process. A preliminary communication [3] described results obtained for the desorption of water, methyl alcohol, and carbon tetrachloride. The present work extends these experiments to desorption of ammonia from silica xerogel of high purity and from xerogels modified by thermal dehydration, and by impregnation with transition metal ions. Figures for the isosteric heats of adsorption of ammonia on these surfaces are also included.

EXPERIMENTAL

Materials.—Davison " 923 " chromatographic grade silica gel (>99·98% pure) was supplied by L. Light and Co., Ltd. This had a particle size range of 76—152 μ and a nitrogen adsorption area of 650 m.²/g.; it was heated at 240° for 2 hr. to activate it, and stored in a desiccator (P_2O_5).

The impregnated gels were all prepared by boiling a 10% w/v solution of the metal salt with gel (100 g.) for 30 min., and then filtering and drying the residue at 140° before activation. Sodium ion exchange was effected by impregnation of 10 g. of freshly activated gel in 100 ml. of 1M-sodium chloride until equilibrium was reached. Analysis showed that the amount of sodium ion exchanged was 212 μg. of ion/g. of gel, with no measurable amount on a blank original (*i.e.*, <5 μg. of ion/g. of gel). Dehydrated gel was prepared by heating activated gel in air for 16 hr. at 850° followed by 16 hr. at 1000°. This treatment removes all the physically adsorbed water and practically all the structural water.[4]

Liquid anhydrous ammonia (99·98% purity) was stored over sodium wire, out-gassed, and redistilled under vacuum several times before use. " White-Spot " nitrogen was dried by passage through calcium chloride and silica gel towers. Other chemicals were AnalaR standards.

Apparatus.—The thermogravimetric balance (Stanton Instruments Ltd.) was modified to include an internal silica furnace tube and a gas box (fitted flush with the furnace base—in the " down " position—and the top of the balance), so that desorption in a stream of nitrogen could

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[1] Beebe and Young, *Anal. Chem.*, 1955, **27**, 1963; Benesi, Bonar, and Lee, *J. Phys. Chem.*, 1954, **58**, 95; Goodman and Gregg, *J.*, 1959, 694; de Boer, " Colston Papers," Butterworths, London, 1958, Vol. 10, p. 68.

[2] Kiselev and Lygin, *Russian Chemical Reviews* (Trans.), 1962, **31**, 175; Kiselev, " Colston Papers," Butterworths, London, 1958, Vol. 10, p. 195.

[3] Darlow and Ross, *Nature*, 1963, **198**, 988.

[4] Henry and Ross, *J.*, 1962, 4265.

be studied. The balance was fitted with a proportionating control system, which allowed the temperature to be kept constant within ±0·05° down to 100°. The initial chart speed was 6 in./hr., in later experiments 12 in./hr.

Static adsorption isotherms were determined in an all-glass vacuum system. The silica gel was suspended in a Nylon bag from a spiral quartz spring of sensitivity 253 mm./g. The spring was enclosed in a deep, cylindrical vessel and the weight of ammonia adsorbed read directly with a cathetometer from the spring extension. The reaction vessel was surrounded by constant-temperature baths or large Dewar flasks, which contained various freezing mixtures. Constant temperatures (*e.g.*, 30 ± 0·5°), which were recorded by mercury or platinum-resistance thermometers, were regularly maintained by the freezing mixtures. The re-distilled, outgassed ammonia was introduced from a reservoir sealed to the vacuum line *via* a three-way stopcock. Pressures were read from a differential mercury manometer, and the vacuum was established by a two-stage mercury diffusion pump backed by a rotary oil pump; the apparatus was easily kept at 10^{-3} mm. Hg for 5 days.

RESULTS

Sorption Rate Studies.—Xerogel samples were placed in a modified vacuum desiccator after activation at 240°. Ammonia was boiled off from a Dewar flask and passed over the samples at 20 ml./min. The samples were left in the container for 30 min., and then transferred quickly to the thermobalance for desorption, which was carried out in a stream of dry nitrogen regulated by needle-valves.

