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THERMO-DIELECTRIC ANALYSIS

Part 2: Zeolites

R. Roque-Malherbe and *A. Montes*

NATIONAL CENTER FOR SCIENTIFIC RESEARCH, P.O.BOX
6880, HAVANA, CUBA

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By means of thermo-dielectric analysis, some natural and synthetic zeolites were studied (clinoptilolite, mordenite, *X*, *Y* and *A*). The results indicate the existence of two effects, one related to water evolution, reflected in a decrease of dielectric constant; the second peak is related to ionic conduction at high temperature. Both peaks characterize zeolites, in thermo-dielectric analysis.

Part 1 [1] described the design and operation of a thermal analyser capable of performing dielectric and thermal analysis simultaneously under the same experimental conditions.

In the present paper the method is applied to a concrete system: the zeolites; the process that occurs during the thermo-dielectric analysis is explained, and the analytical advantages that the method offers for the identification of natural and synthetic zeolites are discussed.

Experimental

The samples under test were: natural clinoptilolite-heulandite from Cuban deposits, denoted HC, CMTC, CC1 and CC2; natural mordenite from Cuban deposits, denoted MC1, MC2 and MP. The elemental and phase analyses of the samples are reported in Tables 1 and 2 [2, 3]. Homoionic samples (90–95% of total exchange) obtained from natural samples by five successive ion exchanges at 373 K with fresh 3 M solutions of sodium and calcium nitrate and ammonium chlorid were denoted Na—CCl, Ca—CCl, NH_4—HC, Na—MP and Ca—MP. Synthetic Na—*X*, Na—*Y* and Ca—*A*, products of REACHIM and LAPORTE, were analysed too.

The thermal analyser used was described in detail in part 1 [1].

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Table 1 Elemental composition of natural zeolites in weigh per cent

Oxide	HC	CC1	CC2	MP	MC1	MC2	CMTC
SiO_2	66.0	61.0	60.2	64.9	60.0	62.0	65.2
Al_2O_3	10.0	10.2	10.8	11.3	8.0	11.0	11.7
Fe_2O_3	1.6	3.0	5.0	2.7	3.0	5.0	2.1
CaO	4.5	5.7	5.0	4.2	4.3	4.2	3.8
MgO	0.0	0.3	0.2	0.7	0.1	0.2	0.6
Na_2O	0.0	0.2	0.2	1.7	0.8	0.1	2.8
K_2O	1.9	2.7	2.2	—	1.8	2.1	1.4
H_2O	14.7	17.8	14.5	15.5	16.0	17.5	13.5

Table 2 Phase composition in weight per cent

Sample	Heulandite-clinoptilolite, %	Mordenite, %	Others, %
HC	80	—	20
CC1	75	10	15
CC2	85	—	15
MP	10	70	20
MC1	—	85	15
MC2	10	70	20
CMTC	75	10	15

The present paper reports curves of the derivative of the output voltage with respect to temperature ($\Delta V_0/\Delta T$) *vs.* temperature (T). The analyser compares the impedance modulus of the sample cylindrical capacitor ($|Z_x|$) to that of the reference capacitor ($|Z_r|$).

The sample and the reference (A1203) are fine powders ($0.1 < d < 0.2$ mm). These are introduced between the plates of the cylindrical capacitors, which are enclosed in a furnace whose temperature is scanned linearly. The referred output voltage is given by:

$$V_0 = \frac{|Z_r|}{|Z_x|} V_i = \frac{\sqrt{(\omega C_x)^2 + (\sigma_x)^2}}{\sqrt{(\omega C_r)^2 + (\sigma_r)^2}} V_i$$

Where V_i is the input voltage for the dielectric circuit sensor [1], C_r and C_x are the capacities of the sample and reference capacitors, respectively, and σ_r and σ_x are the conductivities of the capacitors.

Results and discussion

The experimental results are given in Figs 1 to 4. All curves exhibit two peaks. The first, a negative one ($\Delta V_0/\Delta T<0$), indicates a decrease in V_0 related to an increase of the impedance modulus ($|Z_x|$) in spite of a decrease in C_x related to water desorption during heating (the adsorbed water molecules contribute fundamentally to zeolite polarization in an electric field [4]). The second peak ($\Delta V_0/\Delta T>0$) is related mainly to ionic conductivity in the zeolite, which induces a decrease in Z_x and consequently an increase in V_0 with heating because of an increase in σ_x.

