JOURNAL OF CATALYSIS 8, 173–182 (1967)

Heats of Adsorption of Ammonia on Acidic Catalysts

F. S. STONE AND L. WHALLEY*

From the Department of Physical Chemistry, The University, Bristol, England

Received January 11, 1967

A comparative calorimetric study has been made of the heat of chemisorption of ammonia at 30°C on various preparations of alumina, silica, silica-alumina, and Linde molecular sieve X.

Curves of heat of adsorption (q) versus coverage (θ) for chi, eta, and gamma alumina all have the same general form. A small fraction of the chemisorbed ammonia is very strongly held. An initially high heat of 20–40 kcal $mole^{-1}$ falls over the first few percent of a monolayer to a constant value between 11 and 13 kcal $mole^{-1}$. The highest initial heat was observed for alumina prepared in the absence of alkali metal ions.

Silica-alumina shows a significantly greater integral heat (up to 20% coverage) than alumina, but heats at very low coverage are not higher than those observed on pure alumina. This indicates an equivalent number of strong acid sites but a larger number of weaker acid sites on silica-alumina. The behavior is otherwise similar. The influence of composition on ammonia adsorption has been studied over the range 0–40% Al_2O_3 in silica-alumina.

Calcium X behaves similarly to alumina, and has a higher heat of ammonia adsorption than the corresponding sodium zeolite at all coverages.

No minima or maxima in the q–θ curves, suggesting the existence of strong attractive interactions in the chemisorbed ammonia layer, were found for any of the oxides investigated, contrary to certain earlier calorimetric observations. It is suggested that these effects may be due to differences in calorimetric practice.

INTRODUCTION

In spite of the widespread use of alumina, silica-alumina, and crystalline aluminosilicates as catalysts and catalyst supports, the exact nature of their acidity and its traditional association with catalytic properties are still open questions. The original suggestions (*1*, *2*, *3*) linking the acidity of calcined silica-alumina gels with surface coordination have proved difficult to develop, mainly because of the amorphous nature of these solids. With the publication in 1960 of a paper by Pines and Haag (*4*), establishing the acidic properties of alumina itself, there emerged a new incentive for further research in this area since the various transition aluminas, although not entirely homogeneous structurally, can at least be characterized physically and classified according to the principles of structural chemistry (*5*). At about the same time, there also appeared the first of the extremely significant researches on the catalytic properties of molecular sieves (*6*), where not only the matrix but also the "surface" can to a large extent be crystallographically defined. These developments have brought the discussions on acidity, surface coordination, and carbonium ion generation very much into the foreground at the present time.

In this paper we report a comparative calorimetric study of the chemisorption of ammonia on a variety of preparations of alumina, silica, silica-alumina, and Linde molecular sieves NaX and CaX. The heat of adsorption of ammonia has been measured

---

* Present address: Ministry of Technology, Warren Spring Laboratory, Stevenage, Hertfordshire.

as a function of amount adsorbed up to approximately 50% coverage. The calorimetric results have been obtained at 30°C. The application of gas chromatography to the determination of heats of ammonia adsorption at high temperatures is described in a separate paper (*7*).

The research is complementary to a number of investigations on ammonia adsorption published during the last four or five years. Clark and co-workers (*8*) have determined isosteric heats on silica-alumina of various compositions from adsorption measurements at 100–400°C; MacIver and co-workers (*9*) have investigated ammonia adsorption on eta and gamma alumina as a function of calcination conditions, while Kubokawa (*10*) and Amenomiya and co-workers (*11*) have examined the desorption of ammonia from alumina. Fripiat *et al.* (*12*), Hall and co-workers (*13*), and Peri (*14*) have reported in detail on the infrared aspects of the adsorption of ammonia on various aluminosilicate and alumina preparations, and Hirschler (*15*) has studied the influence of ammonia adsorption on measurements of acidity by carbonium ion indicators. Two calorimetric studies of ammonia adsorption have also been made: Kevorkian and Steiner (*16*) measured heats as a function of coverage on alumina specimens derived from bayerite, and Hsieh (*17*) reported similar results for silica-alumina cracking catalyst. A unique and surprising feature of these calorimetric results was the observation of a *minimum* in the heat of adsorption at moderately low coverage (below 15%), followed by a broad maximum. The rise of the heat of adsorption between the minimum and maximum was up to 4 kcal/mole for alumina (*16*) and 7 kcal/mole for silica-alumina (*17*). The heats evaluated from the indirect measurements (*8*, *11*) reveal no such anomalies, and an examination of this discrepancy was therefore one of our primary aims.

EXPERIMENTAL

Apparatus and procedure. The calorimeter and its application to the measurement of heats of adsorption on powdered adsorbents have been described previously (*18*). The calorimeter normally contained between 10 and 15 g of adsorbent and the water equivalent of the calorimeter and its contents was normally between 8 and 9 g. Before heat measurements the adsorbent was outgassed in the calorimeter at 480°C until the residual pressure dropped below 10^{-5} mm Hg. The calorimeter was then cooled and placed in a thermostat at 30°C.

