Journal of Thermal Analysis, Vol. 10 (1976) 339–356

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

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

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(Received January 20, 1976)

Thermogravimetry, together with DTA, was used to investigate sorption phenomena and surface reactions on solid catalysts. The measurements were carried out with NaX and X-type cation-exchanged zeolites and silica-alumina (Ketjen) treated with sodium hydroxide, in the presence of such hydrocarbons as isobutane, isobutene, heptane, cyclohexane, benzene, toluene, ethylbenzene, cumene, *n*-propylbenzene, *tert*-butylbenzene, biphenyl and naphthalene. On the basis of the quantitative results, it is possible to give an interpretation of the surface phenomena and to prove the existence of various active centres on the surfaces of the catalysts.

Experimental

The adsorption of hydrocarbons was investigated by thermogravimetry on zeolite catalysts and, for comparison, on silica, alumina and silica-alumina gels. A precise description of the method has been given in previous works [1, 2]. The adsorption investigation was carried out either at a constant heating rate or isothermally in order to obtain the equilibrium state at an adsorbate pressure near to one atmosphere. The catalyst was activated in an atmosphere of argon before adsorption. The adsorbate was introduced into the "reaction space" in one batch (a constant amount), or in doses throughout the duration of the measurements. The sample weight was 300 mg, material of the crucible alundum, activation like in Part V. Dosing of the gaseous adsorbate by capillary system to the partial pressure 600–700 torr. In the case of liquid adsorbates 1 ml of liquid substance in the crucible has been introduced at the beginning of the experiment to the "reaction space". The solid adsorbates like diphenyl, naphthalene also in crucible were introduced to the "reaction space" at the beginning of the experiment in the amounts equal to the molar amount of cumene in 1 ml of this substance.

The investigations for one system were repeated many times in order to minimize the errors and to provide a basis for determination of the experimental discrepancies.

Analyses were performed in alundum crucibles by non-isothermal measurements at a heating rate of 6°/min. The mass of the catalyst sample was 300 mg, and the quantity of substance introduced in one batch into the "reaction space" was 1 ml.

Table 1
Adsorption of hydrocarbons on zeolites

Catalyst	Temperature of adsorption maximum, °C	Quantity of remaining H_2O/u.c.	Adsorbate	*A**	*B**	*C**
1	2	3	4	5	6	7
NaX	155	33.2	benzene	25.4	1.92	0.32
	165	14.9	toluene	25.02	1.88	0.31
	185			27.3	2.05	0.34
	220	28.2	*tert*-butylbenzene	7.8	0.59	0.10
	320			10.6	0.80	0.13
	200	31.5	*n*-propylbenzene	6.9	0.52	0.09
	320			11.1	0.84	0.14
	175	36.5	ethylbenzene	14.1	1.06	0.18
	255			18.0	1.36	0.22
	205	25.9	cumene	11.0	0.82	0.14
	300			17.2	1.29	0.21
	275	21.5	biphenyl	1.58	0.12	0.02
	415			1.94	0.15	0.024
	235	31.5	naphthalene	2.8	0.21	0.03
	370			5.1	0.59	0.06
NaHX-9.1	210	17.9	cumene	8.8	0.67	0.12
	310			12.9	0.99	0.18
	125	32.5	benzene	22.5	1.72	0.31
	150	23.4	toluene	19.3	1.47	0.26
	190			22.9	1.75	0.31
	205	13.7	*n*-propylbenzene	7.6	0.58	0.10
	315			11.6	0.88	0.16
	190	19.5	ethylbenzene	11.0	0.84	0.15
	370			16.4	1.25	0.22
	210	26.0	*tert*-butylbenzene	5.2	0.40	0.07
	320			7.5	0.57	0.10
	285	32.5	biphenyl	0.76	0.06	0.01
	420			0.38	0.03	0.005
NaHX-48.2	220	30.7	cumene	5.75	0.46	0.14
	375			6.9	0.55	0.17
	120	24.5	benzene	12.9	1.03	0.31
	150	35.3	toluene	12.9	1.04	0.31
	190	16.3	ethylbenzene	7.6	0.62	0.18
	400			8.6	0.69	0.21
	230	30.7	*n*-propylbenzene	4.6	0.37	0.11
	355			5.1	0.41	0.12
	230	27.2	*tert*-butylbenzene	3.9	0.21	0.06
	380			4.7	0.31	0.09
NaHX-61.2	208	51.2	cumene	3.4	0.28	0.11
	390			2.7	0.23	0.09

* *A:* number of adsorbate molecules per unit cell
B: adsorption in mmole/g zeolite
C: quantity of adsorbate per sodium ion.

