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Adsorption of Amines on Alumina

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The adsorption of a series of aliphatic amines on alumina was investigated. The more weakly bonded species were studied by measuring the adsorption isotherms by the pulse chromatograph technique. The dependence of the isosteric heat of adsorption upon the adsorbed amount was calculated from the adsorption isotherms. The method of temperature programmed desorption (TPD) was employed in the study of strong chemisorption. Most of the amines investigated desorbed in two steps. The steric demands of adsorption do not differ within the series of primary amines. The decrease in the adsorbed amount in the series ethyl-, diethyl-, triethylamine indicates the effect of steric hindrance. Two distinct regions were observed in the dependences of the isosteric heat of adsorption of primary aliphatic amines upon the adsorbed amount. Below 0.3 mmole/g the heat of adsorption increased in the order *n*-butyl- < *n*-propyl- < ethyl- < methylamine, while the order was exactly reversed above 0.5 mmol/g. The type of amine–surface interaction was different in each of these two regions. On the basis of measurements on variously hydrated surfaces it was possible to conclude that hydroxyl groups form a part of the active sites in the region below 0.3 mmol/g. The active sites in the region above 0.5 mmol/g were probably oxide ions. Very strong adsorption on acidic aluminum ions probably occurs at coverages below 0.1 mmol/g and corresponds to the second peak of the TPD chromatogram.

INTRODUCTION

While great attention has been devoted in the literature to the reactions and adsorption of alcohols, there are many fewer papers dealing with the investigation of the properties of the amine–alumina system.

Peri (*1*), on the basis of a study of alumina hydration, proposed (*2*) a surface model of γ-Al_2O_3. According to this model aluminium ions, oxide ions and hydroxyl groups are present on the surface. The active sites, in Peri's view, are incompletely coordinated aluminum ions (strong Lewis acids) and oxide ions (weak Lewis bases). Active sites are formed during the elimination of water from the surface. Peri, by means of ir spectra, identified 5 types of hydroxyl groups whose various properties he related to the number of oxide ions in their immediate neighborhood. The Peri model has been accepted by many authors and has been used to explain the behavior of various substances on the surface of alumina.

Ammonia adsorption on alumina has been studied mainly with a view to the determination of surface acidity. Peri (*3*) and Dunken and Fink (*4*) investigated various forms of bonded ammonia. Medema *et al* (*5*) studied the adsorption of amines while Takeuchi (*6*) measured the adsorption isotherms of ammonia and trimethylamine over alumina and silica–aluminas. Hirota *et al* (*7*), on the basis of spectral studies, came to the conclusion that chemisorbed amine is bonded to alumina by the free electron pair on nitrogen. Parry (*8*), investigating the chemisorption of pyridine, found a strong bond with the surface involving a positive charge on the nitrogen. Stolz and Knözinger (*9*) studied various forms of bonded pyridine and concluded that there are two types of acidic active sites on the surface of alumina. Parrera and Figoli (*10*), on the basis of this conception, assume dissociative adsorption of diethylamine on an acidic–basic site pair and refer to the dissociative adsorption of ammonia determined by Peri.

In a number of papers (*10,12,26*), strong basic sites are proposed in addition to acidic sites.

The present work is directed towards the elucidation of the behavior of amines over alumina and is related to our studies of the reactions of aliphatic amines (*11,12*). Kinetic measurements of the deamination of amines to olefins and of amine disproportionation have shown that the course of these reactions cannot be explained by a simple monomolecular interaction of an amine molecule with a single type of active site on alumina. It was hoped that investigation of the chemisorption proper of amines over alumina would help to confirm the heterogeneity of the alumina surface and, if possible, elucidate the character of the interaction between amines and the surface of the adsorbent. The more weakly bonded amine species were studied by measuring adsorption isotherms by the pulse chromatograph technique in a wide temperature range; the method of temperature programmed desorption (TPD) was used in the study of strong chemisorption.