Increments of coverage were made by admitting doses of ammonia to the calorimeter from a calibrated volume of 270 cm^3. The temperature rise and pressure fall were then measured simultaneously. The gas was normally admitted at about 25 mm pressure, but at high coverages some larger doses at two to three times this pressure were admitted. The volume adsorbed was calculated from pressure measurements made before and after admission using a wide-bore mercury manometer and McLeod gauges. During the adsorption of a dose at low coverage the pressure dropped to about 10^{-2} mm during the first 30 sec and then fell more slowly to about 10^{-4} mm. A succession of 10 to 20 doses was made in each run in order to obtain the heat of adsorption as a function of coverage.

Surface coverages were based on monolayer volumes determined by the BET method using nitrogen at 77°K. An area of 16 Å^2 was assumed for the nitrogen molecule, and the same area was taken for the ammonia molecule. Ammonia coverages were therefore calculated by dividing the volume of ammonia adsorbed by the nitrogen v_m.

Materials. Ammonia was obtained from a cylinder supplied by the British Oxygen Company. The gas was condensed in an ethanol-CO_2 trap and then allowed to evaporate into the vacuum system. It was subjected to several bulb-to-bulb distillations, and the middle fraction was retained and stored in glass bulbs.

Samples of chi alumina, eta alumina, and gamma alumina were kindly supplied by Peter Spence and Sons, Limited. Chi alumina was obtained by calcination of gibbsite at 550°C for 2 hr; eta alumina was prepared by similar calcination of bayerite. Gibbsite and bayerite had been electrolytically prepared, and total metallic impurities

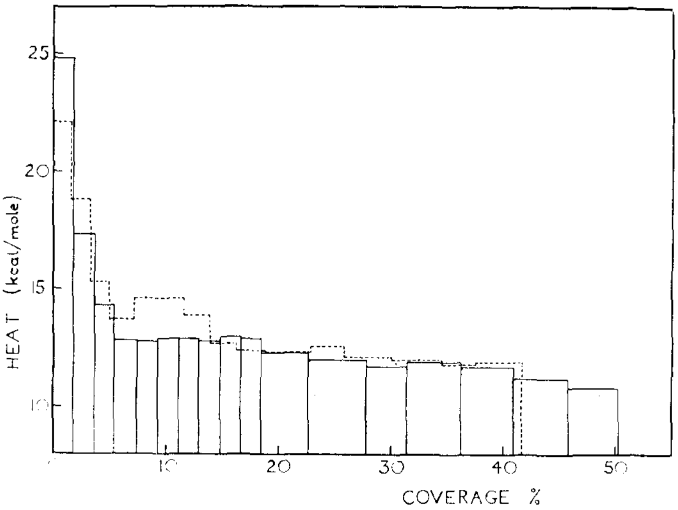

FIG. 1. Heats of adsorption of ammonia at 30°C on chi alumina: ——, first series; - - - - - second series.

were stated as 100 ppm or less. Samples of Linde molecular sieves NaX and CaX were obtained from B.D.H. as extrudates. Silica and silica-alumina samples of several compositions were kindly supplied by Joseph Crosfield and Sons Limited.

A quantity of chi alumina (Spence) was treated with 0.1 *N* KOH solution to examine the effect of contamination with potassium ions. After filtration the alumina was washed with distilled water and dried at 110°C. It was then placed in the calorimeter and baked out in the usual way. The extent of the doping was 2.5 moles KOH per 100 moles Al_2O_3.

One sample of alumina was prepared in the laboratory from aluminium isopropoxide supplied by B.D.H. The isopropoxide was vacuum-distilled, and the supercooled distillate was diluted with an equal volume of isopropanol. The solution was then dropped slowly into a large volume of deionized water contained in a polythene beaker at 0°C. The resulting precipitate was centrifuged, washed once with isopropanol, and twice with deionized water, and then dried at 110°C. An X-ray powder photograph confirmed that the dried precipitate was boehmite. This was calcined at 500°C in a muffle furnace for 9 hr and the product was gamma alumina. This is designated gamma alumina II, and gamma alumina (Spence) as gamma alumina I.

The adsorbents were used in the calorimeter as granules of 30 to 40 mesh. Their surface areas are summarized in Table 1.