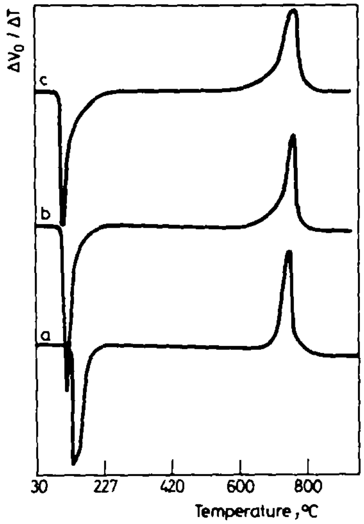

Fig. 1 Thermo-dielectrical curve ($\Delta V_0/\Delta T$ vs. T) of; a: HC, b) CC1 and c: CC2

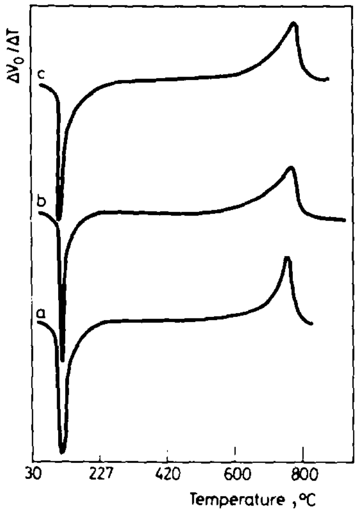

Fig. 2 Thermal curve ($\Delta V_0/\Delta T$ vs. T) of; a: MC1, b: MC2 and c: MP

Both peaks characterize the zeolites in thermo-dielectric analysis. However, notwithstanding the similarities, some individual peculiarities related to structure, ionic content, ionic radii and valence should be mentioned; for example, the sodium and calcium forms exhibit different separations of the two peaks (Fig. 4). This could be explained by the well-known fact that the ionic conductivity of sodium zeolites is higher than that of calcium zeolites [4]. On the other hand, clinoptilolite and mordenite, with an ionic capacity of 2.0–2.3 mequiv/g of zeolite and a pore size less than those of X and Y zeolites, and Zeolites X, Y and A, with an ionic capacity from 4.0 to 5.5 mequiv/g of zeolite, give different separations between the peaks; the difference is less for synthetic zeolites than for natural ones, which is a consequence of the different pore size and ionic capacity.

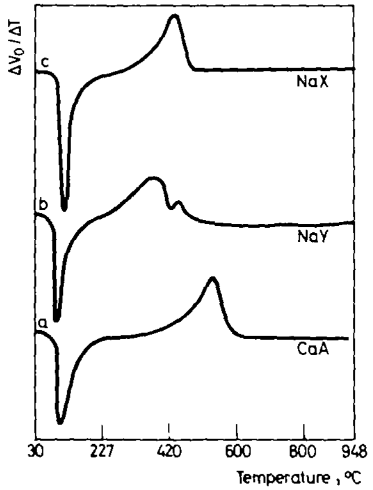

Fig. 3 Thermal curves of synthetic zeolites

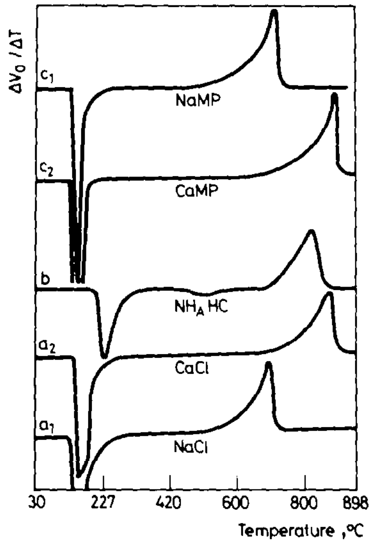

Fig. 4 Thermal curves of homoionic sodium, calcium and ammonium clinoptilolite-heulandite and sodium and calcium mordenite

In short, thermo-dielectric analysis is a useful tool in the study and characterization of zeolites. It permits the identification of different forms of these compounds, and allows inferences about the cationic compositions of different samples.

References

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Zusammenfassung — Einige natürlich und synthetische Zeolithe (Klinoptilolit, Mordenit, *X*, *Y* und *A*) wurden mittels thermodielektrischer Analyse untersucht. Zwei Effekte wurden beobachtet. Der eine ist mit der Abgabe des Wassers verbunden und spiegelt sich in der Abnahme der dielektrischen Konstante wider, der zweite ist durch ionische Leitfähigkeit bei hohen Temperaturen bedingt. Zeolithe können durch beide Effekte charakterisiert werden.

Резюме — С помощью термо-диэлектрического анализа изучены некоторые природные и синтетические цеолиты (клиноптилолит, морденит, *X*, *Y* и *A*). Результаты исследования указали на существование двух эффектов, один из которых связан с выделением воды и проявляющийся в уменьшении диэлектрической постоянной. Второй пик связан с наличием ионной проводимости при высокой температуре. Оба пика являются характерными для цеолитов в термо-диэлектрическом анализе.