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Short Communications

THERMOGRAVIMETRY OF MOLECULAR SIEVES

NOTE 1

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Water-saturated molecular sieves were studied with a derivatograph. Apparent activation energies and orders of reaction were calculated and interpreted on the basis of the structures of the samples.

Up to now, thermal analysis has only been used sporadically for studying synthetic zeolites [1, 2] in papers dealing with other subject, and it has been of minor importance as compared with other methods. However, we consider that the data obtained with the thermogravimetric method provide important information as regards the structures and adsorbency characteristics of molecular sieves.

In this work the TG and DTG curves of molecular sieves are described and interpreted.

Experimental

Commercial molecular sieves Linde 5A, Ingelheim 5A, Bayer 3A and SMP-1 4A were tested. After prolonged saturation (24h) in an atmosphere of water vapour, the products were analysed on a MOM Paulik–Paulik–Erdey derivatograph on 70 – 120 mg samples at a heating rate of 12°/min.

Results and discussion

From a study of the TG and DTG curves of the tested products (Fig. 1), it was ascertained that the desorption of water is not uniform but occurs in two well-separated stages: the first stage occurs at 118 – 155° and the second at 192 – 209°. The quantity of water lost was found to differ for each product and stage (Table 1).

The existence of the two stages as well as the different distribution of the losses lead to the assumption that the bond energies of the water molecules held back by adsorption are different too. To check this, the value of the apparent activation

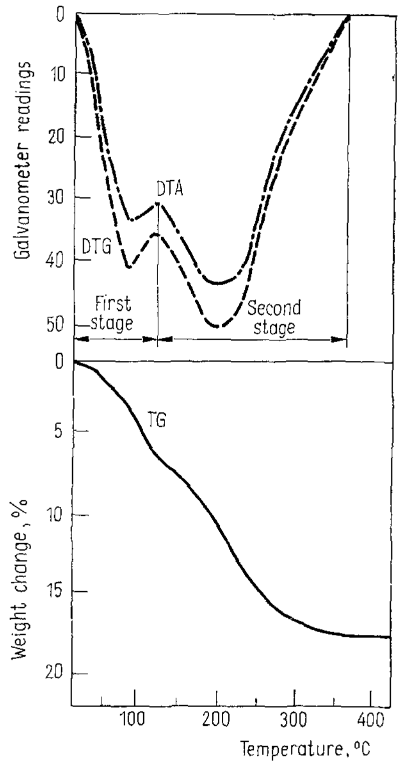

Fig. 1. Typical derivatogram of a water-saturated molecular sieve (Linde 5A)

energy and order of reaction were calculated for each product and each stage, using the Horowitz–Metzger method [3]. The results are given in Table 2.

To find the physical significance of the total order of reaction *n*, and of the apparent activation energy, the following hypotheses were formulated: the numerical value of the reaction order is proportional to the number of the monomolec-

Table 1

Water losses in the endothermic stages

Product	Stage I			Stage II			Total water loss %
	DTG minim. °C	Final temp. °C	Water loss %	DTG minim. °C	Final temp. °C	Water loss %	
Linde 5A	82	128	6	192	360	12	18
Ingelheim 5A	90	122	9	192	330	11	20
Bayer 3A	90	155	11	209	365	10	21
SMP–1 4A	90	118	5	196	315	14	19

Table 2

The activation energy and the order of the reaction of desorption

Product	Stage I		Stage II	
	E_1 (kcal/mole)	n_1	E_2 (kcal/mole)	n_2
Linde 5A	15.2	2.0	19.4	3.8
Ingelheim 5A	9.5	0.9	15.4	2.0
Bayer 3A	13.6	1.9	22.9	3.7
SMP—1 4A	—	—	14.5	1.7

ular layers that constitute the adsorption film of water on the surface of the molecular sieve, and the activation energy is related to the energy of desorption. Indeed, if the activation energy is plotted against the reaction order (Fig. 2), a straight line is obtained.

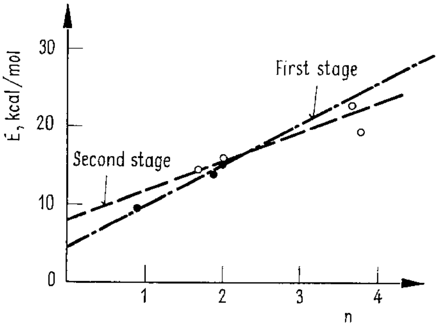

Fig. 2. The change of the activation energy with the reaction order

From the graph the specific energy was calculated for each stage:

$$E_{1\mathrm{spec}} = \Delta E_1/\Delta n_1 = 5.5 \text{ kcal/mole}$$

$$E_{2\mathrm{spec}} = \Delta E_2/\Delta n_2 = 3.7 \text{ kcal/mole}$$

The decrease in the numerical value of $E_{2\mathrm{spec}}$ may be due to the action of the neighbouring walls, an action which, according to the Polányi—Dubinin potential theory of adsorption [4] acquires importance when adsorption takes place in pores close in diameter to the adsorbed molecules.

In conclusion we can formulate the hypotheses that in the thermal analysis of molecular sieves, the two stages occurring on the derivatographic curve are due to the porous structures of the samples. The first stage corresponds to water desorption from the external surface and from pores that have a large radius, and the second to the water desorption from the microporous structures and the internal cavities.

Conclusions

The TG and DTG curves of molecular sieves were studied and interpreted on the basis of the structures of the samples. The water desorption was found to proceed in two steps, the first corresponding to desorption from the surface and from the large pores, and the second to desorption from micropores and internal cavities.

References

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