

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

PART V. ADSORPTION OF CARBON DIOXIDE ON THE SURFACE OF ZEOLITES AND SILICA-ALUMINA GELS TREATED WITH SODIUM HYDROXIDE

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Thermogravimetry and simultaneous DTA were used to investigate the phenomena of adsorption, desorption and surface reactions on solid catalysts. The measurements were carried out with NaX and X-type ion-exchanged zeolites and silica-alumina gels (Ketjen) treated with sodium hydroxide in the presence of carbon dioxide. On the basis of the quantitative results it is possible to give an interpretation of the surface phenomena and to establish the existence of various active centres on the surfaces of the catalysts. In the case of the adsorption of carbon dioxide on X-type zeolites, the quantity of carbon dioxide adsorbed is much smaller on ion-exchanged zeolites than on NaX.

Investigations of carbon dioxide adsorption were carried out by simultaneous TG, DTG and DTA on NaX and NaHX-type zeolite catalysts with various degrees of exchange, and on amorphous silica-alumina doped with sodium hydroxide. The purpose was to examine the change in the strength and the number of electron donor sites (basic centres) on the surfaces of the catalysts as a result of a change in the amount of sodium cations.

The method of catalyst preparation and the methods applied have been described elsewhere [1–3]. The sample weight was 300 mg, material of the crucible alundum, partial pressure of CO₂ 600–700 torr. The activation of the catalysts in the crucible of derivatograph has been performed in flowing dry argon up to the temperature 550° with a heating rate 6°/min, then the catalyst has been cooled to room temperature also in flowing dry argon.

Measurements of carbon dioxide adsorption were performed with a simultaneous method of TG, DTG and DTA at a heating rate of 6°/min. The investigations were carried out in the range 25–600°.

Results

Figure 1 presents typical TG, DTG and DTA curves of CO₂ adsorption on zeolite NaX. The TG curve indicates an increase of mass, with the maximum at 60°, and subsequent desorption up to 200°. Within the range 200–260° there is a plateau, followed by further desorption up to 500°. The only exothermic

effect (DTA curve) is observable in the range of the TG peak. The results obtained are shown in Figs 2–5.

The amounts of CO_2 adsorbed were established (calculating the number of carbon dioxide molecules per unit cell of zeolite) at various temperatures. Index β

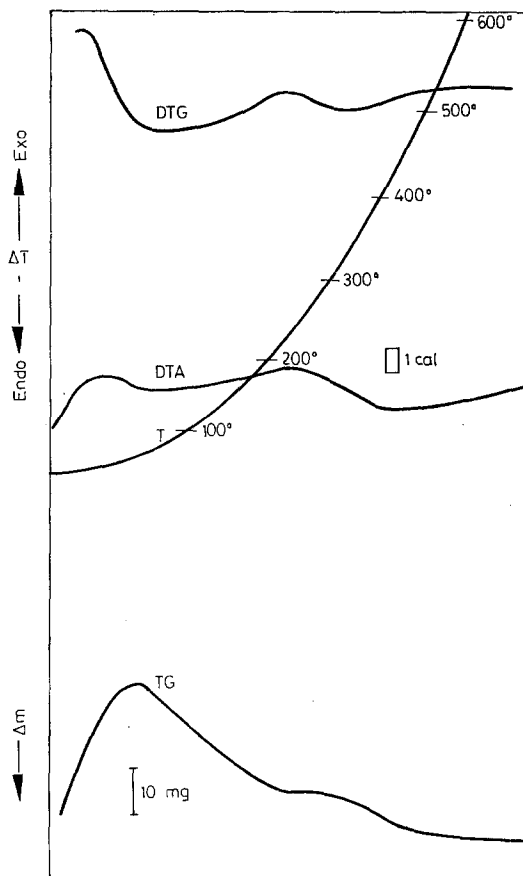


Fig. 1. TG, DTG and DTA curves of adsorption and desorption of CO_2 on zeolite NaX

is the ratio of the numbers of CO_2 and water molecules adsorbed on the zeolite surface (the dehydration course as a function of temperature being known):

$$\beta = \frac{\text{number of } \text{CO}_2 \text{ molecules adsorbed}}{\text{number of } \text{H}_2\text{O} \text{ molecules adsorbed}}$$

The calculation was performed analogously as in the case of ammonia [4]. Similarly as in the case of NH_3 adsorption, the zeolites contained water (about 20 molecules per u.c.).

