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ZEOLITE CONTENT DETERMINATION IN KAOLINIC CLAYS VIA THERMAL EFFECTS

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For application in catalysis and adsorption processes, zeolites are synthesized on the surface of spray-dried kaolin microspheres. Various thermal effects are used for the rapid characterization of the zeolite type and content. From DTA measurements, the exothermic lattice break-down peak gives information on the zeolite type and the thermal stability of the sample. Measurements of the heats of immersion by a very simple and quick method allow conclusions about the type and the sorption properties of the zeolite part of the clay. The most precise method to estimate the zeolite content was a standardized technique of desorption and readsorption of water or organic compounds by means of a thermobalance.

Zeolites and zeolite-containing materials are frequently used in sorption procedures and as catalysts in numerous industrial processes. These substances are often prepared from kaolinic clays by hydrothermal treatment in aqueous sodium hydroxide [1, 2]. In this case, the zeolites are preferably synthesized on the surface of the spray-dried kaolin microspheres used.

By varying the manufacturing conditions, it is possible to obtain different types of zeolites. The problem arose of finding a method of sufficient accuracy for determining the zeolite contents in these catalysts or sorbents, working more quickly than the usual X-ray examination, since the procedure should serve as a manufacturing process control. We have examined the use of thermal effects for characterizing the zeolite types and the contents of our samples.

Experimental

DTA was carried out in a commercial device, using 70 mg samples and a heating rate of 10 deg min^{-1} from room temperature up to 1273 K in air. The inert reference material was standard α-alumina.

Heats of immersion were investigated by a very simple technique, involving wetting 10 g of the substance with an equal amount of water at room temperature

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and following the temperature change during several hundred seconds with a tenth degree scale thermometer. With a thermobalance, a 15 mg sample was linearly heated in a stream of dried air (1.2 l h^{-1}) at a rate of 7 deg min^{-1} up to 723 K, and then held at this temperature for 2 h to remove the residual adsorbed water. The decrease in weight is related to the content of zeolite.

To obtain quantitative information, the sample was cooled down to room temperature in dry air, and then exposed to a stream of wet air (p_{H_2O} = 4 kPa) at a constant temperature of 333 K. The weight increase was recorded during 120 min. The amount of adsorbed water after 100 min was taken as the basis of comparison of the substances.

The method was calibrated with 12 different standard mixtures of pure zeolite with unreacted kaolin.

Results and discussion

The high-temperature exothermic DTA peak originates from the formation of a new solid phase after lattice break-down of the zeolite [3]. Figure 1 shows this peak for several zeolite types. In the case of catalysts and sorbents, *Y* and *A* types are of special interest. It is easy to distinguish between these types by DTA, as seen from Fig. 1.

Especially for their ue as catalysts, it is of great importance to know the thermal stability, i.e. the highest possible temperature of their application in idustrial processes. The stability can be improved by ion-exchange of the sodium in the zeolite [4]. Alkaline earth and rare earth ions show the greatest effects, and by means