Results

For zeolites NaX, NaHX-9.1 and NaHX-48.2, measurements were performed on the adsorption of benzene, cumene, toluene, ethylbenzene, *n*-propylbenzene, *tert*-butylbenzene and biphenyl; for zeolite NaHX-61.2 the adsorption of cumene; and for the alumina, silica and silica-alumina gels the adsorption of toluene and

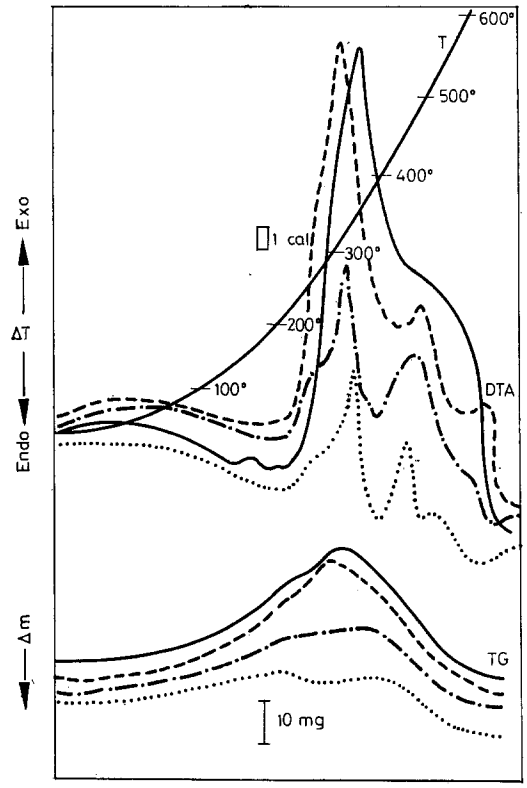

Fig. 1. Cumene adsorption on X-type zeolites; NaX: —, NaHX-9.1 — — —, NaHX-48.2: — · —, NaHX-61.2: · · ·

cumene. For zeolite NaX, the adsorption of naphthalene, isobutane, isobutene, cyclohexane and *n*-heptane and the desorption of previously-deposited triphenylmethane and triphenylchloromethane were also investigated. The results of the adsorption of aromatic hydrocarbons on the sodium and proton X-type zeolites are shown in Table 1.

Comparison of the results obtained revealed that the number of molecules adsorbed per g zeolite decreased with the increase of the exchange of sodium for ammonium cation. Simultaneously, the numbers of molecules adsorbed per sodium cation were similar for the zeolite catalysts investigated. In most cases

the temperatures of the adsorption maxima are also quite close. The two adsorption values are given in the Table for many adsorbates to show the different types of adsorption. The first is always in the range 170–220°, and the other at higher temperatures. Sometimes there are not distinct maxima, but only changes in the curve slopes. The biggest differences in the adsorptions on zeolites NaX and NaHX-9.1 were observed for biphenyl. The data concerning the adsorption of

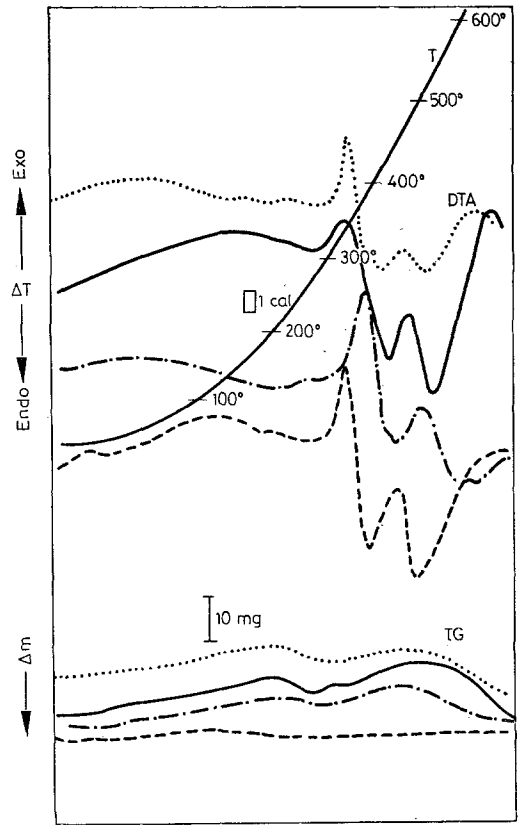

Fig. 2. Cumene adsorption on gels; Ketjen: —, γ-Al_2O_3: — · —, SiO_2: — — —, Ketjen, doped with NaOH: · · ·

hydrocarbons on zeolites obtained by thermogravimetry are of the same order of the magnitude as the results obtained by other investigators using other method of adsorption.