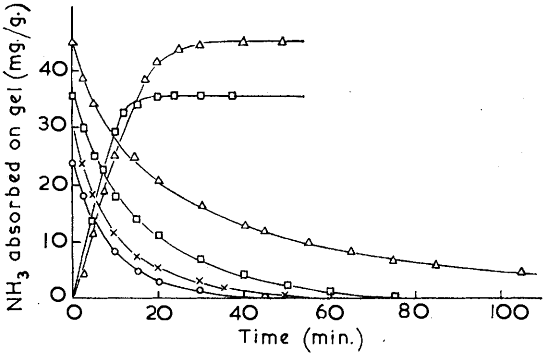

FIG. 1. Ammonia adsorption and desorption patterns on silica xerogel.
△ at 110°; □ at 130°;
× at 150°; ○ at 160°.

Initially, small samples of gel (0·5 g.) were used but, since these did not give very sensitive rate-spreads, the weight was increased to between 2·0 and 2·5 g.

Results obtained for the rates of adsorption of ammonia by using a McBain–Bakr balance proved to be unreliable, and plots of weight adsorbed against time were not reproducible for the conditions investigated; this was due to the very rapid adsorption of ammonia and to the inaccurate method of measuring the extension of a moving quartz spring.

The rapid rate of adsorption is illustrated in the plot of weight adsorbed (mg./g.) against time (min.) obtained by adsorption on the thermobalance (Fig. 1). The ammonia (20 ml./min.) was boiled off from a Dewar flask. It was passed through glass tubing into the heating chamber of the thermal balance *via* a side-arm in the internal silica sleeve. Desorption studies between 100 and 180° indicated that not all the adsorbed ammonia is desorbed at 100 or 110° (Table 1), although it is all desorbed at 130° (Fig. 1).

TABLE 1.

Non-reversible adsorption of ammonia on silica xerogel.

Temp. (°C)	NH_3 adsorbed (mg./g.)	NH_3 desorbed (mg./g.)	NH_3 irreversibly adsorbed (mg./g.)
100	53·6	47·7	5·9
110	44·9	40·5	4·4
130	35·5	35·5	0·0

Microscopic examination (×400) of xerogels after adsorption of ammonia showed no trace of cracking or shattering of the original particles.

In the range 180—240°, adsorbed ammonia appeared to exert a catalytic dehydration effect, and water was detected in the desorption products. At 210°, fully activated gel samples that had been constant in weight for over 2 hr. were shown, on both adsorption and subsequent desorption of ammonia, to have lost an additional 7·3 mg./g. in one case and 7·5 mg./g. in another. The effluent gas from these desorptions was collected by passage through a U-tube at $-20°$, and it was confirmed by i.r. spectroscopy that the liquid collected was water. The weight of water collected was the same as the weight lost by the xerogel, which showed that dehydration had taken place.

An attempt was made to identify this loss of water with the presence of some highly labile silanol groups on the surface of the silica gel, but a similar dehydration effect with sodium-exchanged gel disproved this possibility.

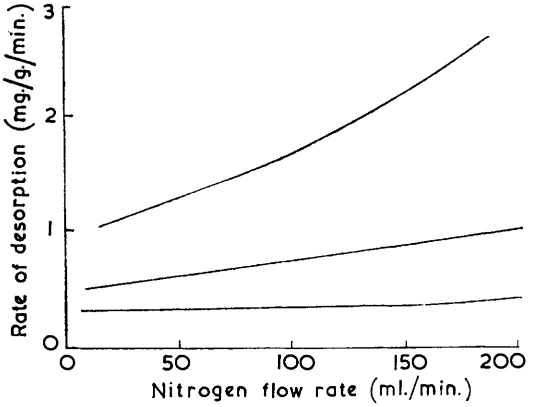

FIG. 2. Variation of desorption rate with nitrogen flow velocity.

Surface coverage: *A*, 13 mg./g.; *B*, 8 mg./g.; *C*, 5 mg./g.

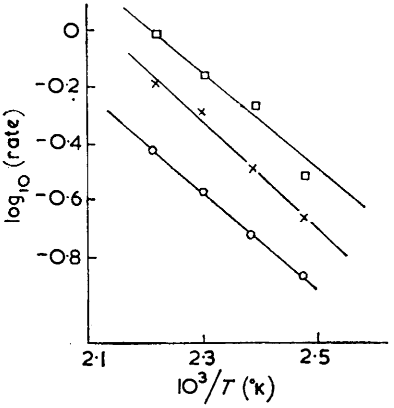

FIG. 3. Effect of temperature on desorption from activated xerogel.