TABLE 1
BET SURFACE AREAS

Adsorbent	Surface area (m^2/g)
Chi alumina	190
Chi alumina impregnated with KOH	175
Eta alumina	190
Gamma alumina I	210
Gamma alumina II, from Al isopropoxide	240
NaX	560
CaX	640
Silica-alumina (40% Al_2O_3)	270
(33% Al_2O_3)	380
(23% Al_2O_3)	230
(14% Al_2O_3)	230
Silica	325

RESULTS

Heats of adsorption of ammonia on chi-, eta-, and gamma alumina. Results for the heat of adsorption of ammonia as a function of coverage on chi alumina are illustrated in Fig. 1. Seventeen increments of ammonia were successively admitted to a fresh sample, giving a total coverage of 50%. The stepped curve shows the extent to which the experiment approaches the ideal of a differential heat measurement. The curve can be seen to consist of two distinct regions. Below about 6% of a monolayer the heat is strongly dependent on coverage, falling from an initial value of 25 kcal/mole to about 13 kcal/mole. Between 6% and 50% coverage, there is a very slight fall to 11 kcal/mole.

After the adsorption run had been completed, the desorption was studied as a function of temperature by isolating the calorimeter and heating it to successively higher temperatures. From the equilibrium pressure observed at each temperature the amount desorbed was calculated, and the results are shown in Fig. 2. A total of 180 cm^3 (STP) had been adsorbed at 30°C, but even at 500°C only 130 cm^3 was desorbed. The 50 cm^3 remaining on the surface at 500°C corresponds to a coverage of 12%. The ammonia held on the more active sites of the chi alumina is evidently not removed by heating to 500°C in a closed system. In order to discover whether the gas adsorbed on these sites could be removed by prolonged heating *in vacuo*, the specimen was outgassed at 480°C and 10^{-6} mm for 36 hr. After cooling to 30°C a second heat of adsorption curve was measured (Fig. 1). The higher heats at low coverage are again apparent, indicating that the outgassing treatment had successfully removed most of the ammonia remaining adsorbed at 500°C in Fig. 2. The heat released by the first increment, however, is a few kilocalories less, suggesting either that the ammonia adsorbed on the most active sites cannot be desorbed even by rigorous outgassing at 500°C or that the strongest sites have been destroyed.

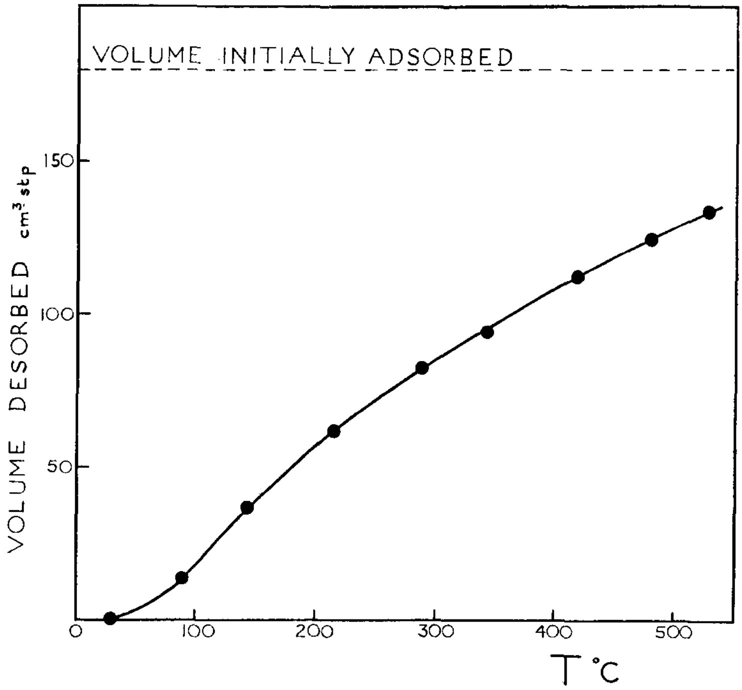

FIG. 2. Desorption of ammonia from chi alumina.

The differential heat curve for eta alumina is shown in Fig. 3. The shape is very similar to those for chi alumina. The initial heat of 21 kcal/mole is somewhat lower than the 25 kcal/mole observed initially for chi alumina, and the decrease in heat with coverage is less steep. The corresponding results for gamma alumina I are also shown in Fig. 3. The initial heat (21 kcal/mole) is the same as that for eta alumina, but the fall with coverage is somewhat more rapid. The heat of adsorption reaches 13 kcal/mole already at 4% coverage. The effect on the heat curves for these aluminas of outgassing at 480°C was similar to that found for chi alumina.

The heat of adsorption curve for the chi alumina that had been treated with potassium ions is shown in Fig. 4. The curve lies slightly below that for the untreated chi alumina in the region between 7% and 25% coverage, but it is unlikely that this difference is experimentally significant.