Figure 1 shows the TG and DTA curves of cumene adsorption on zeolites NaX, NaHX-9.1, NaHX-48.2 and NaHX-61.2. For all of these catalysts, the adsorption is observed as beginning at about 50° on the TG curve, the maxima of which are at 300, 310, 375 and 390°, respectively. At higher temperatures, desorption occurs at a constant rate and ends at about 600°. The quantities of cumene adsorbed

are considerably smaller for the zeolites NaHX-48.2 and NaHX-61.2. For all the zeolites within the range from room temperature up to 200°, very small heat effects are observed (DTA curves). From about 200° a strong exothermic effect begins, the magnitude of which is comparable to those for sodium and low-exchanged zeolites (NaHX-9.1). In the case of zeolites NaHX-48.2 and NaHX-61.2, this effect is considerably smaller. Its maximum is at 320–350°. It is accompanied

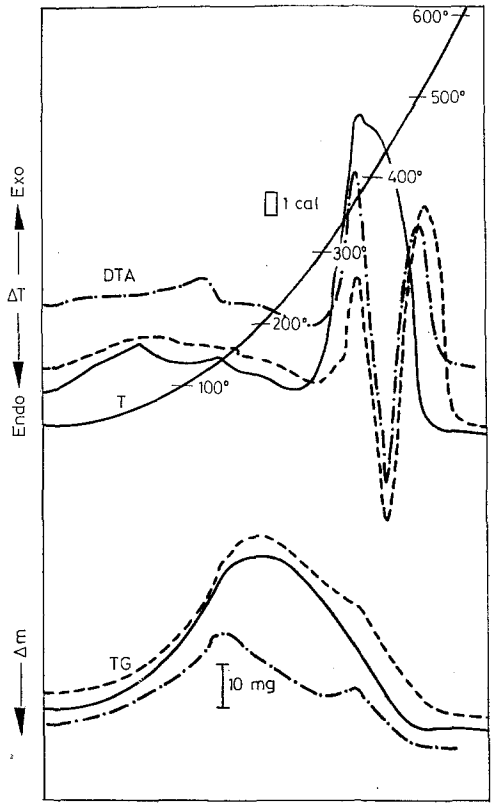

Fig. 3. Toluene adsorption on X-type zeolites; NaX: —, NaHX-9.1: — — —, NaHX-48.2: — · —

by another smaller, exothermic effect, the maximum of which is at about 480°. The magnitude of the effect is in principle independent of the type of the zeolite. In the range of both observed heat effects, vapour samples were taken for chromatographic analysis from over the crucible containing the adsorbate. The presence of benzene and small quantities of toluene was observed. This suggests that the observed effects are connected with catalytic surface reactions. The protonated zeolites are much more active than NaX.

Figure 2 shows analogous TG and DTA curves of cumene adsorption on γ-Al_2O_3 and SiO_2 gels, silica-alumina (Ketjen) and this treated with sodium hydroxide. For all gels (but silica) two distinct adsorption maxima are observed, at about 200° and about 450–480°. The quantities of cumene adsorbed are considerably smaller than in the case of zeolite catalysts. The exothermic effect observed for zeolites with maximum at 350° is very small when amorphous gels are the

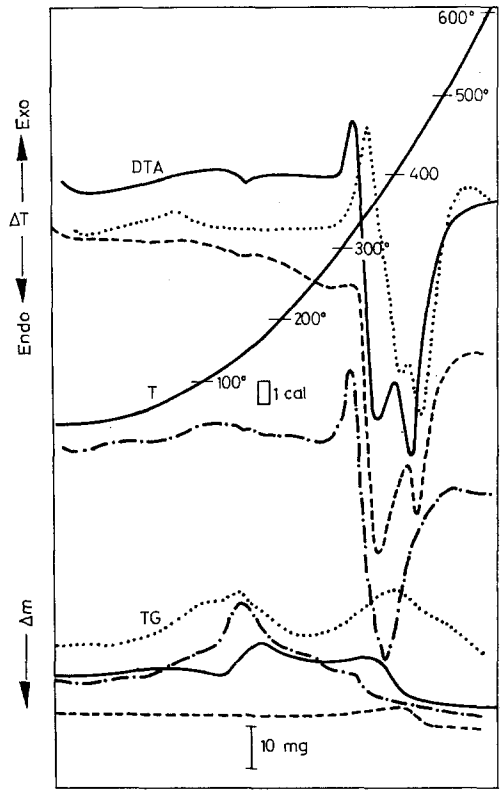

Fig. 4. Toluene adsorption on gels Ketjen; · · ·, SiO_2: —, γ-Al_2O_3: — · —, α-Al_2O_3: — — —

adsorbate, while two endothermic effects appear with maxima at 380° and about 480°. The effects are minimal for γ-Al_2O_3 and Ketjen silica-alumina treated with sodium hydroxide, but quite distinct for the Ketjen and silica gel. For gels no distinct peaks are observed in the DTA curve within the range 20–200°, indicating lack of any surface process.

The results of cumene adsorption are shown in Table 2.