METHODS

Measurement of Adsorption Isotherms

A separate paper (*13*) has been devoted to the application of the pulse chromatograph technique to the amine–alumina system and to a description of the apparatus and conditions of measurement. Adsorption isotherms were measured over alumina whose surface was, before each experiment, treated in the following manner: the adsorbent was washed by atmospheric air for 30 min at 450°C in order to remove adsorbate remaining from the previous measurement. After this the catalyst was activated in a flow of helium at 450°C for 1 hr (helium flow, 150 ml/min). After lowering the temperature to the required value, the adsorption isotherms were measured. Liquid amines were fed by a Zimmermann microsyringe and gaseous amines by calibrated injection syringes.

The adsorbed amount of amine on previously unused alumina was about 10% higher than in experiments over regenerated surface probably due to poisoning of the most active sites. The actual measurements were therefore only made after 3–4 introductory experiments over catalyst of constant properties. In order to limit the amount of physical adsorption to a minimum, the adsorption isotherms were measured at elevated temperatures. The lower limit of the region at which measurements were made was the same for all amines (130°C). The upper limit was set by the occurrence of the decomposition reactions of amines. At temperatures above 250°C the products of desorption were frozen at the temperature of liquid nitrogen and their composition was chromatographically tested. Measurements were stopped at the temperature where there was an identifiable amount of decomposition product present in the frozen sample.

Temperature Programmed Desorption

A detailed description of the apparatus for TPD measurements has been given in a previous paper (*14*). The adsorption column was constructed so as to enable direct temperature measurement in the catalyst bed. The preparation of the surface prior to measuring was the same as for the measurement of adsorption isotherms. Following the activation, the temperature was decreased to 30°C at which temperature amine was fed to the column until the alumina was saturated. After the injection of a further amount for calibration (*13*), the weakly bonded portions were washed from the adsorbent over 30 min. After this period it was no longer possible, using the given means of detection, to detect desorbing amine and further washing had no effect upon the TPD chromatograms. All the desorption measurements were carried out with a linear temperature increase of 14°C/min.

Materials

Alumina was prepared by the standard method used in our laboratory (*15*). It may be assumed that the γ-modification is obtained where this preparative method is used. The specific surface, measured chromatographically, was 180 m^2/g.

The amines used were commercial products further purified to minimally 99.9% by multiple rectification. The purity of methyl-, ethyl- and benzylamine was, however, only 99.8%. Helium was used from pressure cylinders and was purged of oxygen and water over catalytic and liquid purifiers.

RESULTS AND DISCUSSION

The adsorption isotherms of ammonia, methyl-, ethyl-, *n*-propyl-, *n*-butyl-, diethyl-, triethyl- and benzylamine were measured in the partial pressure range 1–200 Torr and in the temperature range 130–340°C at intervals of 10–15°C. The upper limit, which varied (340–270°C) for the different amines, was set by the occurrence of amine reactions over alumina. The dependence of the isosteric heat of adsorption upon the adsorbed amount was calculated from the adsorption isotherms by means of the Clausius–Clapeyron equation.

From the adsorption isotherms of ammonia, methyl-, ethyl-, *n*-propyl- and *n*-butylamine (see Fig. 1) it follows that the adsorbed amount, expressed in moles, is independent of the presence or length of alkyl attached to nitrogen. Steric hindrance does not therefore operate in the adsorption of primary amines. Hence it may be concluded that amines are bonded to alumina by means of the $-NH_2$ group and that the axis of the alkyl group is oriented perpendicular to the surface. Medema *et al.* (*5*) also compared the adsorbed amounts in the same series of aliphatic amines (excepting methyl- and ethylamine). These authors came to the conclusion that the adsorbed amount decreases with increasing size of molecule. According to the cited work (*5*), however, adsorption was studied at relatively low temperatures (20 and 100°C). Under these conditions the differences in the adsorbed amounts were not large (at 20°C the values for *n*-propyl- and *n*-butylamines varied in the range 0.33 to 0.35 mmol/g). Clearly, at low temperature the adsorption is predominantly unspecific. In this case then, increasing length of alkyl group can affect the amount adsorbed. In the event, however, of specific interaction involving the amine group, the alkyl group becomes oriented perpendicular to the surface and so the steric demands do not differ too much in the series of primary amines.

