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THE THERMOANALYTICAL DETERMINATION OF DEACTIVATION TYPES OF CATION-EXCHANGER CATALYST'S

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The dependence of the thermal decomposition of a cation-exchanger catalyst on its deactivation type has been ascertained, and thermal analysis has been suggested as a diagnostic method for the determination of the condition of such a catalyst.

The activity of cation-exchangers used as heterogeneous acidic catalysts usually undergoes a decrease [1—6].

The following processes may give rise to this activity decrease:

- ion-exchange of catalytically-active protons with metallic ions (impurities of feed materials or corrosion products) [1, 7];
- contamination with high-molecular compounds (the formation of which accompanies nearly all organic syntheses, or which are impurities of raw materials) [7];
- splitting-off of functional groups or their reaction with the organic resin [1, 8] as a consequence of overhigh temperatures, or mechanical and chemical destruction of the surface layer of the cation-exchange resin.

Methods affording possibilities for identification of the reasons for these activity decreases in non-active cation-exchanger examinations are not available. In the present paper thermal analysis has been employed for one case based on the dependence of the thermal decomposition of deactivated catalysts (shapes of TG/DTG curves) on the deactivation type.

Experimental

The commercial cation-exchanger resin Wofatit KPS (sulphonated styrene-divinylbenzene copolymer [9]) was the subject of the examinations. In the H-form it was applied as the catalyst of acrylic acid esterification with *n*-butyl alcohol in the pilot plate reactor [10]. After 500 hours of continuous work, samples of catalyst were collected from the first plate. Samples H_0, H_1 and H_2 were taken from different points of the reactor-axis, and R_0, R_1 and R_2 as succeeding cylindrical layers from the reactor wall.

Standard deactivated samples

Deactivated cation-exchanger catalyst samples were prepared from fresh, catalytically-active cation-exchanger in operations which gave only one, definite type of deactivation. Deactivation of ion-exchange type was carried by partial exchanging of H-ions with Fe (sample D_1) deactivation of contamination type by prolonged heating in boiling butyl acrylate (sample D_2), and deactivation of desulphonation type by prolonged heating in the temperature range 420–500 K (sample D_3).

Thermal analysis

Before thermal analysis, air-dried samples were carefully powdered. Experiments were carried out using a Mettler TA-2 instrument. 70 mg of sample was heated in a 0.9 cm^3 cylindrical Pt crucible over the temperature range 300–1200 K at a constant heating rate of 0.133 °/s. A controlled dynamic atmosphere of air was used in the furnace. TG, DTG and DTA curves were recorded.

Results and discussion

DTA, TG and DTG curves obtained during the heating of fresh, catalytically-active cation-exchanger are shown in Fig. 1. The three stages of weight loss visible can be explained by the occurrence of the following processes [11, 12]:

I – an endothermic desolvation process over the temperature range 300–450 K;

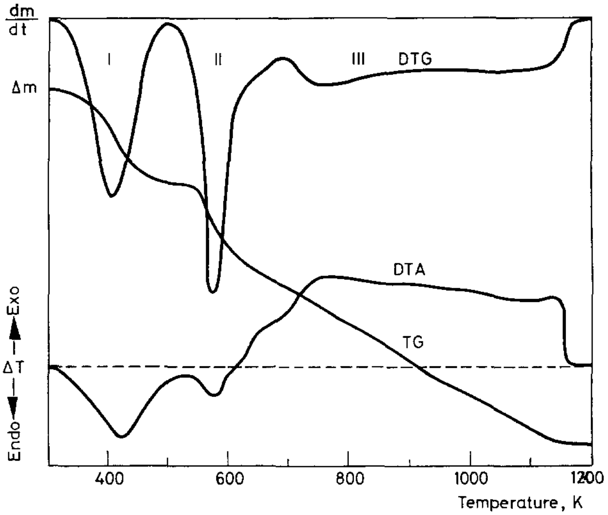

Fig. 1. TG, DTG and DTA curves of the fresh, catalytically-active cation-exchanger Wofatit KPS

II – an endothermic desulphonation process over the temperature range 450–650 K;

III – exothermic processes at thermo-oxidizing resin decomposition, carbonization and complete combustion of crack carbon at temperatures above 650 K.

DTG curves of fresh cation-exchanger and standard deactivated samples are compared in Fig. 2. It can easily be observed that the shapes of the DTG curves of the deactivated cation-exchanger samples vary in accordance with the deactivation type. When the deactivation is of ion-exchange type, the decrease of the desolvation peak, the decrease and disturbance of the desulphonation peak, and the appearance of a new thermal decomposition stage (IV) are observed. The deactivation of polymer contamination type causes a large decrease of the desolvation peak and the appearance of a thermal decomposition step of a settled polymer (V). In the case of the desulphonation type of deactivation, the desolvation and desulphonation peaks decrease nearly proportionally (till disappearance), but essential changes at higher temperatures are not observed.

Owing to such a specific and distinct dependence of the thermal decomposition of the cation-exchanger catalyst on its deactivation type, the type may be identified on the basis of the TG data.

