Journal of Thermal Analysis, Vol. 10 (1976) 73—81

INVESTIGATION OF SURFACE PHENOMENA ON SOLID CATALYSTS BY SIMULTANEOUS TG AND DTA

PART IV. ADSORPTION OF AMMONIA ON THE SURFACE OF ZEOLITES AND SILICA-ALUMINA GELS TREATED WITH SODIUM HYDROXIDE

M. MALINOWSKI,* S. MALINOWSKI** and S. KRZYŻANOWSKI*

* *Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland*; ** *Institute of Organic Technology, Technical University, Warsaw, Poland*

(Received January 20, 1976)

Simultaneous TG and DTA were used to investigate the phenomena of adsorption, desorption and surface reactions of ammonia on NaX and X type exchanged zeolites and silica-alumina gels (Ketjen) treated with sodium hydroxide. On the basis of the quantitative results it is possible to give an interpretation of these surface phenomena and to establish the existence of various active centres on the surface of the catalysts. In the case of the adsorption of ammonia on silica-alumina gels, the quantity of adsorbed ammonia is much smaller than on silica-alumina gel treated with sodium hydroxide.

In the preceding work a measurement technique and an apparatus were described for thermogravimetric investigations of adsorption and surface phenomena occurring on the surface of solid catalysts.

Introducing a series of modifications to the Derivatograph enables us to measure the adsorbed quantity and to analyse the desorbate obtained from the samples investigated. The results of the examinations of water adsorption on zeolite catalysts and some amorphous alumina, silica and silica-alumina gels also containing sodium ions were described previously [2].

The results revealed the existence of specific water adsorption on zeolites.

In the present work, the results of investigations of ammonia adsorption using the same method are described.

The numbers of acid centres on solid surfaces and their character are often defined by adsorption of ammonia. The strength and the character of the centres may also be defined by means of additional investigations in the IR or by the adsorption of amines of various basicities [4, 5].

In this work we set out to determine the number of acid centres and the changes in their strength and character depending upon the temperature.

Experimental

A description of the apparatus and measurement techniques was published elsewhere [1].

The catalysts were also prepared in the previously-described manner [2]. These were X-type ammonium-sodium zeolites which, as a result of activation, changed into sodium-hydrogen forms. NaHX-9.1 means the degree of exchange of sodium by ammonium ions. In the case of the silica-alumina catalyst (Ketjen) treated with sodium hydroxide, the quantity of sodium was 0.025 mole Na^+/100 g of gel.

Results

The NH_3 adsorption investigations were performed with a temperature rise of about 6°/min and for the selected NaX zeolite isothermally.

The isothermal investigations were intended to determine the maximum adsorption (equilibrium) of ammonia on the catalysts and to compare this with the quantities adsorbed under non-isothermal conditions. These data were necessary to check whether the results obtained from thermogravimetry could be compared with the results of adsorption performed by static or chromatographic methods. The next problem was whether the chromatographic methods would be competitive with the described method. Fig. 1 shows the difference in the amount of ammonia adsorbed on NaX zeolite within the range 25–250°. Curve 1 connects points obtained from the adsorption investigations by thermogravimetry (with the given temperature gradient). The data obtained from the isothermal investigations (measured after 200 min) are shown in curve 2. From the curves it is evident that the differences are small, not exceeding 10% at the lowest temperatures, or 6% at the higher temperatures.

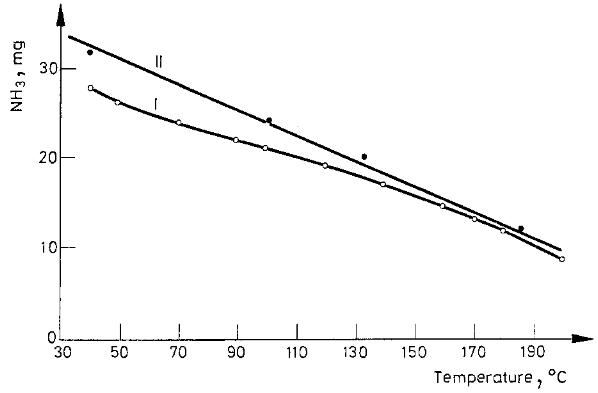

Fig. 1. Comparison of NH_3 desorption from isothermal measurements (curve 2) and with a temperature gradient of 6°/min (curve 1)

The investigations were carried out under a high adsorbate pressure, at about 600 torr.