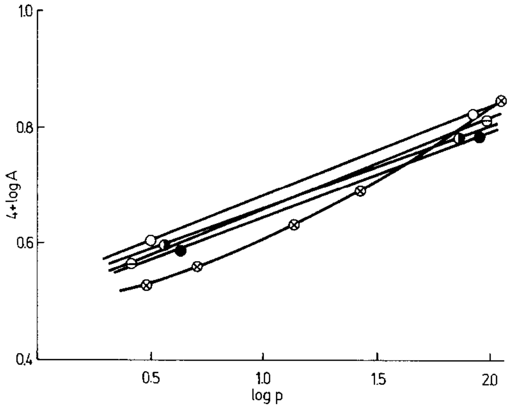


FIG. 1. Adsorption isotherms of primary amines and of ammonia at 229°C; *A* is expressed in mol g^{-1}. (○) Methylamine; (◑) ethylamine; (●) *n*-propylamine; (⊖) *n*-butylamine; (⊗) ammonia.

The decrease in the adsorbed amount in the order ethyl- > diethyl- > triethylamine (Fig. 2) indicates the possible influence of steric hindrance during adsorption. The volume and the space arrangement of the alkyl groups attached to the nitrogen atom of secondary and tertiary amines prevent

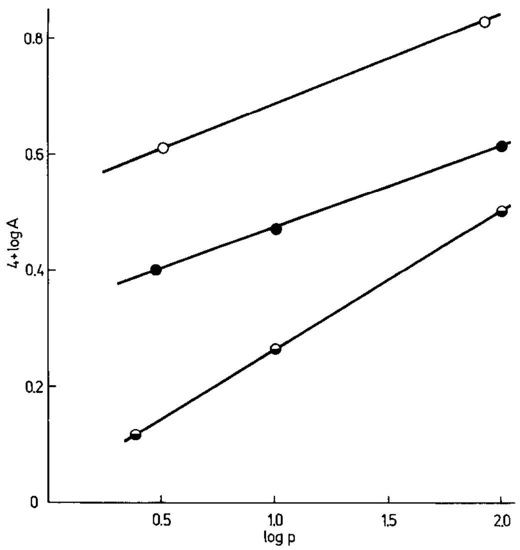
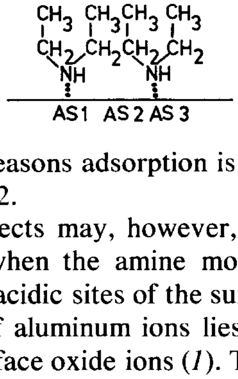


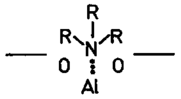
FIG. 2. Adsorption isotherms of ethyl-, diethyl- and triethylamine at 229°C. A is expressed in mol g^{-1}. (○) Ethylamine; (●) diethylamine; (○) triethylamine.

adsorption occurring simultaneously on two adjacent sites.



For these reasons adsorption is impossible on site AS 2.

Steric effects may, however, also come into play when the amine molecules approach the acidic sites of the surface, since the layer of aluminum ions lies beneath a layer of surface oxide ions (*1*). This mutual steric effect between the adsorbed molecule and the adsorbent surface also leads to a weakening of the bond with the surface.



It is not possible, on the basis of the results obtained, to judge which of the two types of steric influence is decisive.

The results of the study of the adsorption of amines by the method of temperature programmed desorption (TPD) indicate that the surface of alumina is nonhomogeneous. Two peaks were observed in the TPD chromatograms of all the amines studied with the exception of ammonia and methylamine. Some TPD chromatograms are given in Fig. 3. Table 1 shows the temperatures corresponding to these maxima.

The existence of two peaks in the TPD chromatograms, in the case of the adsorption of olefins and alcohols, has been directly related to the existence of two types of active sites on the surface of alumina (*16–18*). Ammonia and pyridine, however, whose adsorption on both of the assumed types of sites has been proven (*3,9*), have only one maximum in their chromatograms. Methylamine also shows only one maximum.

