HEATS OF IMMERSION OF CLINOPTILOLITE AND ITS ION-EXCHANGED FORMS
A calorimetric study

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Abstract

The heats of immersion (in water) of outgassed clinoptilolite and its ion-exchanged forms were measured with a Calve calorimeter at 30°C, and the integral heats of sorption were calculated therefrom in order to use zeolites in heating and cooling applications. The immersion and sorption heats were studied as functions of the water saturation degree and the cation contents. The changes observed in the slopes of the sorption curves at low saturation for Ca^{2+} and Mg^{2+} ion-exchanged forms were related to the thermal destruction of the heulandite-type structure.

Keywords: calorimetry, clinoptilolite

Introduction

The property of zeolites in emitting and absorbing water reversibly has found application in a number of technological processes.

One way to examine the sorption properties of zeolites, especially to acquire information on the binding energy of the water within the crystals, is calorimetry. By means of direct calorimetry [1, 2], the immersion heats and the sorption heats can be treated as functions of the amount of water sorbed.

This work reports the use of an isothermal differential calorimeter of Calve type to investigate the immersion heats and thermochemical parameters of clinoptilolite samples, one of the widely distributed natural zeolites of industrial significance.

Experimental

Industrial clinoptilolite tuff from Beli Plast, SE Bulgaria, containing about 80% clinoptilolite and admixtures of montmorilonite, seladonite, crystobalite and clastic minerals, was used. K, Na, Ca and Mg-exchanged forms were prepared from it by means of exchange in 1 M solutions of the corresponding nitrates. The degree of ion-exchange was controlled by electron microscopy. The

results on the chemical compositions of the initial material and the exchanged forms are given in Table 1.

Table 1 Chemical composition of the initial material and the ion-exchanged forms (Wt%) (Philips-SEM 515 with EDAX 9100 microanalyzer. The values for O and H are calculated by EDAX software)

Elements	Natural-	K-	Na-	Ca-	Mg-
			Forms		
Na	0.78(6.05)	–	2.25(2.67)	–	0.63(7.63)
K	2.02(1.34)	5.46(0.80)	1.73(1.53)	1.74(1.51)	1.85(1,48)
Mg	0.45(5.06)	0.39(6.69)	0.43(5.34)	0.44(5.24)	1.01(2.66)
Ca	1.75(1.74)	–	0.45(5.37)	2.09(1.55)	1.04(2.68)
Fe	0.76(5.97)	0.68(7.65)	0.73(6.43)	0.74(6.29)	0.76(6.14)
Al	4.42(0.76)	4.62(0.82)	4.50(0.76)	4.38(0.76)	4.80(0.74)
Si	22.52(0.28)	24.46(0.30)	23.72(0.28)	23.56(0.27)	24.70(0.27)
O	63.30	60.95	62.46	63.19	61.76
H	4.00	3.44	3.72	3.86	3.45

The thermal effects of immersion were measured in a DAC 1-A differential calorimeter, produced in Russia [3], in specially constructed cells. Samples of 0.7 g were placed in glass ampoules which were activated in the temperature interval 100–470°C for 16 h. After the heating was over, the samples were outgassed up to the equilibrium pressure of 3 Pa. The ampoules were broken in water in the cells at 30°C. The effect of ampoule breaking was measured in a separate experiment with an ampoule containing thermally destroyed clinoptilolite; it amounted to 1–2% of the total thermal effect of immersion. An electrical calibration was used, the calibration coefficient being determined before each experiment, with 0.2–0.5% error. The reproducibility of the measurements was ±2.1%.

The degree of activation was assessed as the degree of saturation (θ) of the structure with water. θ was the ratio of the measured loss of water in the unwelded ampoule to the total water content, taken as the water loss from the samples at 800°C.

The clinoptilolite unit cell parameters were measured with a DRON 2YM apowder diffractometer after heating.

Results and discussion

The results on the calorimetrically measured immersion heats (Q_{imm}) of the observed forms are presented at Fig. 1 as functions of the degree of saturation, θ. The increase in the immersion heat at values close to 0 is obvious. The feau-

ter in the curves for the Ca and Mg forms at activation temperatures of 350–470°C (θ = 0.2–0.05) correspond to the thermal destruction of the heulandite-type structure. This is confirmed by the data given by Drebutsak [4] from an investigation of the temperature dependence of C_p for dehydrated heulandite at >417°C. Ca- clinoptilolite is similar in some of its thermal structural properties to heulandite. The thermal destruction begins at 350°C and proceeds through an irreversible decrease in the parameter b of Ca-clinoptilolite unit cell. The work to change the crystal lattice (d = 020–9.00 Å at 20°C, d = 020–8.87 Å after heating to 370°C) is the cause of the decrease in the slope of the immersion curves as θ for the Ca and Mg forms is reduced. For structural
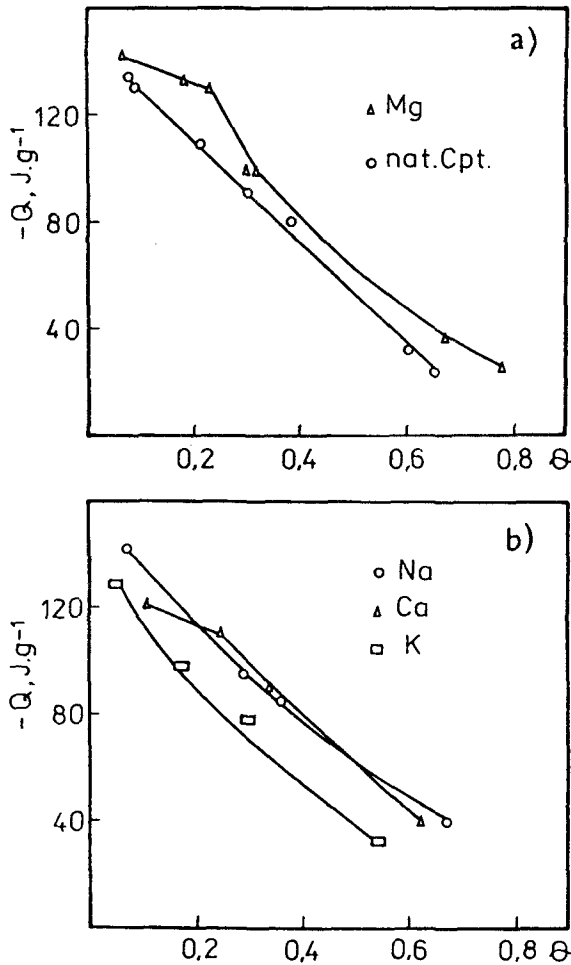