From comparison of the obtained results with the results of adsorption on zeolites, it is found that the quantities of cumene adsorbed are an order of magni-

Table 2

Adsorption of cumene on amorphous catalysts

Catalyst	Temperature of adsorption maximum, °C	Adsorption, mmole/g gel $\times 10^{-2}$	Adsorption, mmole/m² $\times 10^{-4}$
γ-Al_2O_3	190	15.7	5.23
	440	20.4	6.80
SiO_2	120	5.6	3.43
	180	4.2	2.70
Ketjen	190	20.2	3.03
	470	24.5	3.68
Ketjen treated with NaOH	205	18.3	3.77
	440	14.1	2.90

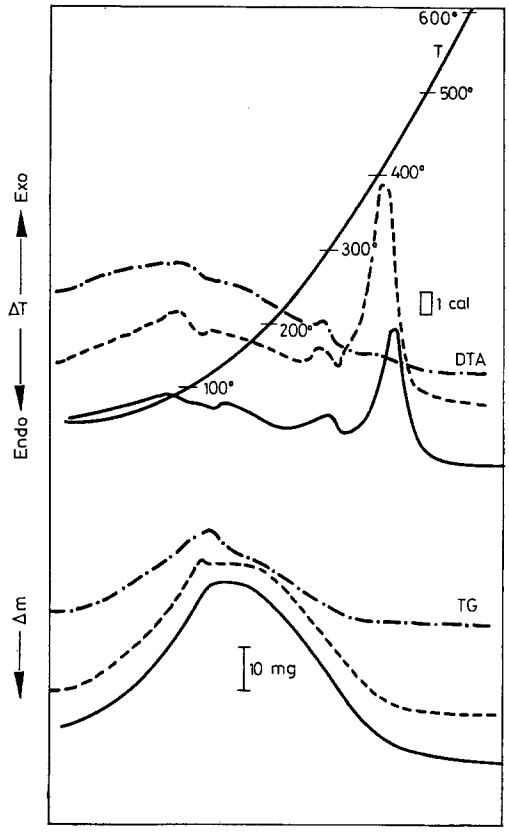

Fig. 5. Benzene adsorption on zeolites; NaX: —, NaHX-9.1: — — —, NaHX-48.2: — · —

tude smaller. Similar results are obtained regarding the quantity of adsorbate per unit of catalyst surface area.

TG and DTA curves of toluene adsorption on zeolites NaX-9.1 and NaHX-48.2 are presented in Fig. 3. The TG curves for sodium and low-exchanged zeolites are similar, but for NaHX-48.2 a local minimum is observed at 410°. Less toluene is adsorbed on this catalyst than on either of the others.

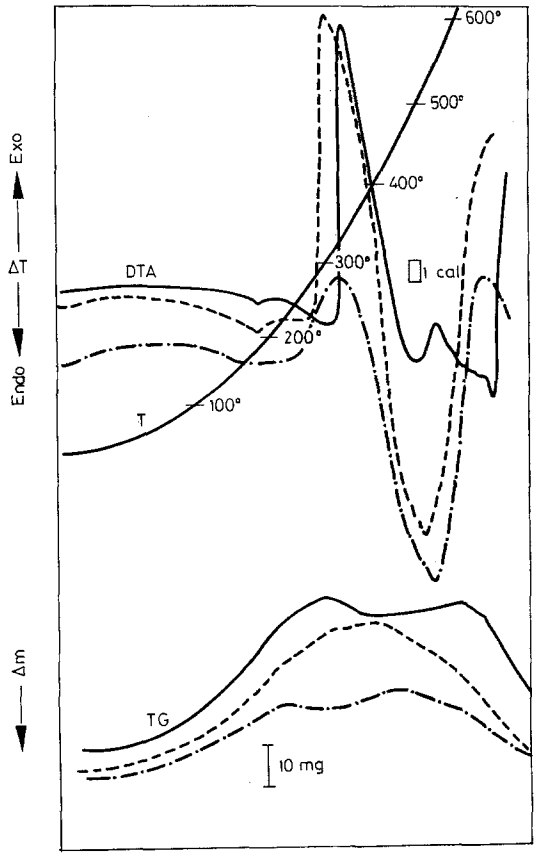

Fig. 6. Ethylbenzene adsorption on zeolites; NaX: —, NaHX-9.1: — — —, NaHX-48.2: — · —

DTA curves within the range 20–300° indicate minimal exothermic effects accompanying adsorption. Above 300° for zeolite NaX, a large exothermic effect is observed, with maximum at 400°. On the other hand, the exothermic effect (also with maximum at 400°) is much smaller for both proton zeolites and becomes an endothermic effect with maximum at 450°. The endothermic effect in the case of proton zeolites changes again to an exothermic one, the maximum of which is

at 530°, for the exchanged zeolites. For NaHX-9.1 it is considerably greater than for NaHX-48.2.

For comparison the adsorption on amorphous catalysts was investigated on α-Al_2O_3, γ-Al_2O_3, SiO_2 and Ketjen silica-alumina. The thermal curves are shown in Fig. 4.