Analysis proved that the desorption products in the region of the second peak are formed mainly by the following reactions of amines over alumina:

1. Disproportionation

$$2\,RNH_2 \rightleftharpoons R_2NH + NH_3,$$
$$2\,R_2NH \rightleftharpoons R_3N + RNH_2.$$

2. Deamination

$$RCH_2CH_2NH_2 \rightarrow RCH = CH_2 + NH_3.$$

The explanation then presents itself that the occurrence of the second peak is connected with these reactions. In the study of the disproportionation of amines over cobalt (*14*), it was experimentally verified that the detector response is independent of the degree of conversion of the starting amine with respect to the disproportionation reaction. This fact is given by the similar heat conductivity values of reactant and product amines and by the considerably different heat conductivity of carrier gas helium. If then the adsorbed amines underwent only disproportionation reactions, without change in the number of moles, there should be no maxima in the TPD.

Deamination is different in that it in-

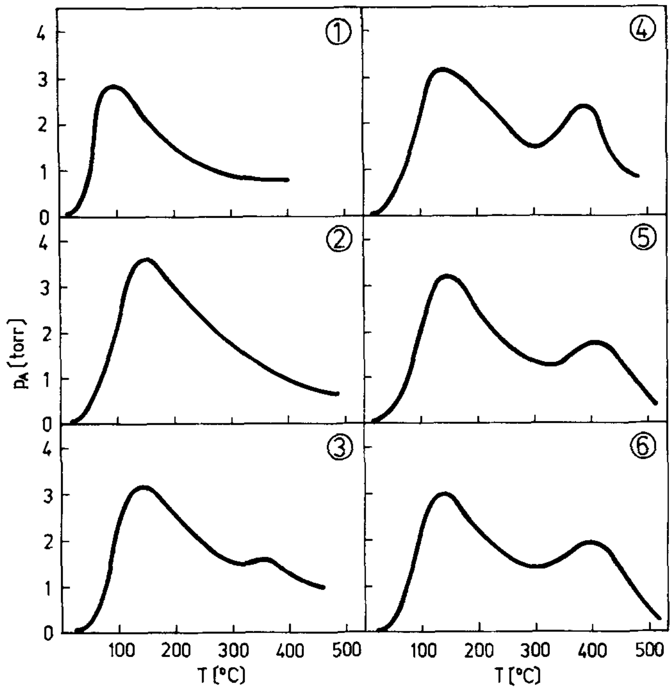


FIG. 3. Temperature programmed desorption chromatograms of ammonia (1), methyl- (2), ethyl- (3), *n*-butyl- (4), diethyl- (5) and triethylamine (6).

volves an increase in the number of moles. Doubling the molar amount of desorbing substances causes an increase in the detector response. With respect to the high value of the activation energy of deamination [52.5 kcal/mol for the deamination of diethylamine (*11*)], the dependence of the reaction rate on temperature is very steep. The second peak, which begins at temperatures about 300°C, at which temperature the first products of deamination were already observed in the adsorption isotherm measurements, may then be attributed to the landslide decomposition of adsorbed amine to olefin. The TPD chromatograms of ammonia and methylamine support this conclusion. Ammonia which is remarkably stable up to 450°C gives only one peak. Methylamine, which also gives only one peak, undoubtedly decomposes but is, however, incapable of forming olefin and so it undergoes mainly disproportionation and perhaps condensation reactions. Analysis of the desorption products of methylamine by mass spectroscopy showed the presence of the following compounds: ammonia, methylamine, dimethylamine, trimethylamine and compounds, of molecular weight 73, 86 and 101, whose exact identity was not investigated.

TABLE 1

TEMPERATURES OF THE MAXIMA OF VARIOUS AMINES IN TPD

Amine	T^1_{max} (°C)	T^2_{max} (°C)
Methyl-	129	—
Ethyl-	128	372
n-Propyl-	135	382
n-Butyl-	134	390
Diethyl-	132	387
Triethyl-	134	397
Ammonia	95	—
Pyridine[a]	208	—
Benzylamine[b]	268	396

[a] Adsorbent saturated and desorption initiated at 40°C.

[b] Adsorbent saturated and desorption initiated at 150°C.