Figures 2 and 3 present the dependences of CO_2 desorption and the value of index β on the temperature. It is seen clearly that the adsorption maxima occur at higher temperatures than in the case of ammonia, and for achievement of the steady state (under conditions of dynamic equilibrium) a longer time is needed.

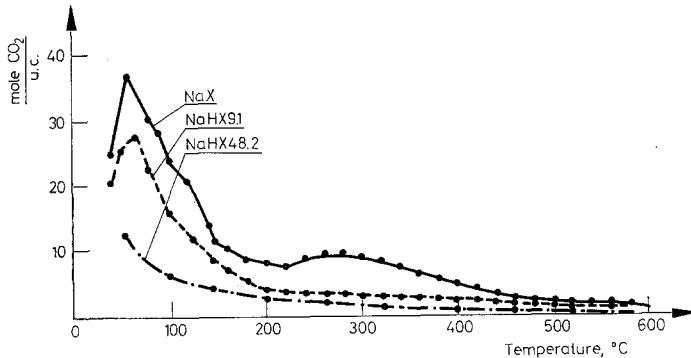


Fig. 2. CO_2 adsorption on X-type zeolites. Quantity of $\text{CO}_2/\text{u.c.}$ as a function of temperature

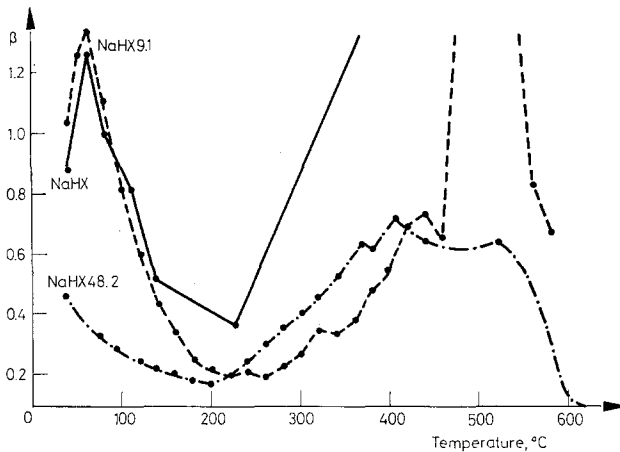


Fig. 3. CO_2 adsorption on X-type zeolites. Index β as a function of temperature

(In the case of ammonia adsorption, the adsorption maximum was obtained almost immediately after introducing the ammonia.) For zeolite NaHX-61.2 it was not possible to determine any dependences. The CO_2 adsorption on this catalyst was so minimal that conclusions as to any regularities might well be erroneous. During the CO_2 adsorption the high-exchanged zeolite NaHX-48.2 behaved slightly differently from NaX and NaHX-9.1. The maximum of the sorption was obtained more quickly than for the other zeolites. (In the investigations

with ammonia, the zeolite showed a much lower acidity than those of the sodium zeolite and a low-exchanged one.)

In both the curve of CO_2 desorption and the curve of the dependence of β upon temperature, the first stage is characterized by a very large negative slope; subsequently ($200\text{--}300^\circ$), the desorption curve is parallel to the temperature axis

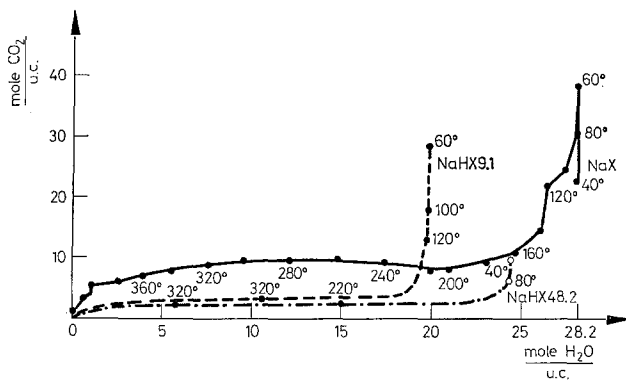


Fig. 4. CO_2 adsorption on X-type zeolites. Quantity of $\text{CO}_2/\text{u.c.}$ as a function of the quantity of water