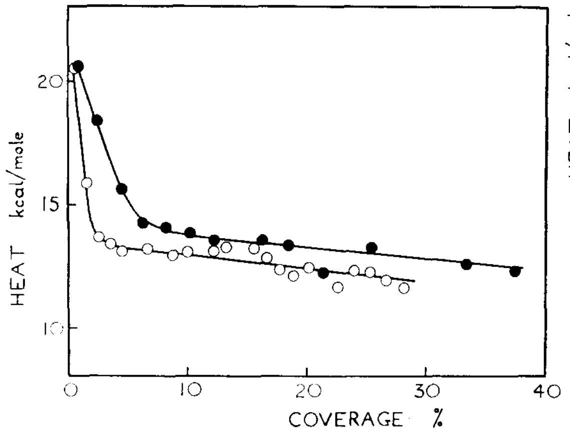

FIG. 3. Heats of adsorption of ammonia at 30°C: ●, eta alumina; ○, gamma alumina I.

The results obtained for gamma alumina II (prepared from the isopropoxide in the absence of alkali metal ions) are quite different from those mentioned so far. As illustrated in Fig. 5, the initial heat of adsorption is 38 kcal/mole, very much higher than on any of the other aluminas. The heat at high coverage, however, is significantly lower.

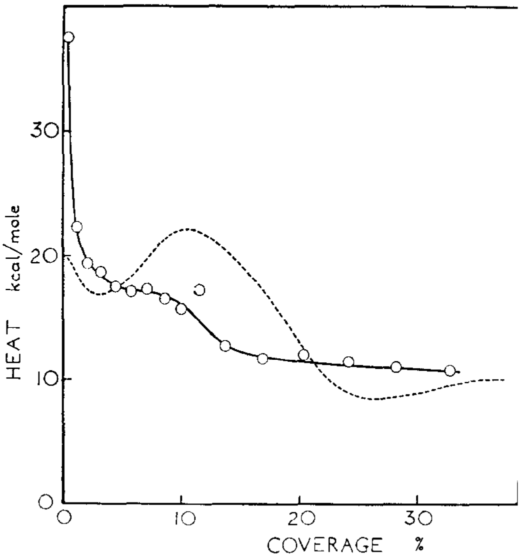

FIG. 5. Heats of adsorption of ammonia at 30°C on gamma alumina II. The broken line shows the result of Kevorkian and Steiner (*16*) for the heat of adsorption of ammonia at 50°C on alumina calcined at 594°C (296 m²/g).

Heats of adsorption of ammonia on silica-alumina. The full differential heat

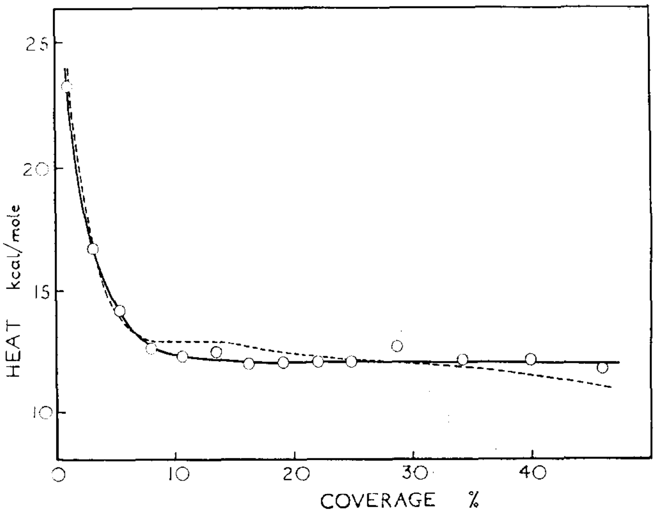

FIG. 4. Heats of adsorption of ammonia at 30°C on chi alumina treated with 0.1 N KOH. The broken line refers to the untreated specimen (Fig. 1).

curve for a typical cracking catalyst (23% Al_2O_3) is shown in Fig. 6. This substance has the highest initial heat of adsorption and integral heat of adsorption of the whole series. The shape of the curve, however, is very similar to those of the aluminas in general. The heat falls abruptly from an initial value of 40 kcal/mole to 12 kcal/mole at 50% coverage.

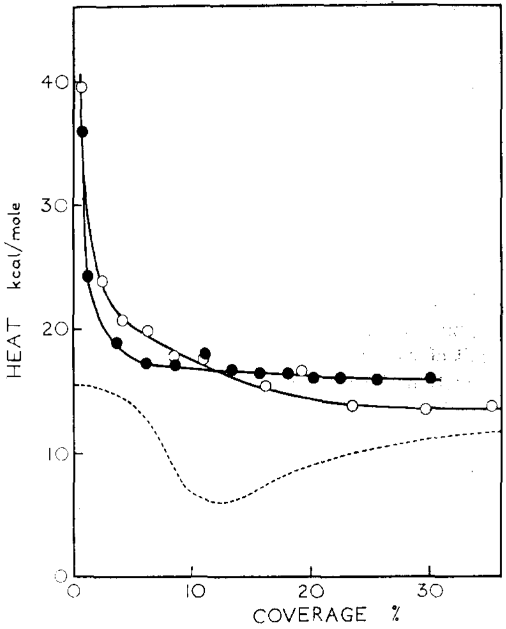

FIG. 6. Heats of adsorption of ammonia at 30°C on silica-alumina (23% Al_2O_3): ○, F. S. Stone and L. Whalley; ●, F. S. Stone and N. K. C. Whalley, separate investigation. The broken line shows the result of Hsieh (*17*) for the heat of adsorption of ammonia at 0°C on silica-alumina (25% Al_2O_3).