Kinetic measurements of the deamination of amines over alumina (*11*) showed that diethylamine deamination is zero order (measurements were made in the temperature range 280–300°C) for a wide range of partial pressures (1–500 Torr). Zero order deamination indicates that the sites over which it occurs are fully occupied. However, it follows from the measured adsorption isotherms of diethylamine (*13*) that the surface of alumina is far from fully occupied [at temperature 280°C and partial pressure 10 Torr the surface coverage is 0.35 assuming a diethylamine cross-sectional area of 43.2 Å^2 (*19*)] and that the adsorbed amount increases with increasing amine partial pressure (measured up to 200 Torr). This of course means that deamination proceeds over a portion of the active sites which have distinct properties. The second peak of the TPD chromatograms may be attributed to products desorbing from sites different to those from which it desorbed in the first peak. It follows from semiquantitive estimates of the desorbed amount that, in the measurement of the adsorption isotherms, we were within the region of the adsorbed amount corresponding to the desorption in the first peak.

Two regions of surface coverage may be distinguished in the calculated dependences of the isosteric heat of adsorption upon the adsorbed amount of primary aliphatic amines (Fig. 4). In the region of lower adsorbed amounts (under 0.3 mmol/g) the heat of adsorption increases in the order: *n*-butyl- < *n*-propyl- < ethyl- < methylamine while in the region of higher adsorbed amounts (above 0.5 mmol/g) the order is exactly reversed. From this it may be concluded that the interactions of the amine with the surface in these two regions are different.

All the dependences of adsorption heat upon adsorbed amount decrease monotonously with surface coverage. Only triethylamine (Fig. 5) shows an increase in adsorption height with increasing surface coverage. Behavior similar to that of triethylamine has been described in the literature for several other adsorbate–adsorbent systems (*20,21*). These maxima are, however, found at surface coverage values approaching the monolayer. At this stage adsorbate–adsorbate interaction may be stronger than any previous adsorbent–adsorbate interaction. In the case of triethyl-

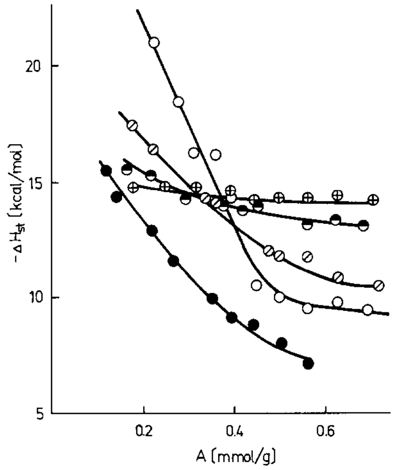


FIG. 4. Calculated dependences of the isosteric heat of adsorption upon the adsorbed amount of primary amines. (○) Methylamine; (⊘) ethylamine; (⊖) *n*-propylamine; (⊕) *n*-butylamine; (●) ammonia.

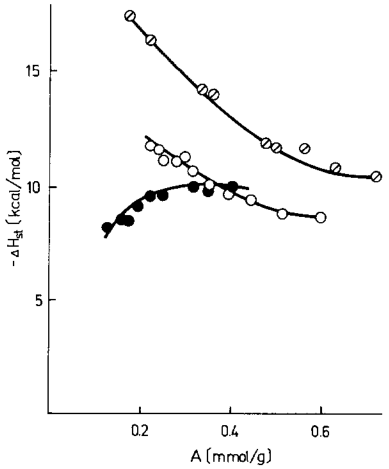


FIG. 5. Calculated dependences of the isosteric heat of adsorption upon the adsorbed amount of ethylamine, diethylamine and triethylamine. (⊘) Ethylamine; (○) diethylamine; (●) triethylamine.

amine, however, the increase in the heat of adsorption occurs at much lower surface coverage [20% for triethylamine of cross-sectional area 43 Å^2 (*19*)]. A similar increase (also at low surface coverage) was found for the system trimethylamine–silica–alumina (*6*). Comparing triethylamine with the other amines investigated we see that it differs in molecular volume and, in particular, is the only one which has no hydrogen attached to nitrogen.