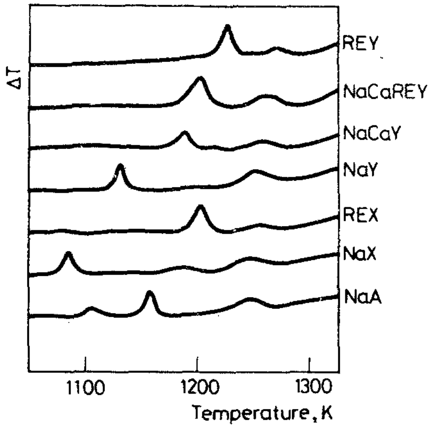

Fig. 1 DTA peaks of lattice break-down

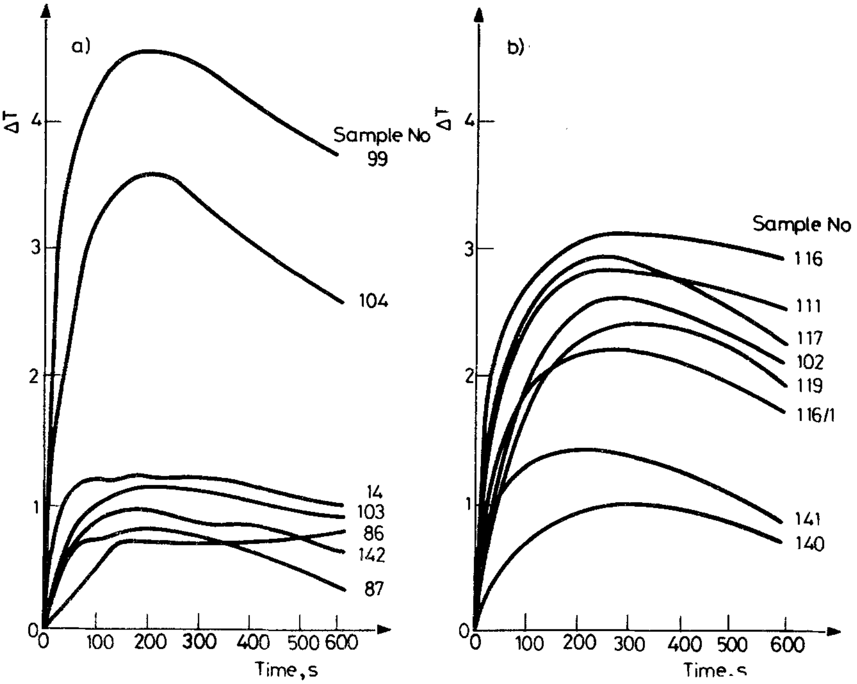

Fig. 2 Temperature changes by immersion
a *A*-type, b *Y*-type zeolites

of DTA the shifting of the exothermic peak to higher temperatures is easy to measure [5] (Fig. 1).

Another means of quick estimation of zeolite contents could be the measurement of the heats of immersion [6], as zeolites are known to show high heats of adsorption of water. However, the exact calorimetric measurement of these data is a difficult and long procedure. Therefore, we merely recorded the temperature increase caused by the heat of immersion. Figure 2 shows the results. With two exceptions, *A*-type zeolites (a) show a temperature increase in the range of 0.5 to 1.2 deg under the given conditions, while *Y*-type containing samples (b) display temperature changes of from 1.5 to 3.2 deg (Fig. 2, Table 1). The maximum temperature change is attained for *A*-type zeolites between 140 and 180 sec, and for those of *Y* type after 200 to 320 sec.

There is not a quantitative relation between zeolite contents and temperature effects. One reason is certainly the recording of the temperature only, instead of a calorimetric heat measurement. On the other hand, the evolution of the heat of immersion not only depends on the zeolite content itself, but is influenced by the crystallinity and distribution of the zeolite crystals in the clay, the surface area, the swelling of the clay, ion-exchange processes, and the pore structure [7, 8]. Nevertheless, measurements in the proposed manner are valuable for a quick screening of the adsorption behaviour of the substances. Large temperature changes correspond to good adsorption properties and active catalysts.

As the zeolite content is always correlated with the adsorption capacity of the substances, we attempted to use thermogravimetric water desorption measurements [3, 9] to estimate the zeolite contents. The decrease of weight should serve as a measure of the zeolite content. The results are shown in Fig. 3. They are not sufficient