Silica-aluminas of other compositions (14%, 33%, and 40% alumina) have recently been investigated in our laboratory by Mr. N.K.C. Whalley, who has also examined a pure silica. The general form of the heat of adsorption curve is similar to that of Fig. 6 in all these cases, but none shows as high an initial heat as the specimen whose characteristics are illustrated in Fig. 6. As is shown in Table 2, the integral heat of adsorption up to 20% coverage is also greatest for the specimen with the composition 23% Al_2O_3, 77% SiO_2.

Heats of adsorption of ammonia on molecular sieves. Linde molecular sieve X (faujasite-type structure) was studied in the form of CaX and NaX. The differential heat curves for ammonia adsorption are shown in Fig. 7. The behavior of the two sieves is quite different. The calcium form gives a curve which is of the same form as the curve for the aluminas, although the initial heat and also the integral heat of adsorption are lower than for any of the alumina specimens. The sodium sieve, on the other hand, does not exhibit the high initial heat of adsorption which is characteristic of the other adsorbents. Indeed this compound has the most uniform heat of adsorption of all the substances studied. The curve for the sodium sieve lies as a whole below that of the calcium sieve, giving an integral heat of adsorption (up to 25% coverage) of 11 kcal/mole

TABLE 2
HEATS OF ADSORPTION OF AMMONIA AT 30°C ON SILICA AND SILICA-ALUMINA[a]

% Al_2O_3	% Silica	Initial heat of adsorption (kcal $mole^{-1}$)	Integral heat of adsorption up to 20% coverage (kcal $mole^{-1}$)
0	100	19	15
14	86	23	17
23	77	36	19
33	67	27	18
40	60	24	18

[a] After N. K. C. Whalley (*19*).

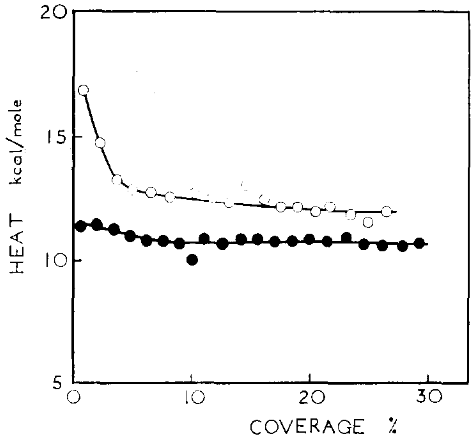

FIG. 7. Heats of adsorption of ammonia at 30°C on Linde molecular sieve X: ○, CaX; ● NaX.

compared to 13 kcal/mole for the calcium form.

Discussion

A rise in the heat of adsorption to give a maximum in the plot of heat of adsorption (q) versus coverage (θ) near the monolayer has been established experimentally in a number of cases of physical adsorption (*20*, *21*), and is satisfactorily explained on the basis of the attractive interactions between adsorbate molecules dominating the effects of surface heterogeneity and repulsive interaction. The observed (and calculated) rises in these cases are normally less than 1 kcal mole^{-1}. In chemisorption, the presence of surface heterogeneity and of endothermic processes related to the transfer of charge in the developing adsorbed layer lead to larger decreases in q than in physical adsorption, with the result that attractive interactions are much less likely to manifest themselves in the q–θ curve. For this reason, the recently published results of Kevorkian and Steiner (*16*) for the chemisorption of ammonia on alumina and those of Hsieh (*17*) for ammonia chemisorption on silica-alumina, examples of which are given in Figs. 5 and 6, respectively, show a most unexpected behavior of the heat of adsorption on coverage. In our experience the results of these authors are unique in showing such large rises of heat of adsorption at such low coverages. If correct, they point to a remarkably specific attractive interaction between localized, oriented ammonia molecules or their reaction products at the oxide surface. Such a phenomenon would almost certainly have consequences for the adsorption and reactivity of other molecules with basic characteristics, and demanded further investigation.

The most important conclusion to emerge from our work is that there are no minima or maxima in the curves of q versus θ for ammonia adsorption on any of the aluminas or silica-aluminas that we have studied. We have deliberately extended the range of specimens to include aluminas of different purity and aluminum-oxygen coordination and silica-aluminas of differing composition about the 25% Al_2O_3 content used by Hsieh. It is difficult, therefore, to account for the discrepancy in terms of differences in preparation. Moreover, the work of Clark *et al.* (*8*) and of Amenomiya and co-workers (*11*) on heats of ammonia chemisorption determined by indirect noncalorimetric methods is in good general agreement with our direct investigation of the heats of adsorption, and does not support the idea of a rise in heat at intermediate coverage. We are led, therefore, to consider the extent to which calorimetric practice might produce anomalous results at intermediate coverages.

