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

PART III. ADSORPTION OF WATER ON THE SURFACE OF ION-EXCHANGE ZEOLITES, SILICA AND ALUMINA GELS TREATED WITH SODIUM HYDROXIDE

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Simultaneous thermogravimetry and DTA were used to investigate the phenomena of adsorption, desorption and surface reactions of water vapour on NaX and NaY-type and NaX-exchanged zeolites, and silica and alumina gels treated with sodium hydroxide. On the basis of the quantitative results, it was possible to give an interpretation of the surface phenomena and to establish the existence of various active centres on the surface of the catalysts. Water in zeolites is probably bound by oxygen-alkali metal bonds.

In our previous work, we found that methods of thermal analysis can be very useful for investigation of surface reactions on solid catalysts. Only qualitative, or at most semiquantitative results are obtained with their help, but with little effort, shortening initial testing. Measurement techniques were discussed previously [1, 2].

In the work we are carrying out at present, we are performing a systematic testing of the adsorption of water, ammonia, carbon dioxide and hydrocarbons on solid catalysts in order to determine surface acidity, the character and distribution of the centres, as well as adsorptivity and catalytic activity in model reactions.

The results of water vapour adsorption on X-type zeolites with various cations, mainly ammonium are presented in this work. The purpose of the work was to determine the types of centres and their distribution on the zeolite surface during the replacement of sodium by other cations.

Experimental

Methods

The Hungarian-made Derivatograph thermobalance adapted for sorptive testing, was used [3]. An identical procedure was applied in all thermogravimetric adsorption measurements; a catalyst was dehydrated by heating it to a temperature of 550° and the system was then cooled (with a constant stream of inert gas) and finally heated again, introducing an adsorbate into the reaction space.

The initial dehydration was carried out with a temperature rise of 6°/min (in some cases 1°/min). Samples of 300 mg were taken for examination (range of weight indications 100 mg). The investigations were carried out in alundum crucibles and nepheline was applied as reference material.

Materials

NaX-type zeolites produced by "Inowrocławskie Zakłady Sodowe" were used.

Ammonium-sodium zeolites were obtained by means of ion-exchange in aqueous solutions.

Silica gel was obtained by moistening Aerosil (produced by the "Deguss" Company) with water, followed by drying and calcination.

The silica-alumina catalyst (produced by the "Ketjen" Company) was used in its initial form or treated with sodium ions by saturation with an aqueous solution of sodium hydroxide.

Results

Figure 1 shows typical thermal curves of water vapour adsorption on zeolite.

In the TG curve, an increase in mass is observed within the range 50–220°; this is the zone of adsorption. The exothermic effect of adsorption is very small. An inflection caused by water desorption from zeolite is observed within the range 220–350°. Desorption proceeds at a constant rate up to 400–450°, at which rapid water desorption associated with a distinct endothermic effect takes place. At higher temperatures, the desorption of the remaining water is also observed, unaccompanied by any heat effect.

The temperature at which water adsorption takes place to the accompaniment of an endothermic effect, depends upon the concentration of water vapour above the surface of the zeolite. The amount of water desorbed from the catalyst (denoted by W_d) and the heat effect connected with it (area of endothermic peak, denoted by S) also depend upon the water vapour concentration. These dependencies are presented in Figs 2–5.

Considering the difficulties of determining the concentration of water vapour in the "reaction space", quantities of water introduced during the periods of measurement are indicated on the ordinate.

Figure 2 represents the interdependence of the peak area of the endothermic effect and the temperature (DTG peak maximum) at which an acceleration of water desorption occurs. From the course of the curves it is evident that the larger the water vapour concentration in the "reaction space", the higher the temperature at which the described phenomenon appears. In the case of evaporation of 0.06 g water in the "reaction space" of the Derivatograph, so that the water is equivalent to that evolved during the zeolite dehydration process, the maximum endo-effect and the highest rate of desorption are at a temperature of about 260°. This temperature is near to that at which the maximum rate of mass decrease was noted in

