THE APPLICATION OF THERMOANALYTICAL METHODS FOR THE CHARACTERIZATION OF ZEOLITE CATALYSTS

H. Siegel[1] and *H. Splinder*[2]

[1]VEB CHEMIANLAGENBAUKOMBINAT LEIPZIG-GRIMMA, G.D.R.;
[2]VEB LEUNA-WERKE "WALTER ULBRICHT", G.D.R.

Through the coupling of a DSC 111 (Setaram) with a gas dosing valve and a catharometer detector, equipment was developed for the investigation of adsorbents and catalysts. This equipment was applied for the determination of differential and integral heats of adsorption of C_2 to C_4 hydrocarbons on zeolites of the pentasile family. The proposed method has sufficient accuracy for the determination of adsorption heats for technical products. The advantages and the problems of the presented method are discussed.

The progress in the development of experimental techniques and theories in recent years has had the result that thermoanalytical methods are applied not only for structural studies but also for the determination of the catalytic and adsorptive properties of zeolites [1, 2]. Through a combination of differential scanning calorimetry with dosing and analyzing units, the determination of adsorption heats is possible [2, 3]. Such equipment has been developed and used for studies of the adsorption of C_2 to C_4 hydrocarbons on ZSM-5 zeolites and on silicalite. These systems were chosen because of the small transport resistance of the hydrocarbons in the channels of the pentasiles. Furthermore, a contribution may be made to the investigation of the adsorption properties of ZSM zeolites. Such studies are of interest in connection with the ability of ZSM zeolites to convert methanol to paraffins and olefins [4, 5]. Little information is available on the adsorption of hydrocarbons on these zeolite catalysts [6–8].

Experimental

The studies were carried out with a combined thermoanalyzer (TG–DTG–DTA) and the DSC 111 (both products of Setaram). The DSC is useful for the detection of adsorption and reaction heats because of its construction design, with two alumina
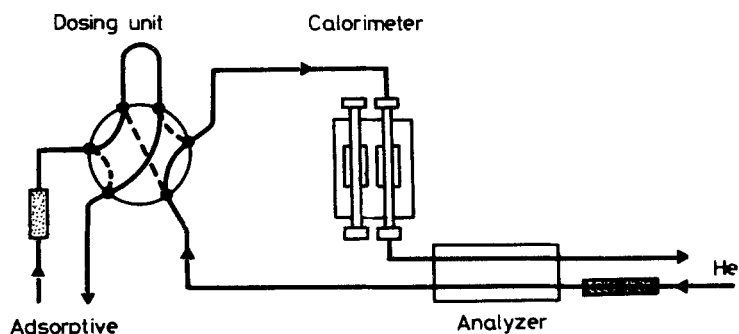
Fig. 1 Scheme of the DSC apparatus for the determination of heats of adsorption

tubes as measuring and reference cell. A scheme of the equipment is shown in Fig. 1. As adsorbents, a laboratory-synthetized silicalite, an industrial-made HZSM–5 zeolite and the sodium forms of this latter, prepared by treatment with 1 N NaCl or with 1 N NaOH solution were used. The compositions of the samples, determined by chemical analysis and by PIGE, were as follows:

Zeolite	Si/Al ratio	Unit cell
HZSM–5	96	$H_{3.27}Na_{0.58}Al_{3.84}Si_{92.16}O_{192}$
(H, Na) ZSM–5	96	$H_{1.91}Na_{1.93}Al_{3.84}Si_{92.16}O_{192}$
NaZSM–5	48	$Na_{7.38}Al_{1.38}Si_{88.61}O_{192}$
Silicalite	—	$(SiO_2)_{96}$ 0.005 atom-% Na

Results and discussion

Thermoanalytical characterization of the zeolites

It follows from the chemical composition that the protons of the HZSM–5 zeolite are not completely exchanged by Na^+ after treatment with NaCl solution. On the application of NaOH solution, the protons are fully removed, but the Si/Al ratio is changed, probably by the dissolution of SiO_2. The information obtained by thermal analysis of the zeolites is summarized in Table 1. The desorption of water from the pentasiles starts at room temperature and is essentially finished at 500 K. The major part of the water is only loosely adsorbed via hydrogen-bonding. The cation-containing zeolites show a small shoulder in the desorption curve at about 370 K, assigned to the cation—water interaction. The desorption of OH groups is responsible for the weight loss between 500 and 800 K. In the DTA curve of the sample treated with NaOH, an exothermic peak is observed at $T < 1100$ K,

Table 1 Water desorption and thermal stability of pentasile zeolites

Zeolite	Water content, %	H_2O/u.c.*	Temperatures, K	
			peak maxima	breakdown
Silicalite	4.3	14.4	324	>1500
HZSM-5	5.9	20.1	325, 415 sh	>1500
(H, Na) ZSM-5	6.0	20.6	337. 420 sh	>1500
NaZSM-5	10.8	39.9	340, 420 sh	1073

* u.c. = unit cell

indicating the breakdown of the framework damaged in the ion-exchange procedure.