In experiments to find the optimum rate of flow of nitrogen for desorption, a series of runs was carried out with activated xerogel and flow rates of 25, 50, 75, 100, and 200 ml./min. at 160°. The results (Fig. 2) are shown as rate of desorption of ammonia (mg./g. of gel/min.) *versus* rate of flow of nitrogen (ml./min.). At surface coverages from 20 to 12 mg./g., the rate of desorption varies with flow velocity. Hence, at the highest surface coverages the desorption rate is clearly a function of the vapour pressure of ammonia above the solid. However, as low surface coverages (around 10 mg./g.) are approached, the desorption rate is hardly affected by gas velocity, until at a surface coverage of 5 mg./g. it becomes independent of it.

Subsequently, the effect of temperature on desorption rate was studied for ammonia adsorbed at 177, 161, 145, and 130° on activated xerogel, and then desorbed at the same temperatures at a flow rate of 50 ml./min. The results (Fig. 3) are plotted as $\log_{10}$ (rate of desorption) *versus* $1/T$ °K for surface coverages of 10·0, 7·5, and 5·0 mg./g. From the slopes of these lines a measure of the dependence of the desorption rate on temperature can be obtained. This is quoted as "experimental activation energy" in Table 2.

TABLE 2.

Influence of temperature on desorption rate from activated silica xerogel at different surface coverages.

Surface coverage (mg./g.)	Experimental activation energy (kcal./mole)
5·0	7·8
7·5	8·5
10·0	9·1

Rates of desorption at 160, 150, and 130° from activated silica gel on which ammonia had been adsorbed at 20° were measured. The figures obtained gave an experimental activation energy of 7·5 kcal./mole for 5 mg./g. surface coverage.

Very little adsorption of ammonia was detected on samples of dehydrated xerogel. After 30 min. adsorption at 20°, only 0·9 mg./g. were adsorbed as shown by subsequent desorption at 190°. The equilibrium amount adsorbed at 190° was 0·7 mg./g.

Sorption studies were completed with xerogel samples impregnated with transition metal ions. Those chosen are frequently supported on silica and used as catalysts in heterogeneous reactions.[5] Activation at 240° of gels impregnated with cobalt and copper nitrates, caused the salts to decompose, but only the cobalt nitrate was completely converted to the oxide. Experiments with gels impregnated with cobalt, nickel, and copper chlorides showed that only the gels containing cobalt chloride were suitable for examination below 240°. The absorbed species on xerogels impregnated with nickel and copper chloride were too stable for measurements of the rates of desorption. The results, Table 3, are presented as " experimental activation energies " for three surface coverages. The cobalt concentrations were 206 and 178 mg./g., respectively, for oxide and chloride impregnates.

TABLE 3.

Desorption activation energy from cobalt oxide and cobalt chloride impregnated xerogels.

Surface coverage (mg./g.)	Experimental activation energy (kcal./mole)	
	Cobalt oxide impregnate	Cobalt chloride impregnate
5·0	9·5	8·5
7·5	9·5	9·2
10·0	9·5	10·5

While the activation energy is independent of surface coverage for oxide-on-gel, the chloride impregnate shows a decrease of activation energy with decreasing surface coverage, which is similar to the trend shown by activated xerogel (Table 2).

Measurements of the ultraviolet and visible spectra of the samples impregnated with cobalt chloride before, after, and during adsorption of ammonia are given in Table 4; the spectra were obtained by reflectance from a mixture of impregnated samples with finely powdered potassium chloride.

TABLE 4.

Reflectance spectra of cobalt chloride impregnated silica gel.

Peaks obtained (mμ).			
Cobalt chloride–silica gel	Cobalt chloride–silica gel with NH_3 adsorbed at 20°	Cobalt chloride–silica gel with NH_3 partially desorbed at 230°	Cobalt chloride–silica gel with NH_3 all desorbed at 230°
685	635	670	690
660	550—560	610—615	660
620—635	520	575 (shoulder)	635—645 (shoulder)
		550 (shoulder)	

The tetrahedral species $CoCl_4^{2-}$ gives [6] peaks at 694, 695, 645, and 621 mμ, whilst $Co(NH_3)_6^{2+}$ gives only one peak at 540 mμ; similar spectra are found in the solid and in solution.

