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Note

DIFFERENTIAL SCANNING CALORIMETRY LEADS TO HIGH PRECISION FOR WATER IN ZEOLITES DETERMINED BY THERMOGRAVIMETRY

A.K. ABOUL-GHEIT, M.A. AL-HAJJAJI, A.M. SUMMAN and S.M. ABDEL-HAMID

Chemistry Department, Faculty of Applied Science and Engineering, Umm Al-Qura University, P.O. Box 3711, Makkah Al-Mukarramah (Saudi Arabia)

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The water content of zeolites is very important to their widespread applications, e.g. as catalysts, molecular sieves, ion-exchangers, adsorbents, etc. The types of water bonding in zeolites have been studied by several authors [1–3]. Thermoanalytical methods, viz. DTA and TG combined with IR spectroscopy, have been used to identify water bondings in natural zeolites [4]. Some zeolites desorbed water through heating in a single step, e.g. natrolite, or in multiple steps, e.g. scolecite and thomsonite.

Water-desorption from many zeolites has been found to cover wider temperature ranges and stronger DSC signals [5] than other non-crystalline solids such as alumina and silica–alumina [6]. Moreover, DSC signals exhibit identifiable peaks with high sensitivity compared with DTA signals [7]. DSC also provides some valuable thermodynamic values such as enthalpy and activation energy [5,6].

MATERIALS

A series of zeolites produced by Norton, OH, was used for determining their water content. Of these zeolites, zeolons 400, 500 and 700 are natural, whereas zeolon 900-Na is synthetic. These materials were dried overnight at 110°C before TG and DSC measurements. Some characteristics of these zeolites are given in Table 1. Silica from Davison was also measured by TG for comparison.

APPARATUS AND MEASUREMENTS

TG analysis was carried out using a Mettler thermobalance system TA 3000 using the conditions: initial temperature, 50°C; rate, 10 K min^{-1}; final temperature, 600°C; plot, 11 cm; range, full scale, 10 mg; weight, 10 mg.

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TABLE 1

Characteristics and thermoanalytical data for zeolons

Zeolon	Mineral	Occurrence	Ring No.	SiO_2/Al_2O_3	Pore diameter (Å)	Void volume ($cm^3\,cm^{-3}$)	Dominant cations	ΔH ($J\,g^{-1}$)	TG wt loss (%)
400	Clinoptilolite	Natural	10	10:1	3.5	0.34	K, Na	281.4	18.15
500	Chabazite/erionite	Natural	8	5:1	4.3	0.47	Ca, Na	149.6	13.18
700	Ferrierite	Natural	10	10:1	3.9	0.28	K, Mg, Na	86.5	10.73
900-Na	Mordenite	Synthetic	12	10:1	7.0	0.28	Na	188.9	14.70

DSC analysis was carried out using a DSC-30 Mettler system TA 3000 at atmospheric pressure and no purge gas was used. The following conditions were used: initial temperature, 50 ° C; rate, 20 K min^{-1}; final temperature; 600 ° C; plot, 10 cm; range, full scale, 25 mW; weight, 10 mg.

RESULTS AND DISCUSSION

Figure 1 shows the TG thermograms obtained for the four zeolites under study (zeolons 400, 500, 700 and 900-Na) throughout the temperature range 50–600 ° C. These thermograms appear as smooth curves devoid of any distinct steps. To differentiate between loss in weight resulting from water desorption and any loss due to any decompositional changes, particularly in the case of unstable zeolites, one can make use of the sensitive endothermic DSC water-desorption signal to determine the exact range of temperature at which only water is desorbed. For the zeolons under study, the percentage weight loss calculated from the TG thermograms indicated by corresponding DSC water-desorption signals is given in Table 1. Figure 2 depicts DSC endothermic water-desorption signals that cover wide temperature ranges. These signals start at 50 ° C for all the zeolons studied. The final temperature is 460 ° C for zeolon 700, 530 ° C for zeolon 500 and 600 ° C for zeolon 400. However, for zeolon 900-Na, two water-desorption peaks appear, a major one between 50 and 460 ° C and a minor one between 500 and 575 ° C.

The enthalpy values ΔH obtained for water desorption from the zeolons are given in Table 1. Accurate determination of water-desorption peaks in a DSC thermogram is of prime importance for obtaining accurate ΔH values. Examples of the dependence of the values of ΔH on the choice of DSC signal temperature range are given in Table 2. Actually, identification of the

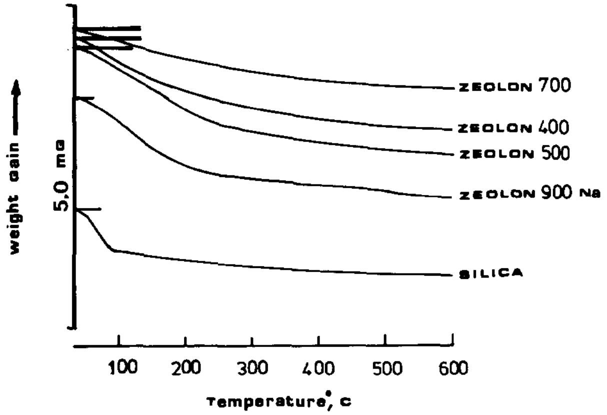

Fig. 1. TG thermograms of zeolons (with silica for comparison).