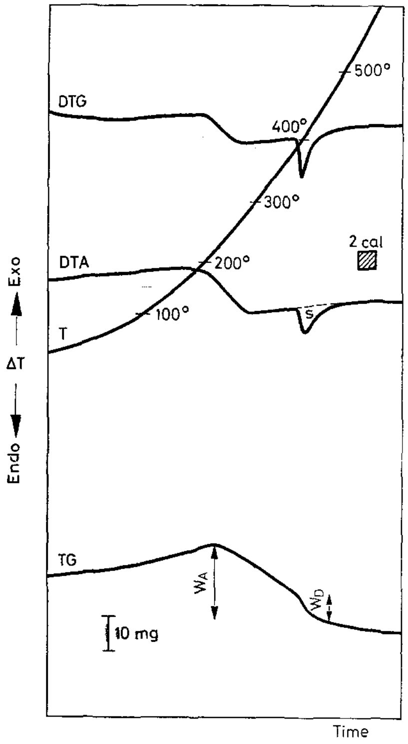


Fig. 1. TG, DTG and DTA curves of water adsorption and desorption (NaX zeolite)

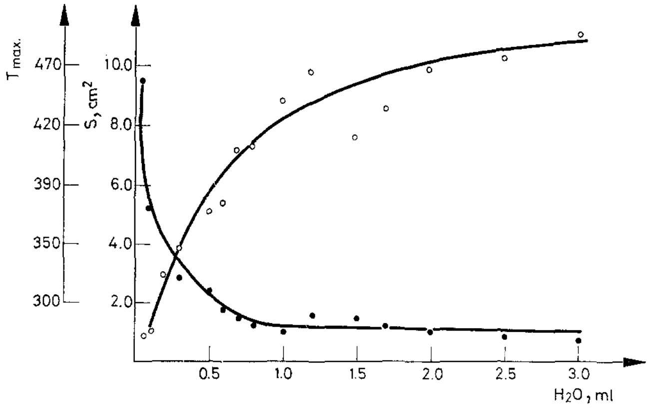


Fig. 2. Water adsorption. Dependence of the endothermic peak area and its maximum temperature on the water vapour concentration (NaX)

the zeolite dehydration process. In the case of dehydration of a maximum water quantity, the water vapour concentration goes up to a pressure of almost 760 mm Hg.

The area of the peak *S*, or the magnitude of the heat effect accompanying this exchange is almost nonvariant in a large range of concentrations, but it increases rapidly at lower water vapour concentrations.

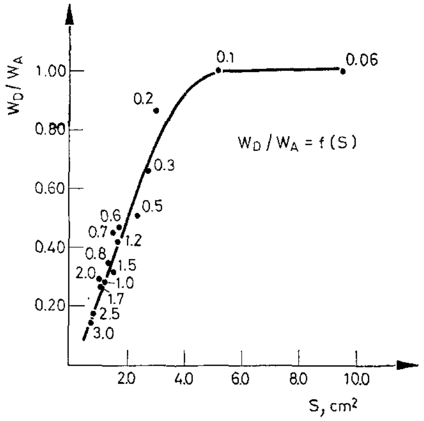


Fig. 3. Water adsorption. Dependence of W_d/W_a on the area of the endothermic peak (NaX)

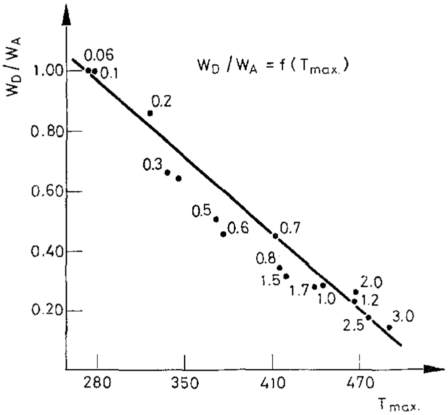


Fig. 4. Water adsorption. Dependence of W_d/W_a on its maximum temperature (NaX)

Figures 3 and 4 show the dependence of the ratio W_d/W_a, the ratio of the quantity of water desorbed in the period of accelerated desorption to the quantity of water adsorbed by the catalyst, on the magnitude of the heat effect accompanying the accelerated desorption and on the temperature at which it occurs.

The dependence on temperature is linear for various quantities of water vapour. The ratio W_d/W_a diminishes at higher temperatures and therefore at higher concentrations of water vapour. Large quantities of water vapour desorb from the catalyst. The area of the peak S goes up to 0.1 and 0.06 g of water with increase of the W_d/W_a ratio. In this range the magnitude of the peak is independent of W_d/W_a.