Equilibrium Studies.—The reversibility of adsorption of ammonia on activated xerogel was tested between 243 and 311°K. At 243°K, 25·54 mg. of ammonia were adsorbed per g. of gel at a pressure of 0·16 mm. Hg. When the temperature was increased to 311°K, the pressure rose to 0·22 mm. Hg and the amount adsorbed fell to 22·52 mg./g. at equilibrium. The temperature was then lowered to 311°K, at which the original readings were obtained. This test was repeated for the same and other samples between 243 and 303°K, and similar evidence of reversibility was found. Further, after ammonia had been adsorbed at 243°K, the temperature was raised to 303°K and the system pumped out for 1 hr. About 5% w/w of the total ammonia adsorbed, which was not removed by this treatment, was removed by continuing the evacuation at 323°K.

The adsorption–desorption isotherm for ammonia on xerogel activated at 240° was determined at 243°K (p_0 = 897 mm. Hg). The sample was out-gassed at 10^{-4} to 10^{-5} mm. for several hours before the ammonia was admitted. Again, some evidence of a stronger residual adsorption between ammonia and the xerogel was obtained (Fig. 4). This is shown by the

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[5] Ciappetta and Plank, " Catalysis," Reinhold, New York, 1954, Vol. 1, p. 315.

[6] Jørgensen, " Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962, pp. 285—286.

irreversibility of adsorption amounting to 7% w/w of the total adsorbed at **897** mm., and is indicated specifically by the non-coincidence of the desorption isotherm with the adsorption isotherm between the origin and hysteresis loop. A B.E.T. plot of the relevant adsorption section of the isotherm is inset in Fig. 4. From the intercept and slope of this line the weight of the adsorbed monolayer was 129 mg./g. From the nitrogen adsorption value of the surface area (650 m.^{2}/g.), this weight of monolayer is equivalent to a coverage of 11·7 μmoles/m.^{2}, which agrees well with the calculated coverage of 11·5 μmoles/m.^{2}, on the assumption of 14·6 Å^2 as the area occupied by an adsorbed ammonia molecule;[7] these results suggest also that one ammonia molecule is adsorbed per surface hydroxyl group.

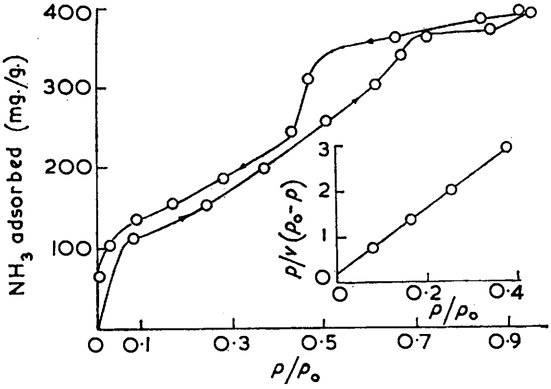

FIG. 4. Adsorption–desorption isotherm on activated xerogel at -30°C. Inset B.E.T. plot.

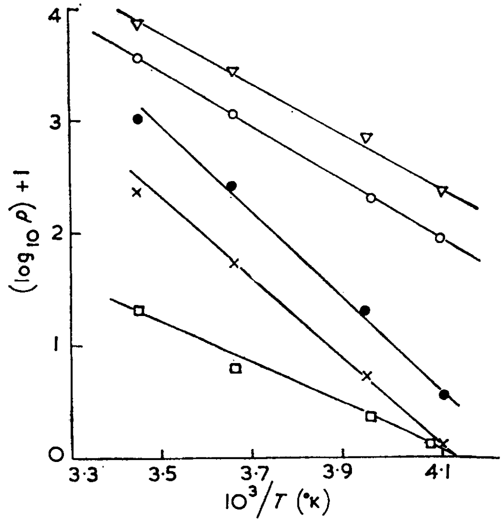

FIG. 5. Adsorption isosteres for various surface coverages.

Values of θ: △, 1·00; ○, 0·80; ●, 0·61; ×, 0·45; □, 0·30.

Adsorption isotherms were determined also at 253, 273, and 290°K. Adsorption isosteres were plotted from the results (Fig. 5) and, from the slopes of the lines, isosteric heats of adsorption were found in the usual way. The variation of q_{st} with surface coverage is shown in Fig. 6. The range illustrated is from θ = 0·1 to 1·0. No figures for values of θ less than 0·1 are included, because doubt remained about the reversibility of adsorption for these coverages.