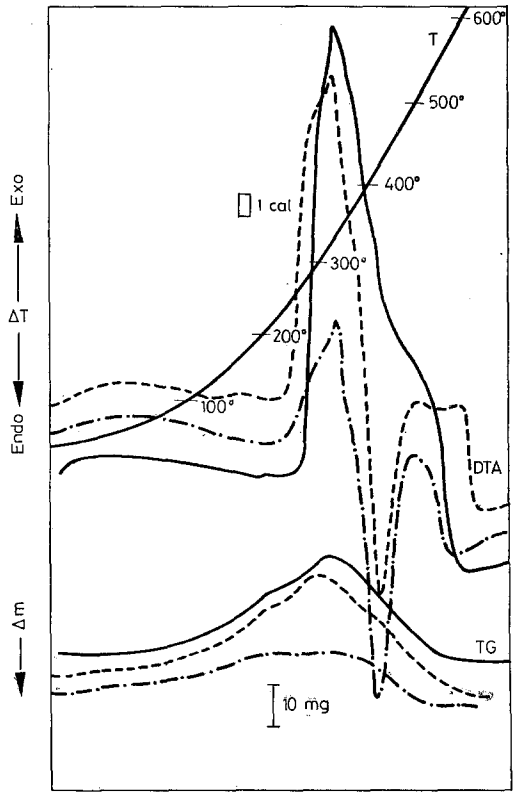

Fig. 7. *n*-Propylbenzene adsorption on zeolites; NaX: —, NaHX-9.1: — — —, NaHX-48.2: — · —

For silica and silica-alumina gels two maxima are observed in the TG curve. On γ-Al_2O_3 there is one toluene adsorption maximum, as on α-Al_2O_3, and the adsorbed quantities are small. In the DTA curves of the catalysts a low plateau is observed in the range 20–300° (similarly as for zeolites), this changing into a small exothermic effect with maximum at 340°. Such an effect was not observed for α-alumina. For all the amorphous catalysts a large endothermic effect occurs, with maximum at 420–480°. The results of toluene adsorption on the above amorphous gels are presented in Table 3.

Table 3

Toluene adsorption on amorphous catalysts

Catalyst	Temperature of adsorption maximum, °C	Adsorption, mmole/g catalyst	Adsorption mmole/m² surface
α-Al_2O_3	440	0.147	0.024
γ-Al_2O_3	160	0.702	0.0023
SiO_2	190	0.378	0.0023
	360	0.334	0.0020
Ketjen	140	0.468	0.00070
	420	0.496	0.00074

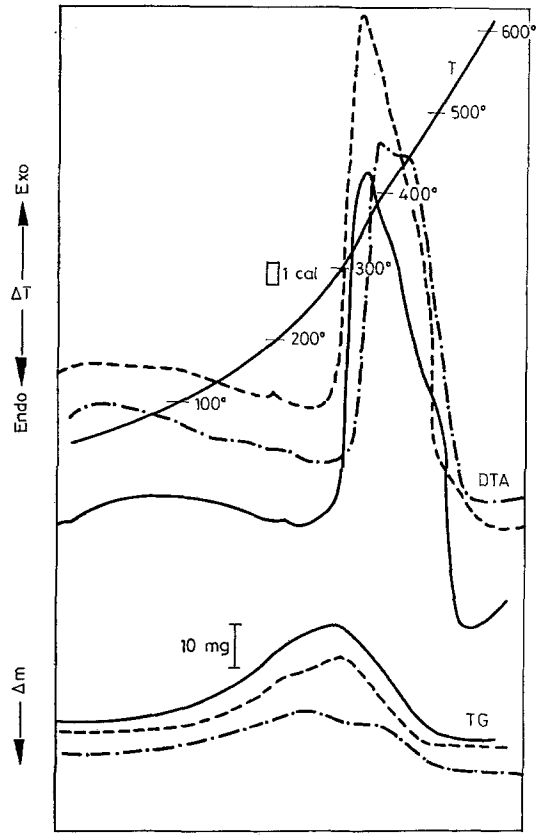

Fig. 8. *tert*-Butylbenzene adsorption on zeolites; NaX: —, NaHX–9.1: — — —, NaHX–48.2: — · —

The lowest surface coating was obtained for pure silica-alumina gel. The quantities of adsorbate per surface unit are very close for silica gel and γ-alumina, while for α-Al_2O_3 it is larger by an order of magnitude. In the case of silica gel, the quantities of toluene adsorbed are almost the same at 190° and 360°.

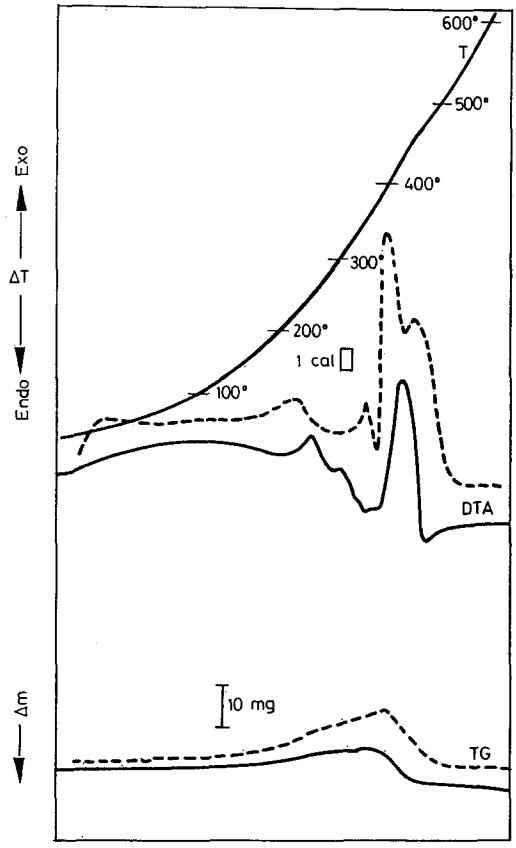

Fig. 9. Adsorption of naphthalene (— — —) and biphenyl (———) on zeolite NaX

The adsorption curves of various hydrocarbons on zeolite catalysts will be discussed in a further part of this work.