All measurements were carried out in the presence of an inert gas (dry argon), in view of the fact that the investigations on the Derivatograph could be performed only under atmospheric pressure in a semiopen system. Figure 2 presents thermal curves of NH_3 adsorption on zeolite.

Ammonia adsorption starts at room temperature and achieves its maximum at temperatures of about 40 – 50°; multistage water and ammonia desorption then begins, which ends at about 600°. In the DTA curve an exothermic effect is initially observed (within the range of adsorption), corresponding to an adsorption heat of about 7 – 9 kcal/mole. The heat was determined by measurement at the peak of the exothermic effect. Calibration of the DTA curve was performed on the basis of the effects accompanying melting and phase changes of standard (benzoic acid, KNO_3, K_2SO_4).

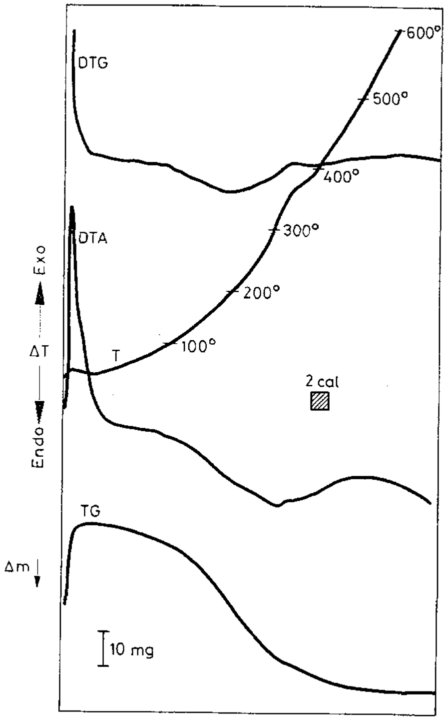

Fig. 2. TG, DTG and DTA curves of NH_3 adsorption–desorption (NaX) zeolite

The results of NH_3 (TG) adsorption, calculated as the number of ammonia molecules per unit cell of zeolite, are given in Figs 3 – 6.

In these plots, the curves of NH_3 desorption for NaX zeolite are compared with the respective curves for X-type ammonium zeolites at various degrees of exchange. The investigations of ammonia adsorption were carried out with the proton forms of these zeolites.

The zeolites being tested for adsorption contained certain quantities of water. The quantities of water and the course of dehydration were also determined by thermogravimetry. Afterwards the curves of ammonia desorption were obtained by subtraction of one curve from the other (desorption of $NH_3 + H_2O$ and desorption of H_2O), assuming that both adsorbates (H_2O and NH_3) desorb independently of each other. The basis for accepting such an assumption was the results of the measurements of NH_3 adsorption for NaX zeolite containing various quantities of water.

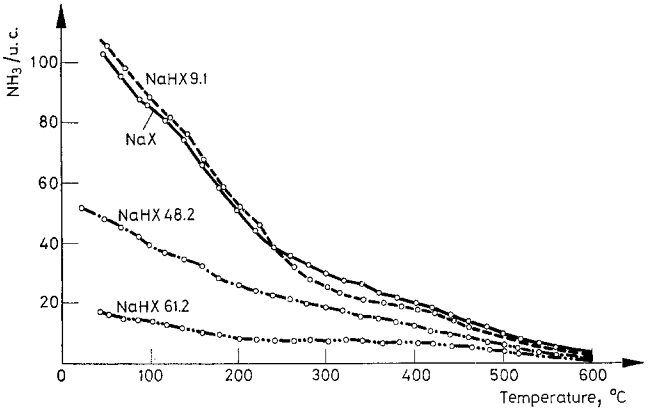

Fig. 3. NH_3 adsorption on X-type zeolites. Quantity of NH_3/u.c. as a function of temperature

The plots in Figs 4–6 present the course of NH_3 desorption from the surface of sodium and hydrogen forms of X-type zeolites as functions of temperature and the quantity of desorbed water. The ratios of the molar quantity of ammonia to the molar quantity of water on the catalyst surface is indicated by the index α. This shows how many molecules of ammonia there are on the zeolite surface at a given temperature per molecule of water.

$$\alpha = \frac{\frac{X}{17}}{\frac{Y}{18}}$$

where X = quantity of adsorbed NH_3 (mg), and
Y = quantity of water on zeolite surface (mg).