Fig. 1 Curves of immersion heats, $-Q$, as functions of water saturation degree, θ.
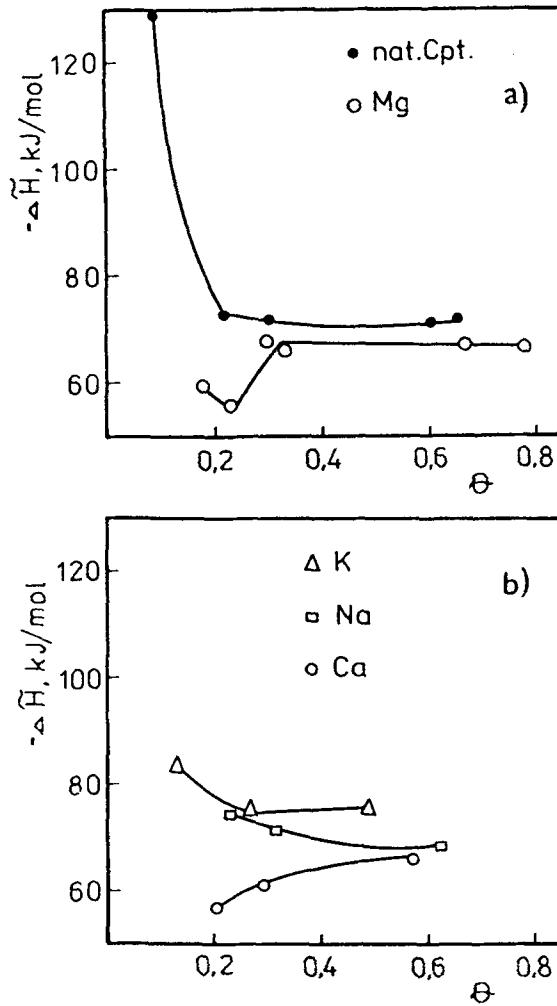   a) natural-, Mg-forms; b) Na-, Ca-, K-forms

Fig. 2 Curves of integral heats of sorption, $-\Delta H$ as functions of water saturation degree, θ.
a) natural-, Mg-forms; b) Na-, Ca-, K-forms

reasons, the Mg form must have the highest thermostability but, because of the low degree of Ca–Mg exchange (Table 1), the slope of the curve is similar to that of the Ca form. From the experimentally found immersion heats, the integral sorption heats of water vapour (ΔH) was defined according to the Barrer and Cram equation [1]:

$$Q_{no}-Q_{ns} = (n_s - n_o) \times (\Delta \tilde{H} - \Delta H_L)$$

where $Q_{no}-Q_{ns}$ are the heats of immersion of the zeolite initially containing n_s and n_o moles of presorbed water per gram, and ΔH_L is the molar heat of condensation of water, taken as 43.97 kJ/mol. The curves shown in Fig. 2 demonstrate how the integral heats of sorption depend on θ for the investigated forms. Once again, the observed features of for the integral sorption heats are confirmed in the slopes of the curves of the Ca and Mg forms at low values of θ.

Conclusions

This work reveals considerable differences in thermal behaviour of various ion-exchanged forms of natural clinoptilolite.

The measurement of immersion heats with a Calve calorimeter is a simple and convenient method for their detailed study. The differences caused by structural and crystallochemical peculiarities can be observed clearly. Additionally, they allow assessment of the thermal stability of the zeolite structure in the low θ area.

The data on the thermostability of the separate forms and their integral heats of sorption show that they can be very effectively used in different temperature intervals for technical purposes: the K and Na forms adsorb water most effectively in a wide temperature interval, while the Ca and Mg forms are applicable for temperatures up to 300°C.

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References

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Zusammenfassung — Mit einem Calve Kalorimeter wurden bei 30°C die Eintauchwärme (in Wasser) von entgastem Clinoptilolit und seiner ionenausgetauschten Formen gemessen und daraus die integrierten Sorptionswärmen berechnet, um Zeolithe bei Erhitzungs- und Abkühlanwendungen einzusetzen. Die Eintauch- und Sorptionswärmen wurden als eine Funktion des Wassersättigungsgrades und des Kationengehaltes untersucht. Die beobachteten Änderungen im Anstieg der Sorptionskurven bei niedriger Sättigung für Ca^{2+}- und Mg^{2+}-ionenausgetauschte Formen wurden der thermischen Zersetzung der Heulandit-Struktur zugeschrieben.