Figure 5 represents TG and DTA curves of benzene adsorption on sodium and proton X-type zeolites. An adsorption with maximum at about 120° is observed in TG curve, followed by desorption at an almost steady rate. An exothermic effect with maximum at 430° is observed in the DTA curve for sodium and low-exchanged zeolite. The effect is not observed for the zeolite NaHX-48.2. The crystal structure of the zeolite was destroyed by about 40%. The curves of ethyl-

benzene adsorption on zeolites are shown in Fig. 6. A strong exothermic effect is observed for the zeolite NaX. This effect is also observed in the case of proton zeolites (for NaHX-48.2 it is considerably smaller), but for these zeolites there is a strong endothermic effect too, with maximum at 500°.

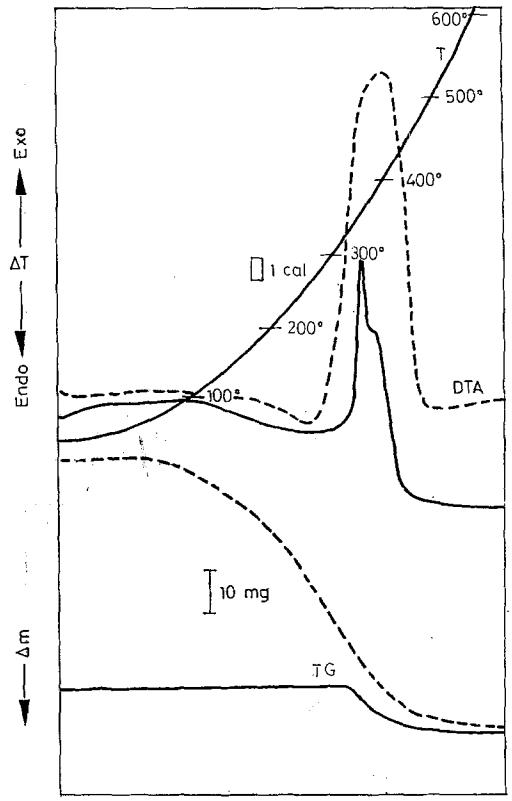

Fig. 10. Desorption of triphenylmethane (———) and triphenylchloromethane (— — —) from zeolite NaX

In the case of adsorption of *n*-propylbenzene on sodium and low-exchanged zeolites, the TG and DTA curves have very similar courses.

On the zeolite NaHX-48.2 (Fig. 7) considerably smaller quantities of hydrocarbon are adsorbed and the exothermic effect is much smaller too. In addition, the endo-effect appears with maximum at 420°, as was also observed for zeolite NaHX-9.1.

The thermal curves of *tert*-butylbenzene (Fig. 8) adsorption on zeolites NaX and NaHX-9.1 are very similar. GLC analysis of samples of desorbate indicates the presence of benzene in the range of temperature in which the exothermic effect occurs.

The exothermic effect was also observed in the case of the desorption of biphenyl or naphthalene from zeolite NaX (Fig. 9), and on the desorption previously adsorbed triphenylmethane, triphenylchloromethane (Fig. 10) and cumene (Fig. 11) but it did not occur during hexane adsorption.

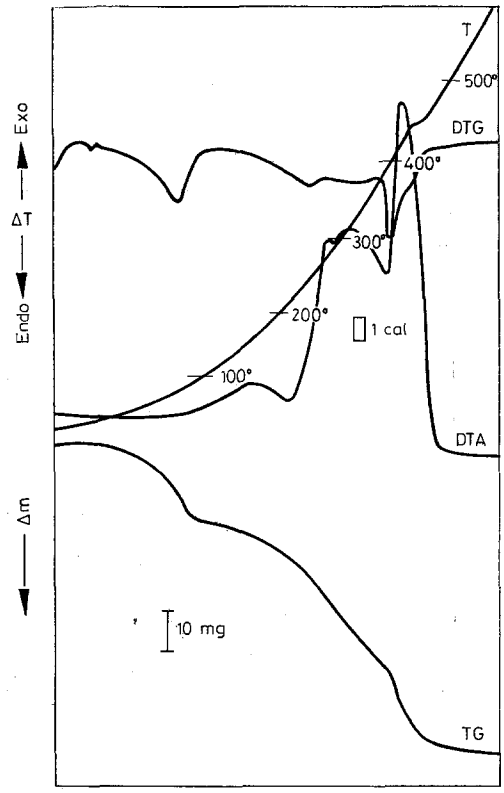

Fig. 11. Desorption of cumene from zeolite NaX

Nor did the exothermic effect occur during the adsorption of a mixture of toluene and water on zeolite NaX (Fig. 12) by the thermogravimetric method, though it does accompany the adsorption of pure toluene. Water adsorption on this zeolite is not accompanied by an endothermic effect strong enough to cause the deterioration of the exo-effect. The above-mentioned effect is also observed during the adsorption of a water-benzene mixture (Fig. 13).