The axes give the numbers of adsorbate molecules (NH_3, H_2O) per unit cell of zeolite (which are comparable with the numbers of NH_3 moles for 1 g of catalyst).

The amount of adsorbed NH_3 in the unit cell (u.c.) can be calculated from the equation:

$$\frac{\text{Molecule } NH_3}{\text{u.c.}} = \frac{M_z Y}{Z M_a}$$

where X = amount of adsorbed NH_3 (mg);
M_z = molecular weight of zeolite;
M_a = molecular weight of adsorbate;
Z = weight of dehydrated catalyst sample.

From the plots presented it is seen that ammonia desorption from the zeolite (as a function of temperature) proceeds in two stages. The stages are shown by straight lines.

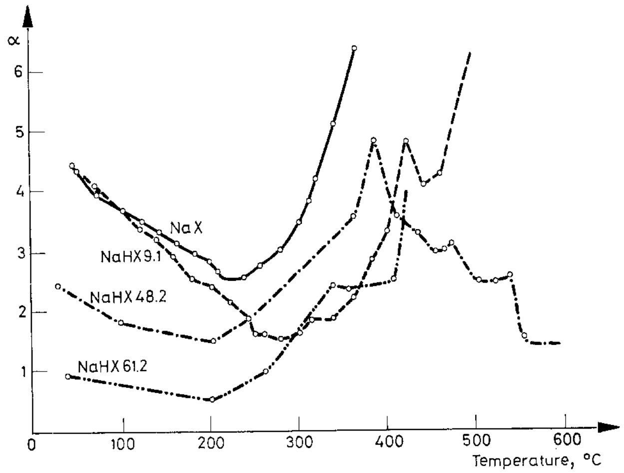

Fig. 4. NH_3 adsorption on X-type zeolites. Index α *vs.* temperature

The limit of these two stages is shown by the minimum in the curve of the dependence of the index α on temperature. These minima, specific for various zeolites, occur within the range 200–280°. In the first stage ammonia desorption proceeds at a higher rate, as shown by the slope of the straight line section. The second stage is slower. The curve $\alpha = f(T)$ decreases to a certain minimum with the increase of temperature, after which it rises rapidly (for NaHX-48.2 zeolite (Fig. 4) a subsequent fall of the curve to the value achieved at the minimum is observed within the range 400–600°). The courses are characteristic for the NaX, NaHX-9.1 and NaHX-48.2 zeolites. The quantities of ammonia adsorbed for 1 g of zeolites are comparable for the first two catalysts, but the NH_3 adsorption reaches only half of the value in the case of the NaHX-48.2 zeolite. However, in that zeolite about 40% of the crystal structure has been destroyed.

The NaHX-61.2 catalyst (with a specific surface of 11.6 m^2/g* and a destroyed structure of about 90%**) behaves differently. In the curve of ammonia desorp-

---

* The specific surface areas was found by the *B* point method.

** The degree of crystalline structure was found by X-ray diffraction [3].

tion for this sample there are local extrema not observed for other zeolites. The amount of adsorbed ammonia is about six times smaller than for NaX zeolite, when the specific surface area is ca. 80 times smaller. The curve $\alpha = f(T)$ shows almost no tendency to fall within the range 110–240°, so that the quantities of desorbing ammonia and water are constant. Above 240° the α value increases rapidly as with other zeolites.

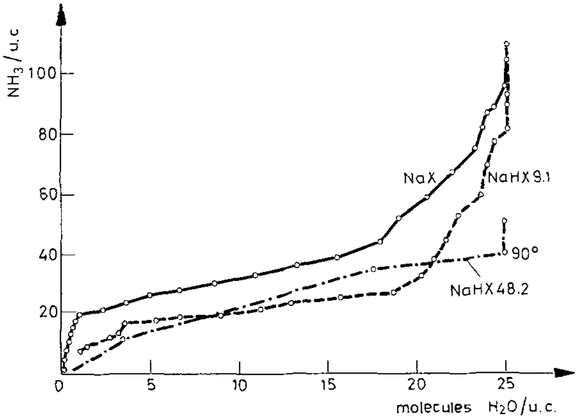

Fig. 5. NH_3 adsorption on X-type zeolites. Quantity of NH_3/u.c. as a function of the quantity of water