Determination of the integral heats of adsorption

The integral heats of adsorption were determined in a simple way by saturation of the well-dehydrated zeolite with the adsorptive, and measurement of the released heat in the DSC cell. For estimation of the molar heats, either the adsorbed amount determined with a vacuum-microbalance or that calculated via a Langmuir model was used. The measured and the calculated heats of adsorption for the C_2 to C_4 olefins and paraffins on pentasiles and on NaY (Si/Al ratio = 2.5) are compared in Table 2. With growing chain length of the hydrocarbons, the adsorption heats increase markedly for all studied zeolites, the heats of adsorption for the paraffins are higher than those for the olefins. Analogous results were found by Messow et al. [11] from measurements of the heats of immersion of longer paraffins (C_5 up to C_{20}). For other types of zeolites, with decreasing strength of the electrostatic field a strong drop in the adsorption heat to below the value for the corresponding paraffin was found [10]. The reason is that, in the case of the Si-rich zeolites, the adsorptives are bound only by dispersion forces [6]. In cation-rich zeolites, the situation is reversed, because the olefins can form additional interactions with cations. Extensive investigations of this topic have been formed by Stach, Thamm et al. [6, 7, 9–11]. The molar heats of adsorption range from 1.5 to 6 kJ mol^{-1}, depending on whether the adsorbed amounts were taken from isotherms or calculated by means of the Langmuir model. Capillary condensation and deviations from the isothermal state or from the model mentioned above can contribute to these differences. The adsorption heats for both *n*-butane and butene–1 differ only little on HZSM–5 and silicalite. These results support the idea of adsorption based on dispersion interactions, in the same way as the small differences between the heats for olefins and paraffins on NaZSM–5, caused by the greater number of cations.

Table 2 Integral heats of adsorption for hydrocarbons on pentasile zeolites

Zeolite	Adsorptive	$\Delta_A H,$ $J \cdot g^{-1}$	$a,$ $mmol \cdot g^{-1}$	$\Delta_A H,$ $kJ \cdot mol^{-1}$	$a_c,$ $mmol \cdot g^{-1}$	$\Delta_A H_c,$ $kJ \cdot mol^{-1}$
NaY	$C_{3=}$	91.8				
	C_3	139.4				
	$C_{4=}$	113.3	2.94 [13]	38.5		
	$C_{4=}$	141.4	3.34 [13]	42.3		
NaZSM–5	C_2	37.4	1.94	19.3	1.78	21.0
	$C_{3=}$	52.0	1.72	30.2	1.64	31.7
	C_3	51.8	1.79	28.9	1.65	31.4
	$C_{4=}$	59.5	1.63	36.5	1.43	41.6
	$C_{4=}$	58.2	1.68	34.8	1.50	39.1
HZSM–5	C_2	43.8	3.62	12.1		
	$C_{3=}$	64.3	2.21	29.1		
	C_3	62.7	2.63	23.8		
	$C_{4=}$	73.8	1.65	44.7		
	C_4	72.4	1.98	36.6		
	$i–C_4$	54.9	1.45	37.9		
Silicalite	C_2	48.9	1.87	26.1		
	$C_{3=}$	73.0	2.01	36.5	1.92	38.0
	C_3	72.2	2.75	26.2		
	$C_{4=}$	81.5	1.74	46.8	1.65	49.4
	C_4	79.4	2.21	35.9		

Differential heats of adsorption

In order to determine the differential heats of adsorption, small amounts of the adsorptive were introduced in a stream of helium which flowed through the zeolite layer within the calorimeter. The amounts of hydrocarbons not adsorbed in the cages of the zeolites were determined with a catharometer.

The differential adsorption heats for n-butane show a small progressive rise with increasing coverage (Fig. 2). This is characteristic for microporous adsorbents. Such a course is to be expected for adsorbate—adsorbate interactions if the adsorption sites are energetically homogeneous. The proportion of this effect is small for narrow-pore zeolites however, because only the terminal methyl groups are in contact with one another [6]. Similar high values for the differential heats of adsorption were found by Thamm et al. [6, 7, 10] from calorimetric studies of n-butane on silicalite. They explained this finding in terms of the formation of optimal adsorption structures in the narrow channels. In zeolites with larger cages, the values of the adsorption heats are smaller [9, 10]. Only at smaller adsorbed amounts (< 0.3 mmole g^{-1}) is the heat of butene-1 higher than that of butane; it drops with
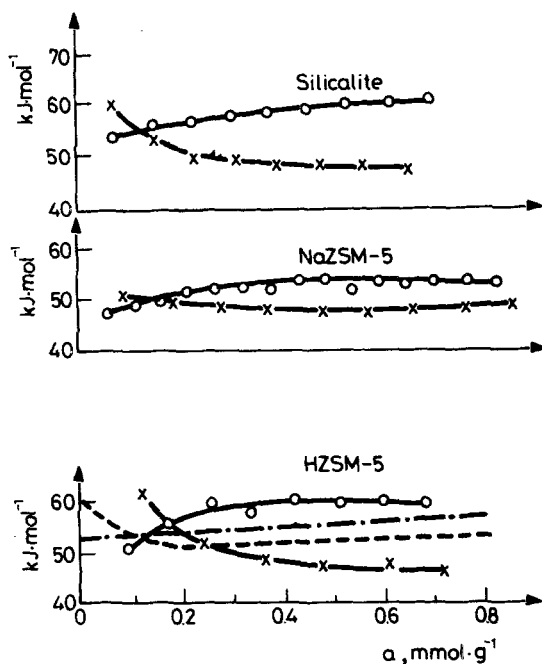
Fig. 2 Differential heats of adsorption for hydrocarbons on pentasile zeolites. ○ butane, × butene