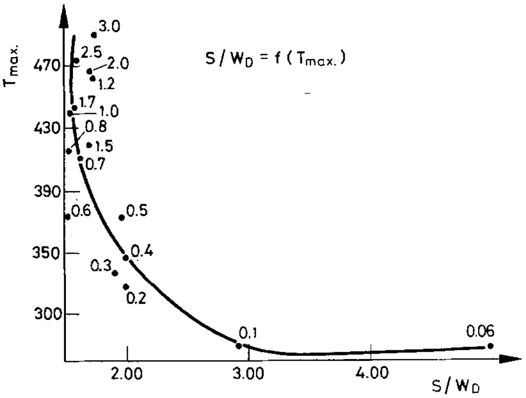


Fig. 5. Water adsorption. Dependence of S/W_d on the temperature of the endothermic effect (NaX)

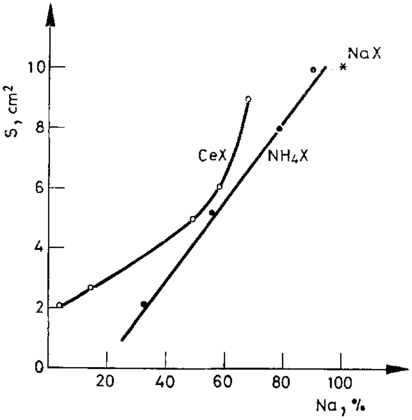


Fig. 6. Water adsorption. Area of the endothermic peak (S) as a function of Na cation-exchange

W_a changes imperceptibly with the concentration of water vapour, and as W_d rises, the heat effect accompanying desorption must also grow. The ratio S/W_d can be called a heat unit. Figure 5 show its dependence on temperature. It decreases with an increase of temperature and the concentration of water vapour. In the low concentration range, it increases with a drop in concentration, nearly independently of temperature.

Further investigations of water adsorption on zeolite catalysts were carried out on X-type zeolite, with exchanged cations. It was observed that the discussed phenomenon of accelerated water desorption is connected with the presence of sodium or calcium cations. Figures 6 and 7 show the magnitude of the heat effect accompanying acceleration and the quantities of water adsorbed on zeolite as a function of sodium cation-exchange for ammonium, cerium or cobalt. The effect is decreased with increase of the degree of exchange of sodium and calcium, while certain deviations are observed for the polyvalent cations. The effect is also connected with the zeolite surface, as it was observed that it did not occur in the case of water adsorption on pure silica gels and on those treated with sodium, but its magnitude is minimal for alumina and silica-alumina gels. Fixing limits here is quite difficult because, with the exchange of sodium ions for ammonium ions, a loss of the crystalline structure of the zeolite often occurs. In the case of silica gels the phenomenon did not occur, and in the case of alumina gels it was independent of sodium, so it might be connected with the zeolite structure. On the other hand, the deviation for polyvalent cations and the dependence of the magnitude of the effect on the quantity of sodium allow us to presume that it is connected with the presence of sodium cations in zeolite centres.

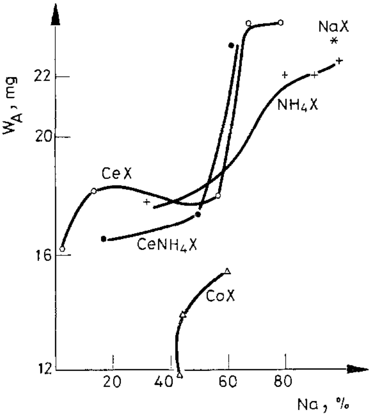


Fig. 7. Water adsorption. Quantity of water vapour adsorbed as a function of Na cation-exchange

The investigations of water adsorption at various rates of temperature rise showed that this is an effect appearing at a particular temperature (in the case of a temperature rise of 1°/min and 1 g of introduced water, the temperature is 250°), but the course of the curve of mass decrease (desorption) can be compared with the course of the curves of mass change registered in the case of substance boiling, beginning precisely at the particular temperature.

Figure 8 shows the results of water adsorption in isothermal investigations on NaX zeolite. The investigations were carried out to establish the TG curve for

0.1 g H_2O/min. The system attained an equilibrium state after about 20 minutes. A distinct break in the water adsorption curve at 225–250° corresponds to the temperature at which accelerated desorption was observed in the non-isothermal measurements (temperature rise 1°/min) and this was accompanied by the discussed endothermic effect. The quantities of water adsorbed within the range 150–250° are larger than in the case of non-isothermal investigations.