The resistance thermometer calorimeter which we have used is designed to minimize the adverse effects of local heating during rapid adsorption. It has also a relatively large thermal capacity, containing 10–15 g of adsorbent. Furthermore, we dosed ammonia at fairly high pressure (25 mm) to achieve good equilibration of heat. The thermocouple calorimeters used by Kevorkian and Steiner (*16*) and by Hsieh (*17*), on the other hand, were apparently of low thermal capacity (1–2 g of adsorbent) and relied on a single junction to measure the temperature rise. Experience in our own laboratory (*22*) inclines us to think that single-junction calorimeters in designs where there is rapid cooling to the surroundings may not register the full heat liberated in very fast chemisorption processes. It should be noted that the heats observed by Hsieh in the range up to 30% coverage (which covers the whole of the anomalous region) are *very* much lower than those observed by us and those reported by Clark *et al.* (*8*). Poor thermal response up to $\theta = 0.3$ would simultaneously account for a minimum and a maximum in the q–θ relation, since the extremely high heats of adsorption for initial doses (Fig. 6) can be expected to show through in spite of a poor response, albeit with arbitrarily low numerical values. At higher coverages the adsorption becomes less rapid; local heating at a distance from the thermocouple is less likely to occur and the calorimeter is then able to register more correctly the heat liberated in the adsorption. The same observations are pertinent with respect to the comparison between our results on pure alumina and silica and those of Kevorkian and Steiner (*16*), although the anomalous effect in their calorimeter would not appear to be so great. Thus, in the absence of further experiments with more elaborate isothermal calorimeters, we consider that it is the calorimetric method, combined with the special characteristics of ammonia adsorption on these high area solids in respect of the rate of heat release, which is probably responsible for the minima and maxima rather than unique properties of the adsorbed ammonia. The rate of adsorption is certainly dependent on coverage, being very rapid at low θ, and it is worth remarking that one apparent small rise in q which we observed (Fig. 1, Curve 2) occurred when an abnormally large increment of coverage was made. Such rises are certainly within experimental error in our calorimeter.

Adsorption of ammonia on alumina. The plots of q versus θ have the same general form for all the aluminas studied. An initially high heat of 20–40 kcal mole^{-1} falls very rapidly over the first few percent of the monolayer to flatten out at about 13 kcal mole^{-1}. Thereafter q decreases very slowly with θ, reaching ~11 kcal mole^{-1} at 50% coverage. The infrared studies of Parry (*23*) and of Peri (*14*) lead us to suppose that the great majority of the strong ammonia chemisorption at 30°C results from its reaction as a base with Lewis acid sites on the oxide surface. On this view, and assuming 1:1 correspondence between ammonia molecules and acid sites, the upper limit for the strong adsorption ($q > 14$ kcal mole^{-1}) of 7% implies a concentration of not more than 4×10^{13} per cm^2 for the acid sites on alumina (1 monolayer $\equiv 6 \times 10^{14}$ molecules cm^{-2} for $A_0 = 16$ Å^2). Of these, approximately 20–25% have $q > 20$ kcal mole^{-1} (strong sites). Chi alumina and eta alumina, which are derived directly from the respective $Al(OH)_3$ compounds gibbsite and bayerite, have more acid sites than the corresponding gamma alumina I derived indirectly from $Al(OH)_3$ via boehmite. Gamma alumina and eta alumina have very similar structures, both being related to that of spinel, $M_{tet}[M_2]_{oct}O_4$, with oxygen ions in cubic close packing. Gamma alumina, however, shows a tetragonal distortion from the spinel structure, and the cation vacancies demanded by the stoichiometry of Al_2O_3 ($\square_{\frac{1}{3}}\ Al_{2\frac{2}{3}}O_4$) are thought to be located exclusively on the tetrahedral sites, $(\square_{\frac{1}{3}}\ Al_{\frac{2}{3}})_{tet}[Al_2]_{oct}O_4$ (*24*). In eta alumina, the work of Krischner (*25*) indicates that the distortion from the cubic structure is absent, which may imply a different distribution of the cations. However, bearing in mind the results for gamma alumina II (Fig. 5), there does not appear to be an intrinsic property of the structure which determines ammonia adsorption heat behavior, although catalytic behavior is reportedly different (*26*). Other variables, such as hydroxyl content and alkali metal ion content, to which we refer below, are presumably more significant. Our figure of 4×10^{13} per cm^2 (maximum) for the surface density of acid sites on alumina is lower than that given by Webb (*27*) (10×10^{13} per cm^2) from ammonia chemisorption, but close to that determined by Pines and Haag (*4*) (2×10^{13} per cm^2) from trimethylamine adsorption. The latter authors consider that the number of acid sites capable of isomerizing cyclohexene was only 8×10^{12} per cm^2. This discrimination in favor of a fraction of acid sites more active than others is entirely supported by our observation of a steeply falling q–θ curve at low coverages. Analogy implies that activity for cyclohexene isomerization corresponds to sites with heats of ammonia chemisorption greater than about 20 kcal mole^{-1}