increasing coverage, because the dispersion interactions prevail. The high initial heats of adsorption for the olefin are caused by adsorption on crystal defects and catalytically active sites.

At temperatures > 295 K, the heats increase strongly, due to the oligomerization of butene–1 [1]. As mentioned for the integral adsorption heats, the cations do not significantly influence the adsorptive process. The differences between the differential heats of the olefins and paraffins are small in completely exchanged NaZSM–5. The reason for this effect is the increased content of Al^{3+} and also of Na^+. Therefore, the specific interactions of the olefinic double bonds make a marked contribution.

Conclusions

Through the combination of a DSC 111 with dosing analyzing units, measuring equipment was developed which is suitable for the determination of adsorption heats. With this apparatus the processes of adsorption of hydrocarbons on zeolites were investigated. The integral heats of adsorption could be reproduced within 5%.

Comparison with literature data shows that the proposed method has an accuracy sufficient to characterize technical catalysts and adsorbents. Nevertheless, the measuring time is substantially shorter than in conventional adsorption calorimetry. It is noteworthy that, during work in a stream of carrier gas, displacing heats are measured which are smaller by the heat of adsorption for the used gas. This heat, however, is small in the case of helium. For the measurement of differential heats, irreversible adsorption is necessary.

References

1 B. Wolf, Dissertation, Karl-Marx-University, Leipzig 1985.

2 H. Lechert, Zeolites, Science and Technology, eds F. R. Ribeiro et al. M. Nijhoff, Den Haag 1983.

3 P. Gravelle, Adv. Catalysis, Vol. 22, Academic Press, New York 1972.

4 F. Janowski and K. H. Bergk, Z. Chem., 22 (1982) 277.

5 U. Törk, Dissertation, Ruhr University, Bochum 1982.

6 H. Thamm, H. Stach, W. Schirmer and B. Fahlke, Z. Phys. Chem., (Leipzig) 263 (1982) 461.

7 H. Thamm, H. Stach and W. Fiebig, Zeolites, 3 (1983) 95.

8 H. Siegel, Dissertation B, Karl-Marx-University, Leipzig 1986.

9 H. Stach, K. Fiedler and W. Schirmer, Prepr. Workshop "Adsorption of Hydrocarbons in Zeolites" Acad. Sci. of GDR, Berlin 1979, p. 94.

10 H. Stach, U. Throl, H. Thamm and K. Fiedler see [9], p. 108.

11 U. Messow. K. Quitzsch and H. Herden, Zeolites, 4 (1984) 255.

12 J. Hofmann, Adsorption Isotherms Data ORZ, Karl-Marx-University, Leipzig.

13 R. Harlfinger, D. Hoppach, H. P. Hofmann and K. Quitzsch, Z. Phys. Chem. (Leipzig), 261 (1980) 33.

Zusammenfassung — Durch Kombination eines DSC-Geräts (Setaram Typ 111) mit einem Gasdosierventil und einem Wärmeleitfähigkeitsdetektor wurde ein Gerät für die Untersuchung von Adsorbentien und Katalysatoren geschaffen. Dieses Gerät wurde zur Bestimmung differentieller und integraler Adsorptionswärmen von C_2- bis C_4-Kohlenwasserstoffen an Zeolithen der Pentasil-Familie eingesetzt. Die vorgeschlagene Methode ist ausreichend genau, um Adsorptionswärmen technischer Produkte zu bestimmen. Vorzüge und Probleme der Methode werden diskutiert.

Резюме — Посредством соединения ДСК 111 (Сетарам) с газ-дозирующим клапаном и катарометром-детектором, разработана аппаратура для исследования адсорбентов и катализаторов. Аппаратура была использована для определения дифференциальных и интегральных теплот адсорбции углеводородов с длиной углеродной цепи от C_2 до C_4 на цеолитах семейства пентасила. Предложенный метод достаточно точный для определения теплот адсорбции технических продуктов. Обсуждены преимущества и проблемы представленного метода.