Figure 14 presents the thermal curves of cumene adsorption on zeolite NaX under isothermal conditions.

In Fig. 15 the curve of cumene adsorption on zeolite NaX, obtained by the thermogravimetric method, is shown for a heating rate of 1°/min. Comparing the

maxima of the adsorption on the TG curve and the heat effects on the DTA curve with those obtained at a heating rate of 6°/min, we observe that the heat effects and also the adsorption curves exhibit similar characters (see Fig. 1). The above-

Table 4

Adsorption of hydrocarbons on zeolite NaX

Adsorbate	Temperature of adsorption maximum, °C	Adsorption, molecule/u.c.	Adsorption, mmole/g
Isobutane	4	22.7	1.71
Isobutene	40	24.6	1.85
n-heptane	130	17.6	1.33
Cyclohexane	140	17.1	1.29

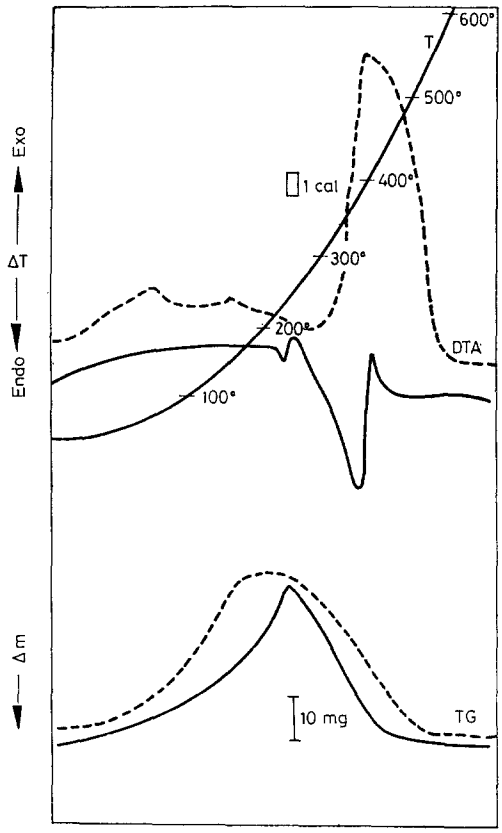

Fig. 12. Adsorption of toluene (— — —) and a mixture of water and toluene (———) on zeolite NaX

mentioned effects, however, occur at temperatures lower by approximately 65°. This proves that the thermal system cannot keep pace with the high heating rate, but it confirms that the thermogravimetric method can be used for adsorption measurements.

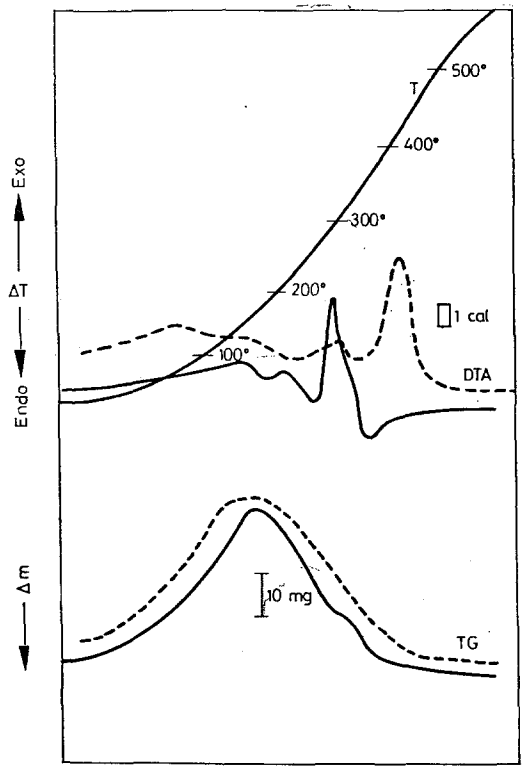

Fig. 13. Adsorption of benzene (— — —) and a mixture of water and benzene (———) on zeolite NaX

Table 4 gives results of the adsorption of various hydrocarbons on zeolite NaX, obtained from thermogravimetric measurements.

The results obtained for many aliphatic hydrocarbons correlate with the literature data obtained by the classical methods of adsorption [3].

Discussion

The purpose of the present work was to obtain data on the adsorption of various hydrocarbons on zeolites and, for comparison, some amorphous catalysts. The results shown in the Tables and Figures correspond to measurements obtained

under isobaric conditions with a high concentration of adsorbate. The desorption curves (TG) presented are isobaric.