The presence of alkali and alkali metal salts in alumina reduces the acidity (*4*, *16*). Our results confirm that alumina is poisoned more easily by adventitious exposure to alkali metal ions during preparation than by impregnation after calcination. The most active of our aluminas (gamma alumina II) was one prepared by avoiding contact of solutions with glass or aluminosilicates. It is interesting, however, that the digestion of chi alumina with KOH did not reduce q at low θ; indeed, there was almost no effect. Chi alumina, it should be recalled, is prepared from gibbsite, which probably has to contain sodium to be stable (*28*). Kevorkian and Steiner (*16*) also observed that impregnation with KOH did not completely destroy acidity.

The lowest heat of adsorption measured (~11 kcal mole^{-1} at 50% coverage) is still much higher than the heat of liquefaction of ammonia, which is ~5 kcal mole^{-1} at 30°C. Peri (*14*) has shown in his infrared work that the O–H stretching frequencies of the residual hydroxyl content of outgassed alumina are affected by ammonia adsorption beyond the range of the strong chemisorption. Thus the enhanced heat is at least partly due to a contribution from hydrogen bonding supplementing the energy of physical adsorption, an effect which is well known in the adsorption of –OH or –NH containing vapors on hydroxylated surfaces (*29*).

The experiment illustrated in Fig. 2 fully accords with the experience of Peri (*14*) that an appreciable fraction of the ammonia chemisorbed on alumina cannot be removed by outgassing at 500°C. As shown by Peri (*14*), the adsorbed ammonia can react at high temperatures as a Bronsted acid with oxide ions to form NH_2^- and OH^-; attempts to desorb ammonia also result in loss of some water of constitution (*15*). It follows that adsorption equilibria studied below 500° refer to only a part of the adsorbed ammonia. This adversely affects attempts to measure the heat of adsorption at high temperatures by noncalorimetric methods (*7*).

Adsorption of ammonia on silica-alumina and Linde X. The silica-aluminas which we have investigated embrace the range of composition (70–90% SiO_2) which is generally regarded as being most active for cracking, isomerization, and polymerization catalysis. The ammonia adsorption heats (Table 2) provide a further illustration of the well-established trend (*1*) towards increasing acidity as alumina is admixed with pure silica, and a maximum in the heat occurs for the 23% Al_2O_3 specimen. The maximum, however, is rather flat and arises in our work because of the very high heat of the 23% Al_2O_3 specimen over the first 1% of coverage (Fig. 6). The *initial* heats of adsorption on the silica-aluminas are not noticeably different from the spread of initial heats of adsorption observed with the aluminas, but taken over a broad range of coverage they have a significantly higher integral heat. Assuming this reflects differences in acidity, the conclusion is that the silica-aluminas have a larger number of weaker acid sites than pure alumina. This agrees with the view that silica-alumina has appreciably more Bronsted acidity than pure alumina. The ammonia heat results of the present paper do not add further to the current dialogue on the amount and nature of the acidity in these materials, but it should be noted that they are free from certain drawbacks (*15*) associated with the determination of acidity distributions from ammonia desorption at high temperature.

To accommodate greater reliability in the calorimetric measurements with regard to the q–θ variations reviewed in the first part of the Discussion, the zeolites NaX and CaX were not employed as the pure fine powders but as coarser granules obtained by crushing the commercially available extrudates of CaX and NaX, which presumably contain a proportion of binder. This qualifies the absolute significance of the numerical values of the heats obtained, and may account for our NaX curve (Fig. 7) being somewhat flatter than that reported by Kiselev (*29*) for a similar adsorbent, but internal comparison between our CaX and NaX results is less likely to be affected. With this provision, the results with Linde X are of interest in that CaX is known to be a much more effective cracking catalyst than NaX. Moreover, the respective cracking patterns reported (*30*) are such that the process over CaX is characteristic of carbonium ion reactions (as with the acidic silica-alumina) while that over NaX is more characteristic of free-radical (thermal) cracking. The ammonia adsorption data presented in Fig. 7 show a clear discrimination in the direction of greater heats of adsorption on CaX compared to NaX, similar to the comparison between silica-alumina and alumina mentioned in the preceding paragraph. There appears to be a correlation between catalysts which support carbonium ion cracking and greater ammonia adsorption heat in the region of medium coverage. Although the matter is still debated, the activity of the zeolite catalysts in carbonium ion formation has been attributed to specific action of the multicharged ions (*31*) lodged in the matrix rather than to Bronsted or Lewis acidity. In this connection it is of interest that CaX behaves so differently from silica-alumina towards ammonia adsorption at very low coverage. Although acidic to some degree, there are obviously no strong acid sites on CaX or NaX as we have studied them which are comparable to those on silica-alumina or pure alumina.