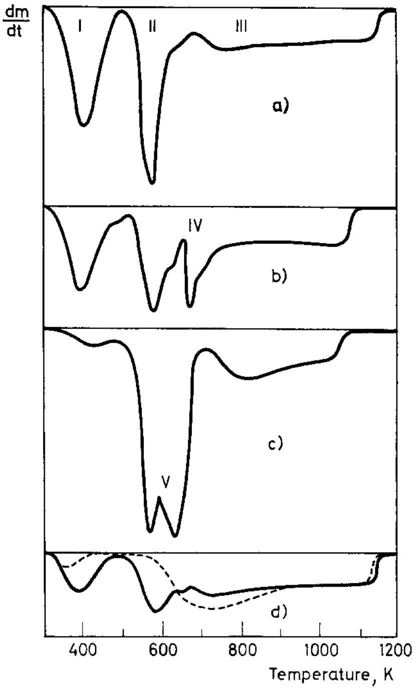

Fig. 2. DTG curves of Wofatit KPS. a. Catalytically-active sample; b. sample D_1 (deactivation of ion-exchange type); c. sample D_2 (deactivation of polymer contamination type); d. sample D_3 (deactivation of desulphonation type: full line — partial; broken line — complete)

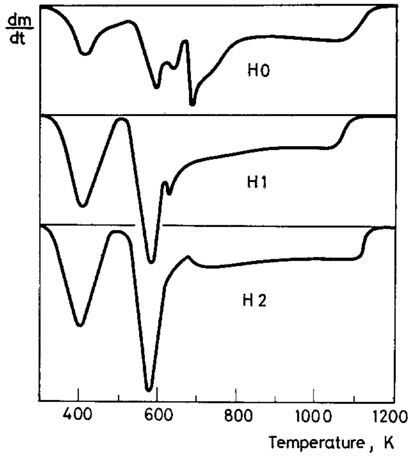

Fig. 3. DTG curves of catalyst samples (*H* series)

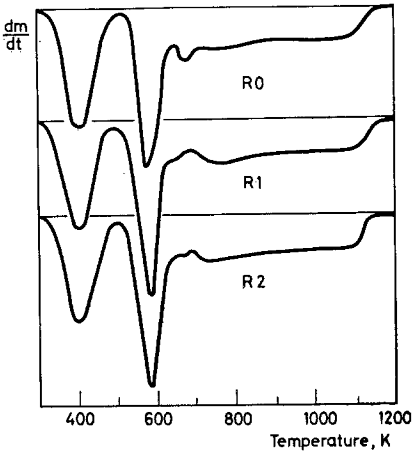

Fig. 4. DTG curves of catalyst samples (*R* series)

The above possibility has been made use of during an examination of cation-exchanger catalyst samples taken from the reactor (*H* and *R* series). DTG curves of the examined samples are shown in Figs 3 and 4. Analysis of these curve shapes with consideration to the contents of exchangeable hydrogen ions in the samples (Table 1) permits the following conclusions about the condition of the examined cation-exchanger catalyst. (1) In the direction of reagent flow, the ion-exchange type of deactivation occurs; to a great extent, the catalyst is deactivated only in the top layers of the bed. The same type of deactivation also results in the thin layer near the reactor wall [2]. Deactivations of polymer contamination and desulphonation types are not observed.

Table 1

Contents of hydrogen ions in cation-exchanger samples collected from the reactor

Sample	Part of bed		Content of exchangeable hydrogen ions, meq/g of dry resin [13]
	distance from the top of bed, mm	distance from the reactor wall, mm	
fresh	average value		5.11
H_0	0	in reactor axis	0.45
H_1	50		3.37
H_2	100		4.92
R_0	total bed-depth of the first plate	0–10	2.08
R_1		10–20	2.80
R_2		20–30	4.62

The above interpretation of the results suggests that the presence of inorganic impurities in the reagents is the main reason for catalyst deactivation in the given process.

Conclusions

The ascertainment of the distinct dependence of the thermal decomposition of a sulphonic cation-exchanger on its condition (especially the deactivation type when it is used as catalyst) permits the use of thermal analysis (TG mainly) as a diagnostic method for an investigation of cation-exchangers. This method affords a possibility of observing catalyst deactivation and its extent. Methods used up to present for cation-exchanger catalyst examination do not give the same data. The described method is therefore a good supplementary one because it gives qualitatively new information. It will be more than usually serviceable when the regeneration of non-active catalyst is carried out and checked on.

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Zusammenfassung — Die Abhängigkeit der thermischen Zersetzung eines Kationaustauscher-Katalysators von seinem Inaktivierungstyp wurde bewiesen und die Thermoanalyse als diagnostische Methods für die Bestimmung des Zustandes eines solchen Katalysators vorgeschlagen.

Резюме — Установлена зависимость термического разложения катионообменного катализатора от типа его дезактивации. Указано, что термический анализ может быть методом для определения такого состояния катализатора.