Plots of the dependence of ammonia desorption and of the index α on the quantity of outgoing water (Figs 5 and 6) indicate certain convergences. The curves of ammonia desorption within the range 40–70° are segments of a vertical line. Therefore, the ammonia desorption from the zeolite surface for that temperature range is not connected with water desorption. Within the range 90–220° for the NaX zeolite, three stages of water desorption are observed with a lack of ammonia desorption, and then two stages with a constant ratio of desorbing $NH_3 + H_2O$. For the NaHX-9.1 zeolite similar, but four straight segments are observed within the ranges 120–140°, 140–160°, 180–200° and 200–260°. From the NaHX-48.2 zeolite ammonia is desorbed at a constant rate within the range 90–200° (as a function of the increase of temperature at the rate of 6°/min).

For the above-mentioned catalysts within the range 200° (260° for NaHX-9.1)–500° ammonia desorption as a function of water loss was steady. Plots for the index α are analogous with the curves of desorption, but from 200–260° they show a tendency to rise. Such curves for NaHX-61.2 zeolite have different courses than in the case of sodium or proton-form zeolites (NaHX-9.1 and NaHX-48.2). The desorption exhibits a decreasing curve within the range 45–120°, but in all the remaining temperature ranges there is a certain kind of plateau. Similarly, in the initial range of temperatures, the curve for α is not a decreasing function.

Table 1

Adsorption of ammonia on zeolites and silica-alumina

Catalyst	Adsorption, mmole NH_3 / g. cat.	Adsorption, 10^{-2}mmole NH_3 / m^2 surf.	Adsorption, molecule NH_3 / 1 atom Na	Temperature of maximum adsorption, °C
Ketjen	0.70	0.105	—	120
Ketjen treated with sodium hydroxide	4.39	0.905	17.56	40
NaX	7.79	0.83	1.29	40
NaHX-9.1	8.24	0.88	1.49	40
NaHX-48.2	4.18	0.90	1.25	40
NaHX-61.2	1.43	12.32	0.54	40

For a comparison with amorphous catalysts, investigations were carried out on completely amorphous silica-alumina (Ketjen) without or with deposited sodium hydroxide in an amount of 0.025 mole on 100 g of gel. The pure Ketjen material proved to be a catalyst having a very low number of acid centres, with a maximum NH_3 adsorption at 120°, while with those silica-aluminas treated with sodium hydroxide a strong NH_3 adsorption was observed even from 40° (similarly to the zeolites). An exothermic effect accompanying the adsorption raised the system temperature up to 40°. The results obtained are shown in Table 1.

For silica-alumina containing 0.025 mole Na^+ per 100 g of gel the NH_3 adsorption calculated per 1 g of gel and per 1 m^2 of surface is similar to that of the NaHX-48.2 zeolite, the crystal structure of which was destroyed by about 40%.

The quantities of sodium calculated per 1 g of gel are about 40 times larger in the case of NaX. The NaX zeolite adsorbs more ammonia per unit mass than the amorphous gel treated with sodium.

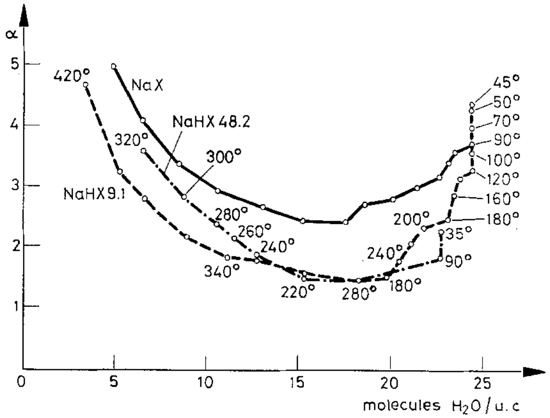

Fig. 6. NH_3 adsorption on X-type zeolites. Index α as a function of the quantity of water

Calculated per sodium atom, the ammonia adsorption is near that for NaHX-48.2, while the NaHX-9.1 zeolite shows much more acidity and affinity for ammonia.