Samples impregnated with cobalt chloride were activated at 260° for 2 hr. under vacuum, and became deep blue in colour. When ammonia at 17° was admitted, the colour changed to a violet-purple with 50·37 mg./g. of ammonia adsorbed at an equilibrium pressure of 2·91 mm. If the sample was cooled to -32°, the colour became lighter and 59·22 mg./g. were adsorbed at 0·44 mm. When the temperature was brought back to 17°, the colour darkened and 53·10 mg./g. were adsorbed at 2·06 mm. The cycle was repeated with similar results, which are

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[7] Emmett and Brunauer, *J. Amer. Chem. Soc.*, 1937, **59**, 1553.

indicative of irreversible adsorption. On final exposure at 57°, the colour became deep blue, but strong evacuation did not remove all the adsorbed ammonia, which amounted to 47·99 mg./g.

A similar set of experiments was carried out with unactivated impregnated samples containing 10% w/w of adsorbed water; evidence of irreversibility was again pronounced. After final evacuation at 53°, some of the solid was treated with sodium hydroxide solution and ammonia was evolved.

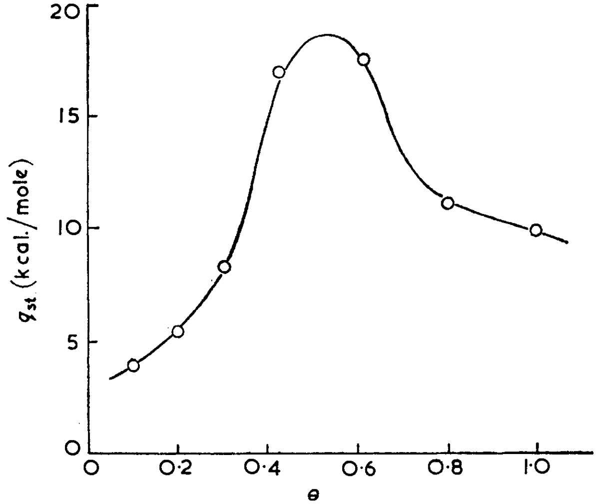

FIG. 6. Variation of heat of adsorption with surface coverage.

A set of isotherms was obtained for the activated cobalt chloride samples. These all gave isosteres that dropped parabolically towards the temperature axis. The departure from linearity was most marked from −20 to −30°C.

DISCUSSION

Both the kinetic and thermodynamic experiments show that the pattern of ammonia adsorption on silica xerogel is complex. The results suggest that the effect lies on the boundary between physical and chemical adsorption.

From 100—180°, the rate studies showed adsorption to be fairly rapid. Thus at 130°, on a total adsorbed amount of 35·5 mg./g., 10 mg./g. were adsorbed in 3—4 minutes, and 30 mg./g. in 10 minutes; the desorption rate was much slower. At the same temperature, 10 mg./g. were desorbed in about 8 minutes and 30 mg./g. in 35—40 minutes. Further, the desorption behaviour is only consistent within certain temperature ranges; for example, at 100—130° the amount of ammonia irreversibly adsorbed is about 10% of total adsorbed weight. This may be explained by the presence of a chemisorbed NH_3 species, which implies that alternative bonding arrangements between ammonia and surface hydroxyl groups are possible.

From 130 to 180°, plots of $\log_{10}$ (rate of desorption) *versus* $\log_{10}$ (weight adsorbed) gave straight lines of unit slope for surface coverages from 0 to 10 mg./g.; these plots indicate that the desorption rate may be interpreted in terms of a first-order kinetic law. There were no discontinuities in these plots, and no evidence of irreversibility of adsorption could be detected by experiment. The irreversible process that occurs at lower temperatures was swamped, which may indicate that this process has a desorption activation energy of less than 10 kcal./mole and thus cannot be separated at the higher temperatures. Above 180°, dehydration sets in, and this most likely involves elimination of surface hydroxyl groups from the pre-activated xerogel.