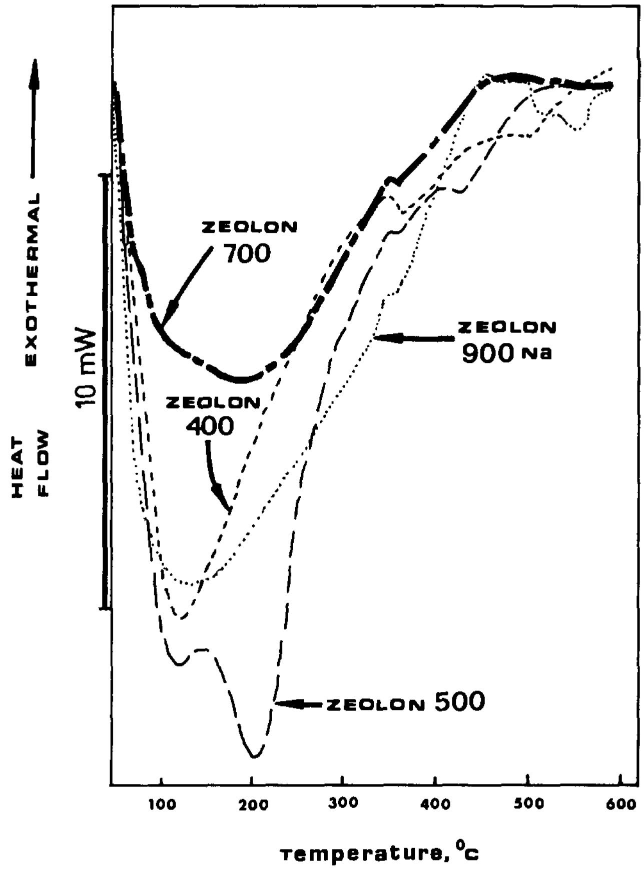

Fig. 2. DSC thermograms of zeolons.

DSC signal temperature range is simple in the case of horizontal base lines, but needs much care to identify the true baseline in case of steep ones. In the present work, baselines 7 and 8 are found adequate for whole peaks. The ΔH values are evaluated using either "peak integration" or "kinetic analysis" programs.

TABLE 2

The change of ΔH and E_a values with changing temperature range

Temperature range (°C)	ΔH (J g^{-1})	E_a (kJ g^{-1})	Reaction order
170–370	109.8	98.0	2.38
180–370	96.0	111.2	2.40
180–400	105.5	102.0	2.37
180–420	111.7	93.5	2.31
180–440	121.0	92.2	2.43

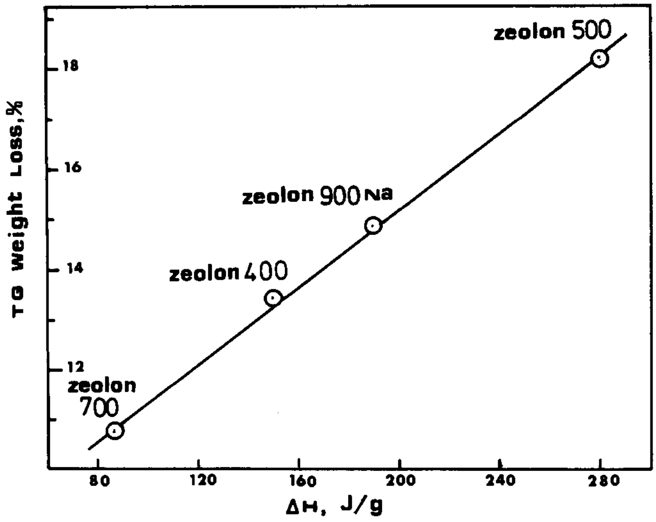

Fig. 3. Relationship between ΔH by DSC and percentage weight loss of water from zeolons by TG.

Table 2 shows that decreasing the temperature range through increasing the value of initial temperature and/or decreasing the peak end temperature, gives lower ΔH values and larger activation energy values, and vice versa. The kinetic order of desorption is almost unaffected by the temperature range. The kinetic order and activation energy have their significance in kinetic analysis programs [6].

Figure 3 gives a plot of the zeolites weight loss calculated from the TG thermograms throughout a temperature range determined by DSC water desorption signal (Table 1) vs. ΔH obtained for such water desorption (Table 1). Since ΔH is related to mass [6], the straight line obtained in Fig. 3 may indicate the independence of the DSC water-desorption signal on the type of zeolite, although these zeolites possess different modes of water bonding due to their different structural characteristics. Table 1 shows that these zeolites possess different ring numbers, pore diameters, void volumes and different cationic composition. Such independence may justify the use of this procedure for determining water in zeolites. Nevertheless, a large number of other zeolites has to be investigated before making a stronger generalization.

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