Conclusions

The results of ammonia adsorption on zeolites of sodium and proton X type prove the occurrence of several kinds of ammonia bonds with the zeolite surface. The strengths of these bonds vary, as shown by the fact that the desorption appears stepwise over a wide range of temperatures and at various rates.

Every stage corresponds to a certain binding strength of NH_3-sodium cation, or NH_3-Broensted centre, by which a molecule of water can also be adsorbed. Curve-analysis indicates that there are about 20 strong acid sites and the same number of medium acid centres in one cell of NaX zeolite. For the NaHX-9.1 zeolite the number of each type of site is about 18. As the degree of change increases, the number of medium acid centres decreases, but the number of strong acid centres decreases only insignificantly. A certain number of strongly acid centres are maintained independently of the exchange of sodium and of partial loss of the crystal structure.

The number and types of acid centres in zeolites depend on the activation temperature.

From the above it appears that the amount of ammonia adsorbed does not depend on the quantity of adsorbed water (within the range 20 – 40 molecules of H_2O per unit cell), but is the amount adsorbed when the catalyst is cooled after preliminary activation and dehydration. The desorption curves for zeolites containing various amounts of water exhibit no differences.

In pure silica-alumina gel (Ketjen) there is a very small number of acid centres, which rises rapidly after the deposition of sodium ions on the surface. The numbers of acid centres for gels doped with sodium hydroxide and for zeolites are of the same range as regards specific surface area.

References

1. M. Malinowski, S. Krzyżanowski and P. Wierzchowski, Thermal Analysis, Proceedings of the IV. ICTA Budapest, 1974, Vol. 3, p. 233.
2. M. Malinowski, S. Malinowski, and S. Krzyżanowski, J. Thermal Anal., 10 (1976) 65.
3. P. Wierzchowski, S. Majchrzak and S. Krzyżanowski, Chemia Stosowana, 19 (1975) 347.
4. J. Datka, Bull. Acad. Sci., Ser. Chim., 22 (1974) 11.
5. A. Bielanski and J. Datka, J. Catal., 37 (1975) 383.

RÉSUMÉ — La thermogravimétrie et l'analyse thermique différentielle ont été appliquées simultanément à l'étude des phénomènes d'adsorption, de désorption et de réactions en surface sur des zéolites échangeuses d'ions de type NaX et X ainsi que sur des gels de silice-alumine "Ketjen" traités par l'hydroxide de sodium en présence d'ammoniaque. Les résultats quantitatifs permettent de proposer une interprétation des phénomènes de surface et d'établir l'existence de plusieurs centres actifs à la surface des catalyseurs. Dans le cas de l'adsorption de l'ammoniaque sur les gels de silice-alumine, la quantité d'ammoniaque adsorbée est beaucoup plus faible que sur les gels de silice-alumine traités par l'hydroxyde de sodium.

ZUSAMMENFASSUNG — Simultane TG und DTA wurden zur Untersuchung von Adsorptions-, Desorptions- und Oberflächenerscheinungen an Zeoliten der Ionenaustauschtypen NaX und X, sowie an mit Natriumhydroxid in Gegenwart von Ammoniak behandelten Silika-Aluminiumoxid-hydroxid-Gelen "Ketjen" eingesetzt. Aufgrund der quantitativen Ergebnisse ist es möglich eine Deutung der Oberflächenerscheinungen zu geben und die Existenz verschiedener aktiver Zentren an der Oberfläche der Katalysatoren festzustellen. Bei der Adsorption von Ammoniak an Silika-Aluminiumoxid-Gelen ist die Menge des adsorbierten Ammoniaks viel geringer als an Silika-Aluminiumoxid-Gelen, welche mit Natriumhydroxid behandelt wurden.

Резюме — Одновременно были использованы термогравиметрия и DTA для исследования явленций адсорбии, десорбции и реакций на поверхности на NaX и X типа ионно-обменных цеолитах и силико-алюмогелях типа "Кетьен", обработанных гидроокисью натрия в присутствии аммиака. На основании количественных результатов, представилось возможным интерпретировать поверхностные явления и установить наличие различных активных центров на поверхности катализаторов. В случае адсорбции аммиака на силико-алюмигелях, количество адсорбированного аммиака намного меньше, чем на алюмо-силикагеле обработанного гидроокисью натрия.