The inversion in the order of the heats of adsorption of primary aliphatic amines in the region below 0.3 mmol/g and above 0.5 mmol/g may be explained only by a change in the character of the interaction of the amine with the surface in these two regions. In the series methyl-, ethyl-, *n*-propyl- and butylamines, several physical chemical constants may be found which increase from methyl- to butylamine (boiling point, alkyl inductive effect, molecular size and the increasing steric demands in adsorption following from it). All these parameters may contribute to the size of the heat of adsorption. In order to find out which of the parameters mentioned is decisive, we measured the dependence of the heat of adsorption upon adsorbed amount for benzylamine which has the advantage that the values of all the above-mentioned constants, with the exception of the inductive effect, lie beyond that of butylamine, while its negative inductive effect comes before that of methylamine. The calculated values of the heats of adsorption of benzylamine (in Fig. 6 compared with the values for methylamine), are less than those of methylamine in the region of higher adsorbed amounts. On account of the ease of benzylamine decomposition at higher temperatures, it was not possible, using the given technique, to determine the heat of adsorption for lower values of surface coverage. From the trend of the measured dependences, however, it is possible to deduce that, for low surface coverages, the heat of adsorption of benzylamine would be higher than that of methylamine. On this basis the probable influence of the inductive effect of the alkyl group upon the strength of amine adsorption on the surface of alumina may be conjectured. This effect, however, acts in a different way in the two regions under consideration.

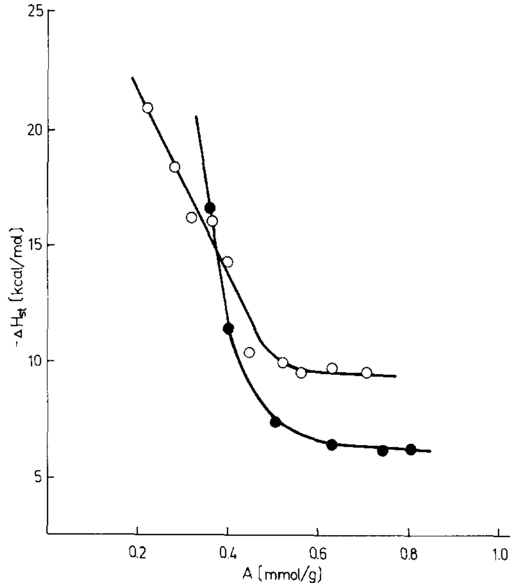


FIG. 6. Calculated dependences of the isosteric heat of adsorption upon the adsorbed amount of methylamine and benzylamine. (○) Methylamine; (●) benzylamine.

The results of investigations of basicity and acidity in the gas phase (*22–24*) have led to interesting conclusions. Both basicity and acidity are influenced by the polarizability stabilization effect of alkyl. This means that both basicity and acidity increase with increasing size of the alkyl group. In the case of basic interaction (interaction of the free electron pair on nitrogen with surface acidic site) and in the case of acidic interaction (interaction of the hydrogen on nitrogen with surface oxide ion), the highest value of adsorption heat in the series of primary amines should be that of *n*-butylamine. This is true, however, only in the region of higher adsorbed amounts (above 0.5 mmol/g). It seems that the interaction of the amine with the surface at lower adsorbed amounts cannot be classed among the simple types mentioned above.

In addition to the acidic (aluminum ions) and basic (oxide ions) sites already considered, hydroxyl groups are also present on the surface of alumina. The number of surface hydroxyl groups may be reduced by raising the activation temperature of the alumina. A change in the hydration of the surface may also cause a change in the relative representation of the individual types of sites (*1*,*2*). The measured values of the heats of adsorption of methylamine on variously hydrated surfaces are illustrated in Fig. 7. The temperature of activation was 450 or 550°C. Measurements were also made on alumina activated at 350°C. These latter results, however, were affected by the displacement of water from the alumina surface in the course of methylamine adsorption. The shape of the chromatographic peak was affected by desorbing water and, in addition, the surface was changed in an undefined way as a consequence of the removal of water.