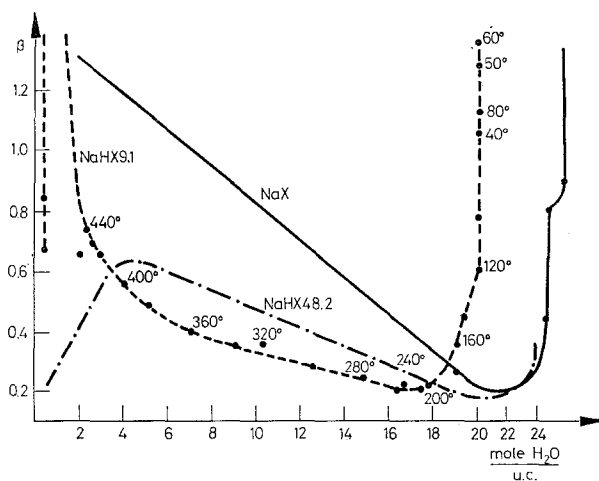


Fig. 5. CO_2 adsorption on X-type zeolites. Index β as a function of the quantity of water

(for zeolite NaX a very weak maximum occurs at 260°). The final part of the desorption curve is a straight line. In the first stage the curve of the dependence of β on the temperature behaves similarly to the desorption curve; it then increases rapidly beginning from 220° for NaX, 260° for NaHX-9.1 and 200° for NaHX-48.2.

For both the proton zeolites within the range 500–600° one observes a repeated decrease in β . Comparison of the CO₂ adsorption on the zeolite NaX containing various quantities of water reveals the dependence of the number of CO₂ molecules adsorbed on the number of water molecules adsorbed on the zeolite. As the quantity of water increases, the CO₂ adsorption decreases.

Figures 4 and 5 present curves of CO₂ desorption and the dependence of β on the water content. For the three zeolites (for zeolites NaHX-61.2 the minimal quantities of adsorbed CO₂ made it impossible to perform calculations) the first stage is CO₂ desorption from the catalyst surface, not associated with the loss of water. The curves of desorption and of the index β are linear up to 80° for NaX, up to 120° for NaHX-9.1 and up to 80° for NaHX-48.2. The second stage is further rapid CO₂ desorption (up to 160–180°). Within the range from 160–180° up to 360–420° the quantity of adsorbed carbon dioxide remains at the same level, but it afterwards quickly drops to zero. The curve of the dependence of β on the quantity of water in the zeolite exhibits a minimum at 180° for NaX and NaHX-48.2, and at 260° for NaHX-9.1. The values of β next rise rapidly, but for the proton zeolite they again diminish within the range 500–600°.

For comparison with amorphous catalysts, investigations of CO₂ adsorption were carried out on amorphous silica-alumina (Ketjen) and that containing 0.025 mole Na/100 g gel. For both a very weak adsorption of carbon dioxide was observed. The gel doped with sodium hydroxide exhibited a CO₂ adsorption 5 times greater than that of the pure gel.

Table 1
Carbon dioxide adsorption

Catalyst	Maximum temperature of adsorption, °C	CO ₂ adsorbed, mmole/g of catalyst	CO ₂ adsorbed, mmole/m ² of surface	CO ₂ adsorbed, molecule CO ₂ /atom of Na
Ketjen	45	0.09	0.013×10^{-2}	—
Ketjen treated with Na ⁺	45	0.34	0.070×10^{-2}	0.03
NaX	60	2.79	0.298×10^{-2}	0.46
NaHX-9.1	60	2.05	0.219×10^{-2}	0.37
NaHX-48.2	40	0.94	0.202×10^{-2}	0.28
NaHX-61.2	40	0.48	4.13×10^{-2}	0.19

An adsorption maximum was observed for both catalysts at 40°, i.e. lower than in the case of the zeolites. The occurrence of CO₂ adsorption and desorption on amorphous silica-aluminas is not accompanied by any distinct heat effect in the DTA curve. The obtained results in comparison with analogous ones for zeolites, are shown in Table 1.