Studies[8] of the dissociation of an ammonia–alumina–silica solid complex have shown

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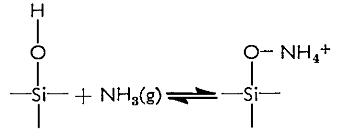
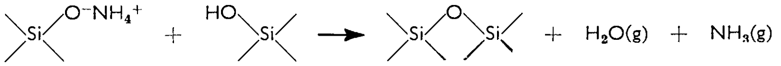
[8] Roper, quoted by Tamele, *Discuss. Faraday Soc.*, 1950, **8**, 270.

that dissociation of the ammonium ion begins at 180°, and that this is accompanied by a large increase in loss of water. A similar mechanism may be involved on surfaces where adsorbed ammonia acting as a Lewis base initially neutralises labile hydroxyl groups:



(1)

Felden[9] has also suggested this step to explain decreasing ionic mobilities of surface protons in high-frequency dielectric studies of ammonia adsorbed on silica gel. On desorption, the ammonium ion may react as a cation acid with a neighbouring silanol group, or with a silanol group on an adjacent particle, to form an oxygen-bridge bond; gaseous ammonia and water are evolved:



(2)

The reflectance spectra indicate that on the gel impregnated with cobalt chloride, the $CoCl_4^{2-}$ species exists in tetrahedral form. On exposure to ammonia this is converted partially into the $Co(NH_3)_6^{2+}$ octahedral species. Ammonia molecules involved in complex formation of this type would be expected to have a higher desorption activation energy, as was observed (8·5—10·5 kcal./mole). During ammonia adsorption, there will, of course, be a change in the stabilisation energy of the crystal field of the cobalt ion and, at the same time, desorption may include displacement of ammonia from surface Cl′ sites. These additional factors may partly account for the differences in desorption-activation energies for gels impregnated with cobalt chloride and cobalt oxide. The latter gave 9·5 kcal./mole, independent of surface coverage. It is unlikely that ammonia would interact strongly with the oxygen species in the oxide. Also, since the surface coverage with cobalt ion is not complete (4·6 μmoles/m.^{2} in the halide impregnate), a considerable amount of normal adsorption of ammonia will take place on intrinsic xerogel sites. The increase of activation energy with surface coverage on the cobalt chloride gels may then be explained by the existence of a greater proportion of the $Co(NH_3)_6^{2+}$ species at the higher coverages.

Recently, several authors[10,11] have studied the thermodynamics of ammonia adsorption on silica–alumina surfaces by using isothermal methods; these were designed mainly to obtain information on the surface properties of the materials in relation to their application as cracking catalysts. While such solids generally have quite different physical properties (*e.g.*, density and surface area) from those of the simple silica xerogel system, some grounds for comparison may be found, especially with regard to variations of heat of adsorption with coverage.

Our results show conclusively that some 5—7% w/w of the total ammonia adsorbed at 243—303°K is not truly reversibly adsorbed. This feature does not appear to have been observed in studies with the silica–alumina system.[10,11] Otherwise, the trend of q_{st} with θ from 0·1 to 1·0 is very similar to that found by Hsieh[10] with a " fresh " silica–alumina catalyst (25% Al_2O_3) of surface area 525 m.^{2}/g. A similar rise to a maximum value of q_{st} at $\theta = 0{\cdot}4$—0·5, along with the subsequent decline, can be detected. The numerical values of the heats of adsorption are also similar over the range, except for the respective maxima, which lie at about 18 kcal./mole for xerogel and nearer 13 kcal./mole for silica–alumina.

The irreversibly adsorbed ammonia is similar in amount to that taking part in the surface dehydration at higher temperatures in the kinetic experiments. The rise in q_{st} to its maximum at about 50% coverage will then involve $-OH-NH_3$ attachment. This

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[9] Felden, *Compt. rend.*, 1959, **249**, 682.

[10] Hsieh, *J. Catalysis*, 1963, **2**, 211.

[11] Clark, Holm, and Blackburn, *J. Catalysis*, 1962, **1**, 244; 1963, **2**, 21.

has been suggested by Yates [12] from spectroscopic studies, and would amount to Lewis acid sites interacting with ammonia, according to the terminology adopted by Hsieh.[10]

Such attachment would involve polarisation of the adsorbed molecule, whilst the ultimate equilibrium condition may involve surface species of the type shown in equation (1). These species would attract further ammonia molecules approaching the surface, which would explain the rise in q_{st} to its maximum value. The subsequent fall in q_{st} to 11—12 kcal./mole at $\theta = 1$ would arise from the growth of the repulsive contribution as the surface becomes increasingly populated by neighbouring adsorbed NH_4^+ species interacting on each other.

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[12] Folman and Yates, *J. Phys. Chem.*, 1959, **63**, 183; Yates, Sheppard, and Angell, *J. Chem. Phys.*, 1955, **23**, 1980.