It is evident from the dependences of the isosteric heat of adsorption upon the adsorbed amount, measured on alumina dehydrated at 450 and 550°C, that the deflection is shifted towards lower adsorbed amounts with decreasing number of hydroxyl groups. From this it may be concluded that those sites of which hydroxyl groups form a part are being occupied in the region of low adsorbed amount (below 0.3 mmol/g at activation temperature 450°C). Amine interaction with surface hydroxyl groups may be taken to be hydrogen bridge type bonding. This essentially, then, involves electrostatic interaction, whose strength is dependent upon the size of the charges and the distance between them. Quantum chemical calculations (*25*) have shown that, with increasing length of alkyl group and with increasing number of alkyl groups on the nitrogen atom, the negative charge on nitrogen decreases. From this it follows that, with increasing alkyl size the strength of interaction with hydroxyl group is diminished. Using the conclusion, from measurement on variously hydrated surfaces, that hydroxyl groups form a part of the sites which are being occupied at low surface coverages, it is possible to explain the order of the heats of adsorption of primary aliphatic amines in this region by the interaction of amine with hydroxyl groups. This interaction should, by all accounts, be very weak (the heat of adsorption should be around 5 kcal/mol). The considerably higher values measured by us indicate that, in addition to adsorption of amine on surface hydroxyl group, interaction with neighboring surface oxide ion may simultaneously occur. Our conclusion is therefore consistent with the Knözinger conception of the basic site (*26*):

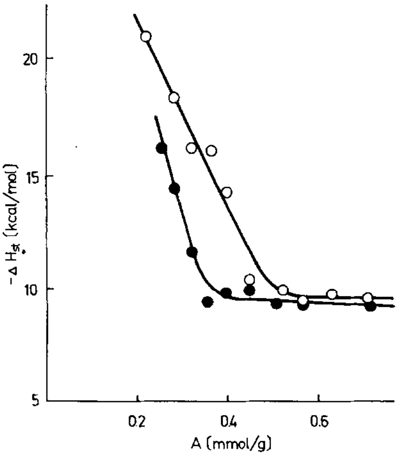
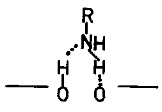


FIG. 7. Calculated dependences of the isosteric heat of adsorption of methylamine on variously hydrated surfaces. Activation temperature (°C): (○) 450; (●) 550.



Adsorption probably occurs on these sites in the region 0.1–0.3 mmol/g. The concept of interaction with both acidic and basic sites conforms to the measured order of adsorption heats of primary aliphatic amines in the region above 0.5 mmol/g. As followed from the Peri simulated model of the alumina surface, and as later asserted also by Stolz and Knözinger for pyridine adsorption (*9*), the number of exposed aluminum ions (strong acidic sites), capable of bonding a nucleophilic agent, is very small – 3 to 4 per 1000 Å^2 – which for our type of alumina of specific surface 180 m^2/g represents adsorption of less than 0.1 mmol/g. Adsorption on strong acidic sites therefore occurs in the region of very low coverages and, in view of its irreversibility, could not be investigated by means of the methods used for measuring the adsorption isotherms.

A semiquantitative estimate of the amount desorbing during the temperature programmed desorption suggested that the region in which the adsorption isotherms were measured corresponds to the first peak in the TPD chromatograms. Clearly the second peak corresponds then to desorption from the very strong sites which is possible only in the form of decomposition reaction products.

The relatively weak adsorption at coverages above 0.5 mmol/g is evidenced by the low values of the measured heats of adsorption in this region as well as by the rapidity and reversibility of the adsorption–desorption process during the measurement of the adsorption isotherms. On the basis of the given facts we assume that, at coverages greater than 0.5 mmol/g, amine is more likely to interact with basic sites (oxide ions) even if interaction also with weakly acidic sites cannot be ruled out in this region.

In the discussion so far we have not deàlt with the behavior of the other investigated amines. For di- and triethylamine a simple assessment of the influence of structural factors is complicated by the simultaneous action of various steric hindrances during adsorption. Ammonia, which is the zero member of the homologous series investigated, fits in with the discussed conception of surface heterogeneity only at higher adsorbed amounts. In the region below 0.3 mmol/g the value of the heat of adsorption of ammonia should be considerably higher. We are unable to explain unambiguously this disagreement.

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