The occurrence on zeolites of sorption processes accompanied by an exothermic effect in the range of desorption of aromatic hydrocarbons and olefines is worthy

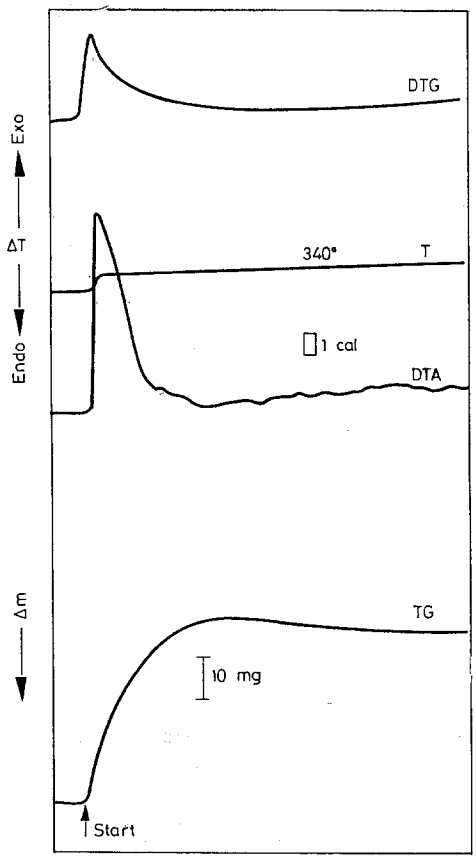

Fig. 14. Cumene adsorption (isothermal) on zeolite NaX. Rate of dosing: 0.5 ml/min

of consideration. In our opinion it might be attributed to the occurrence of molecular polycondensation in the zeolitic cavities. The polymerized molecules cannot leave the zeolites. This surface reaction accompanied by the exothermic effect (which became smaller with loss of the zeolite structure) did not occur in the case of amorphous catalysts.

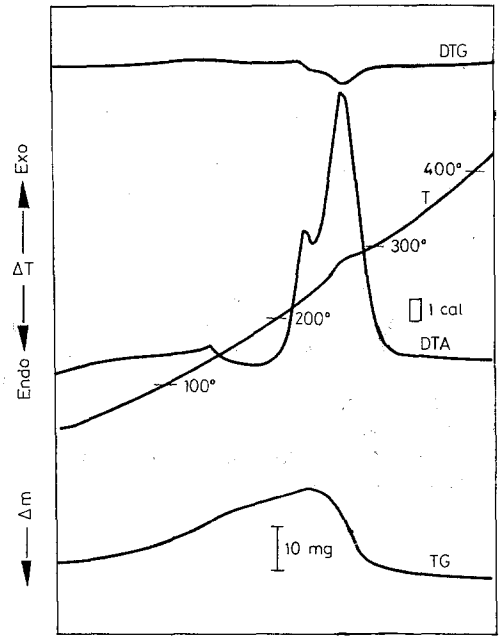

Fig. 15. Cumene adsorption on zeolite NaX. Heating rate: 1°/min

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RÉSUMÉ — Application de la TG et de l'ATD à l'étude des phénomènes de sorption et des réactions de surface sur des catalyseurs solides. Les mesures ont été effectuées à l'aide de zéolites échangeuses cationiques de type NaX, X ainsi qu'à l'aide de gels silice-alumine "Ketjen" traités par NaOH en présence des hydrocarbures suivants: isobutane, isobutène, heptane, cyclohexane, benzène, toluène, éthylbenzène, cumène, *n*-propylbenzène, *tert*-butylbenzène, diphényle, naphtalène. 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.

ZUSAMMENFASSUNG — Die Thermogravimetrie wurde zusammen mit der DTA-Methode zur Untersuchung von Sorptionserscheinungen und Oberflächenreaktionen an festen Katalysatoren eingesetzt. Die Messungen wurden an NaX, an Kationenaustauscherzeoliten des Typs X und an Silika-Aluminiumoxid "Ketjen" durchgeführt, welche mit Natriumhydroxid in Gegenwart der Kohlenwasserstoffe Isobutan, Isobuten, Heptan, Cyclohexan, Benzol, Toluol, Äthylbenzol, Kumol, *n*-Propylbenzol, *tert.* Butylbenzol, Diphenyl und Naphthalin behandelt worden waren. Aufgrund quantitativer Ergebnisse ist es möglich die Oberflächenerscheinungen zu deuten und das Vorliegen verschiedener aktiver Zentren an der Katalysatorenoberfläche zu beweisen.

Резюме — Совместно с методом DTA, была использована термогравиметрия для исследования явления сорбции и поверхностных реакций на твердых катализаторах. Измерения были проведены с катион-обменными цеолитами типа NaX и X, а также с кремний-алюминиевыми гелями типа «Кетьен», обработанных едким натром в присутствии таких углеводородов, как изобутан, изобутен, гептан, циклогексан, бензол, толуол, этилбензол, кумол, н-пропилбензол, трет-бутилбензол, дифенил и нафталин. На основании количественных результатов, стало возможным дать интерпретацию поверхностного явления и доказать существование различных активных центров на поверхности катализаторов.