ACKNOWLEDGMENTS

The authors are much indebted to Mr. N.K.C. Whalley for his help with some of the calorimetric measurements. They also wish to express their thanks to Peter Spence & Sons, Ltd. and to Joseph Crosfield and Sons, Ltd. for kindly supplying special preparations of alumina and of silica-alumina and silica, respectively.

REFERENCES

1. THOMAS, C. L., *Ind. Eng. Chem.* **41,** 2564 (1949).
2. TAMELE, M. W., *Discussions Faraday Soc.* **8,** 270 (1950).
3. MILLIKEN, T. H., MILLS, G. A., AND OBLAD, A. G., *Discussions Faraday Soc.* **8,** 279 (1950).
4. PINES, H., AND HAAG, W. O., *J. Am. Chem. Soc.* **82,** 2471 (1960).
5. TERTIAN, R., AND PAPÉE, D., *J. Chim. Phys.* **55,** 341 (1958); SAALFELD, H., *Proc. Intern. Symp. Reactivity Solids, 4th, Amsterdam, 1960,* p. 310 (Elsevier, Amsterdam, 1961); LIPPENS, B. C., Thesis, Delft, 1961.
6. RABO, J. A., PICKERT, P. E., STAMIRES, D. N., AND BOYLE, J. E., *Actes Congr. Intern. Catalyse, 2ᵉ, Paris 1960,* p. 2055 (Technip, Paris, 1965).
7. STONE, F. S., AND WHALLEY, L., to be published.
8. CLARK, A., HOLM, V. C. F., AND BLACKBURN, D. M., *J. Catalysis* **1,** 244 (1962).
9. MACIVER, D. S., TOBIN, H. H., AND BARTH, R. T., *J. Catalysis* **2,** 485 (1963).
10. KUBOKAWA, Y., *J. Phys. Chem.* **67,** 769 (1963).
11. AMENOMIYA, Y., CHENIER, J. H. B., AND CVETANOVIC, R. J., *J. Phys. Chem.* **68,** 52 (1964).
12. FRIPIAT, J. J., LÉONARD, A., AND UYTTERHOEVEN, J. B., *J. Phys. Chem.* **69,** 3274 (1965).
13. UYTTERHOEVEN, J. B., CHRISTNER, L. G., AND HALL, W. K., *J. Phys. Chem.* **69,** 2117 (1965).
14. PERI, J. B., *J. Phys. Chem.* **69,** 231 (1965).
15. HIRSCHLER, A. E., *J. Catalysis* **6,** 1 (1966).
16. KEVORKIAN, V., AND STEINER, R. O., *J. Phys. Chem.* **67,** 545 (1963).
17. HSIEH, P. Y., *J. Catalysis* **2,** 211 (1963).
18. GALE, R. L., HABER, J., AND STONE, F. S., *J. Catalysis* **1,** 32 (1962).
19. WHALLEY, N. K. C., unpublished.
20. BEEBE, R. A., AND YOUNG, D. M., *J. Phys. Chem.* **58,** 93 (1954).
21. KISELEV, A. V., *Quart. Rev. Chem. Soc.* **15,** 99 (1961).
22. DELL, R. M., KLEMPERER, D. F., AND STONE, F. S., *J. Phys. Chem.* **60,** 1586 (1956).
23. PARRY, E. P., *J. Catalysis* **2,** 371 (1963).
24. SAALFELD, H., AND MEHROTRA, B., *Ber. Deutsch. Keram. Gesell.* **42,** 161 (1965).
25. KRISCHNER, H., Habilitationschrift, Techn. Hochschule, Graz, 1964.
26. MACIVER, D. S., WILMOT, W. H., AND BRIDGES, J. M., *J. Catalysis* **3,** 502 (1964).
27. WEBB, A. N., *Ind. Eng. Chem.* **49,** 261 (1957).
28. TORKAR, K., AND BERTSCH, L., *Monatsh. Chem.* **91,** 450 (1960).
29. KISELEV, A. V., *Discussions Faraday Soc.* **40,** 205 (1965).
30. FRILETTE, V. J., WEISZ, P. B., AND GOLDEN, R. L., *J. Catalysis* **1,** 301 (1962).
31. PICKERT, P. E., RABO, J. A., DEMPSEY, E., AND SCHOMAKER, V., *Proc. Intern. Congr. Catalysis, 3rd, 1964,* p. 714 (North-Holland, Amsterdam, 1965).