The quantities of CO₂ for 1 g or 1 m² of silica alumina surface are one order of magnitude smaller than in the case of the zeolites.

For zeolites NaX, NaHX-9.1 and NaHX-48.2 the quantities of adsorbate per unit of surface are similar, but the number of CO₂ molecules per atom of sodium diminishes with the degree of exchange of sodium ions for proton.

Discussion

CO₂ adsorption on zeolites and amorphous silica-aluminas is small. Carbon dioxide is a gas with Lewis acid properties; it has an electron deficiency on the carbon, while there are free electron pairs on the oxygen; under suitable conditions these can coordinate with strong Lewis acid centres. According to Wolkenstein's three models of adsorbed CO₂ molecules, the most favoured is the bonding between carbon and basic surface centres. It is also possible to form carbonates in the presence of sodium.

The CO₂ adsorption diminishes as the sodium ions are exchanged for protons. It is possible that this exchange decreases the acidity of the oxygen, and hence the CO₂ adsorption on lattice oxygen. The CO₂-zeolite bonds are considerably weaker than the H₂O-zeolite bonds: as the temperature rises, CO₂ is desorbed nearly completely first, and water only afterwards.

Comparison of the CO₂ adsorption on silica-alumina gel with that on those containing deposited sodium ions shows that the presence of sodium ions in a gel causes an increase in CO₂ adsorption; this may be caused by the higher basicity of the lattice oxygen due to Na-O-Si and Na-O-Al bonding types, and by the formation carbonates. The rapid CO₂ adsorption at low temperatures suggests the former possibility rather.

References

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RÉSUMÉ — Application de la TG et de l'ATD simultanées à l'étude des phénomènes d'adsorption, de désorption et de réactions de surface sur des catalyseurs solides. Les mesures ont été effectuées avec des zéolites échangeuses d'ions de type NaX et X ainsi qu'avec des gels "Ketjen" silice-alumine traités par NaOH en présence de CO₂. Les résultats quantitatifs permettent de donner une interprétation des phénomènes de surface et d'établir l'existence de divers centres actifs à la surface des catalyseurs. Dans le cas de l'adsorption de CO₂ sur les zéolites de type X, la quantité de CO₂ adsorbé est beaucoup plus faible que sur les zéolites de type NaX.

ZUSAMMENFASSUNG — Thermogravimetrie und simultane DTA wurden zur Untersuchung der Adsorptions-, Desorptions-Erscheinungen und Oberflächenreaktionen an festen Katalysatoren eingesetzt. Die Messungen wurden an NaX und Zeolithen des Typs X sowie an Silika-Aluminiumoxidgelen "Ketjen" durchgeführt, welche mit Natriumhydroxid in Gegenwart von Kohlendioxid behandelt worden waren. Aufgrund der quantitativen Ergebnisse ist es möglich eine Deutung der Oberflächenerscheinungen zu geben und die Existenz verschiedener aktiver Zentren an der Katalysatorenoberfläche nachzuweisen. Im Falle der Adsorption von Kohlendioxid an Zeolithen des Typs X ist die Menge des adsorbierten Kohlendioxids am Ionenaustauscher viel niedriger als am NaX.

Резюме — Одновременно были использованы термогравиметрия и ДТА для исследования явления адсорбции, десорбции и поверхностных реакций на твердых катализаторах. Измерения были проведены с ионно-обменными цеолитами типа NaX и X и силико-алюминиевыми гелями марки «Кетъен», предварительно обработанные едким натром в присутствии двуокси углерода. На основании количественных результатов представилось возможным дать интерпретацию поверхностных явлений и установить наличие различных активных центров на поверхности катализаторов. В случае адсорбции углекислого газа на цеолитах типа X, количество его на этих ионно-обменных цеолитах немного меньше, чем на цеолитах типа NaX.