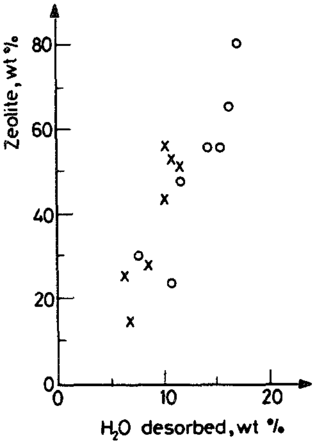

Fig. 3 Water desorption vs. zeolite contents
○ *A*-type, x *Y*-type zeolites

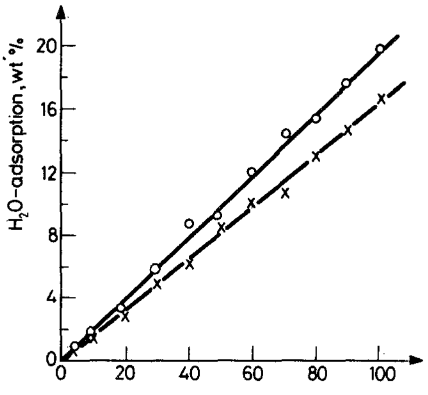

Fig. 4 Water readsorption calibration
○ *A*-type, x Y-type zeolites

Table 1 Thermoanalytical data, zeolite types and contents

Sample number	Lattice break-down from DAT, K	Zeolite type	Heat of immersion		Water adsorption at 333 K, wt.%	Zeolite contents, wt.%	
			T, K	T_{max}, sec		from TG	from X-ray
14	1160	*A*	1.2	100	4.8	24	~10
86	1158	*A*	0.7	140	8.7	44	—
87	1103/1158	*A*	0.8	160	11.1	56	15–20
99	1103/1158	*A*	4.5	165	15.9	80	>20
103	1108/1163	*A*	1.1	165	11.0	55	>10
104	1163	*A*	3.6	180	5.9	30	>5
142	1103/1158	*A*	0.9	180	12.8	65	—
102	1133	*Y*	2.6	300	4.6	28	5–10
111	1123	*Y*	2.8	210	7.8	48	15–20
116	1130	*Y*	3.1	210	8.3	51	>20
116/1	1130	*Y*	2.2	210	4.4	26	~10
117	1128	*Y*	2.9	250	6.9	43	5–10
119	1128	*Y*	2.4	240	8.7	53	>20
140	1130	*Y*	1.0	315	2.3	14	—
141	1128	*Y*	1.4	205	8.7	53	>20

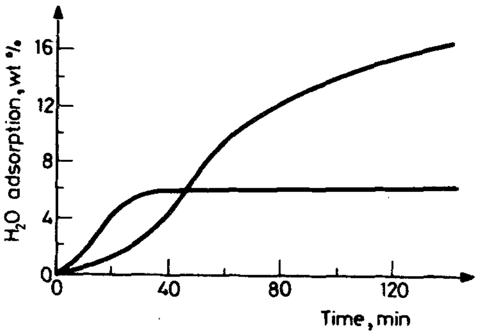

Fig. 5 Quick and slow readsorption of water

for the determination of zeolite contents, since the amount of water adsorbed on zeolites depends on the humidity of the ambient air, and constant starting conditions are not guaranteed. Therefore, after cooling down, the readsorption of water at 333 K was carried out. This procedure was undertaken with the calibration mixtures, too, and a linear relation was obtained between the zeolite content and the uptake of water. Figure 4 presents this correlation for *A* and *Y*-type zeolites. The zeolite contents of our substances as found by the described technique are listed in Table 1. It is to be seen that they are much more accurate than those estimated from simple X-ray diffraction patterns obtained with a comparable expenditure of time.

Additionally, the slope of the curves allows an interpretation of the adsorption properties. Figure 5 shows the weight increase curves of two different substances, a slowly and a quickly adsorbing one.

Conclusions

The simple thermogravimetric sorption method described allows the determination of the zeolite contents of catalysts and sorbents prepared from clay minerals with a higher accuracy than that of normal X-ray diffraction analyses, provided that the manufacturing process is the same in all cases and an equivalent raw material is used. The type of zeolite and the thermal stability can be obtained via DTA investigations.

Information on the sorption properties and the zeolite types is given by the temperature course during immersion in water and by the shape of the thermogravimetric adsorption curves.

In this way it is possible to utilize simple thermal effects for the quality control of zeolitic catalysts and sorbents, and for the supervision of manufacturing processes.

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Zusammenfassung — Zur Anwendung in der Katalyse und bei Adsorptinsprozessen werden Zeolithe auf der Oberfläche sprüh-getrockneter Kaolin-Mikrokugeln eingesetzt. Verschiedene thermische Effekte werden zur schnellen Charakterisierung des Zeolith-Typs und -Gehalts genutzt. Der exotherme DTA-peak beim Gitterzusammenbruch liefert Informationen über Zeolith-Typ und thermische Stabilität der Probe. Eine sehr einfache Schnellmethode zur Messung der Immersionswärmen erlaubt Schlussfolgerungen über Typ und Sorptionseigenschaften des zeolithischen Anteils des Tons. Die genaueste Methode zur Bewertung des Zeolithgehalts war eine standardisierte thermogravimetrische Desorptions- und Readsorptions-Methode mit Wasser oder organiscen Verbindungen.

Резюме — На поверхности микросферического каолина, высушенного распылением, синтезированы цеолиты, используемые в каталитических и адсорбционных процессах. Различные термические эффекты были использованы для быстрой характеристики типа цеолита и его содержания. ДТА измерения показали, что экзотермический пик разрушения решетки дает информацию о типе цеолита и термоустойчивости образца. Измерения теплоты погружения, проведенные очень простым и быстрым методом, позволили сделать заключение о типе и сорбционных свойствах цеолитной части минерала. Наиболее точным методом оценки содержания цеолита был стандартный метод десорбции и реадсорбции воды или органических соединений, проведенный с помощью термовесов.