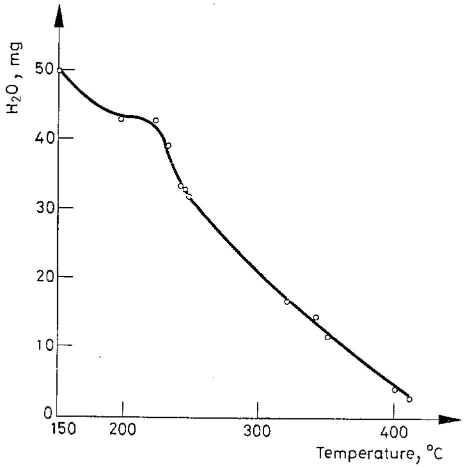
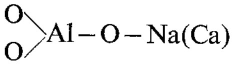
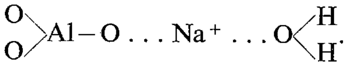


Fig. 8. Water vapour adsorption. Data from isothermal measurements (NaX)

It appears from this that, under conditions of a programmed temperature increase, the adsorbent system (in the case of the H_2O–NaX system) is far from the equilibrium state.

Conclusions

Water desorption from zeolites proceeds at various rates at various temperatures. The quantity of water adsorbed on the X-type zeolite depends upon the amount of sodium ions. Certain deviations caused by polyvalency were observed for calcium ions. The investigations of water adsorption on zeolites at various temperature gradients and various concentrations of water vapour, and similarly for silica, alumina and silica-alumina gels (sodium-treated and sodiumless), suggest that the effect is connected with the system  $\begin{smallmatrix}O\\O\end{smallmatrix}\!>\!Al-O-Na(Ca)$ and water coordinated with it. Water is probably strongly bonded in oxygen alkali metal bonds as it is in the system  $\begin{smallmatrix}O\\O\end{smallmatrix}\!>\!Al-O\ldots Na^{+}\ldots O\!<\!\begin{smallmatrix}H\\H\end{smallmatrix}$. The bond is broken at quite a high temperature, characteristic for the system, to the accompaniment of an endothermic effect.

The water molecules adsorbed at the different centres of the zeolite or gel desorb within a wide range of temperatures. The endothermic effect appears during water desorption from alumina and silica-alumina gel surfaces (though to a minimal degree), but does not occur in the case of silica gels.

In the case of NaY zeolite the effect is smaller in that the quantity of alumina and sodium atoms per unit cell is smaller than in NaX zeolite.

The deviations observed for CaX and CeX zeolites are caused by the polyvalent atoms interacting with water, thereby leading to a certain lowering of the polyvalency.

References

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2. S. Szczepańska, M. Malinowski and W. Kiewlicz, J. Thermal Anal., 9 (1976) 165.
3. M. Malinowski, S. Krzyżanowski and S. Szczepańska, J. Thermal Anal., 4 (1972) 281.

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 NaY et NaX ainsi que sur des gels de silice et d'alumine traités par la soude en présence d'eau. 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 les zéolites, l'eau est probablement liée par des liaisons oxygène-métal alcalin.

Zusammenfassung — Thermogravimetrie und DTA wurden simultan zur Untersuchung von Adsorptions-, Desorptions- und Oberflächenreaktionserscheinungen an Zeolit-Typen von NaX und NaY und NaX Ionenaustausch sowie an mit Natriumhydroxid in Gegenwart von Wasser behandelten Silika- und Aluminiumoxid-hydroxid-gelen eingesetzt. Aufgrund der quantitativen Ergebnisse war es möglich eine Deutung der Oberflächenerscheinungen zu geben und die Existenz verschiedener aktiver Zentren an der Oberfläche der Katalysatoren festzustellen. In Zeoliten ist Wasser wahrscheinlich durch Sauerstoff–Alkalimetallbindungen fixiert.

Резюме — Одновременно были использованы термогравиметрия и DTA для исследования явлений адсорбции, десорбции и реакций на поверхности на NaX, NaУ и NaX ионнообменного типа цеолитах, а также на силикагеле и алюмогеле, обработанных гидроокисью натрия в присутствии воды. На основании количественных результатов, стало возможным интерпретировать поверхностные явления и установить наличие различных активных центров на поверхности катализаторов. Возможно, что вода в цеолитах связана связями типа кислород–щелочной метал.