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 "Inowroclawskie Zaklady 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

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