

Dielectric properties of faujasites: comparison between types X and Y during dehydration

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Abstract

The dielectric properties of two faujasites, X and Y, were studied in a wide range of frequencies (10–10⁶ Hz) at several temperatures and for various outgassing temperatures TT (100–400°C). Conductivity measurements were undertaken with the aim of describing the possible mechanisms of conduction in these materials. The polarization conductivity is ascribed to the cations in the large cages (supercages). The d.c. conductivity is related to the migration of the exchangeable cations over relatively large distances. The corresponding activation energies vary from 0.58 to 0.9 eV for NaX and from 0.61 to 0.85 eV for NaY. These energies vary with TT in a different way for each zeolite. Two relaxation domains, attributed to the cations on sites II and III', are a function of the dehydration temperature. The activation energies are 0.41–0.58 eV. These two processes are shown by the technique of the thermally stimulated currents–relaxation map analysis. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Complex impedance spectroscopy (CIS) can assist in understanding the movement of cations in zeolites at different degrees of hydration [1], since the movement of the charge carriers can be analyzed by two techniques of relaxation. In the

first, the CIS refers to the action of an alternating field applied to the solid. In the second, the thermally stimulated currents (TSC) technique, the applied electric field is static, and relaxation is obtained by a temperature rise. The two methods provide complementary information about the dielectric properties and allow the investigation of the orientation polarization which corresponds to a hopping process.

Zeolites very easily adsorb a given amount of water without topological modification of their aluminosilicate framework, and the degree of hydration is relevant for most zeolite properties

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and applications. Dielectric properties of anhydrous and hydrated zeolites have been studied extensively. Information about the electric field affecting cations in hydrated and fully dehydrated faujasites (zeolites X and Y) has been collected by Mortier and Schoonheydt [2]. Indeed, the dielectric properties of zeolites strongly depend on the amount of adsorbed water [3,4]. Nevertheless, experiments on zeolites at various water contents have been limited to hydration levels not lower than 65% [5], and the pattern of evolution of dielectric properties as a function of the degree of hydration has been clearly established. In faujasites X and Y, multiple domains of relaxation were observed near ambient temperature for dehydrated [3–9], hydrated or partially hydrated zeolites [10–12]. No agreement was reached in the literature concerning interpretations of the double relaxation pattern.

Thus, in hydrated zeolites, Matron et al. [13] assigned two relaxations to cations located in different sites, while Jansen and Schoonheydt [8] and Schoonheydt et al. [12] considered that the two relaxations correspond to a Maxwell–Wagner effect at low frequency and to cation relaxation at high frequency. In hydrated zeolites, two relaxations were attributed to the exchangeable cations, the water molecules or the Maxwell–Wagner effect [8,12,13]. In recent work [1,10,14], we described several examples of conductivity in zeolites, due to the migration of exchangeable cations.

Surprisingly different values for the d.c. activation energies, E_{dc} , depending on the hydration state of zeolites X and Y, have been reported by several authors. A decrease of E_{dc} with increasing water content has sometimes been observed [3,15] when an opposite effect is also reported for the same solids [16]. Constant values of E_{dc} are also mentioned for a zeolite X [9,11], whereas increasing values of the same parameter are reported under the same conditions [13].

To solve the literature disagreement on this point, and to obtain an insight into the processes and the mechanism of conduction, it appears interesting to compare two zeolites of the faujasite type by using two complementary techniques, viz. CIS and the technique of TSC. Comparison between the results obtained by the two techniques and the

known cation positions of these zeolites enables us to ascribe all relaxations to cations located on energetically different sites. We follow the evolution of the two relaxation domains with the state of hydration of the zeolites to explain the differences in the electric behavior between zeolites X and Y.

2. Experimental methods

Two faujasites were used: (1) NaX provided by Aldrich, (2) NaY synthesized according to Ref. [17]. The anhydrous compositions determined by chemical analysis are the following: $\text{Na}_{84}(\text{AlO}_2)_{84}(\text{SiO}_2)_{108}$ for NaX corresponding to $\text{Si}/\text{Al}=1.29$ and $\text{Na}_{61}(\text{AlO}_2)_{61}(\text{SiO}_2)_{131}$ for NaY corresponding to $\text{Si}/\text{Al}=2.12$. The crystallinity of the samples was verified by X-ray diffraction.

Zeolite powder was compacted under a pressure of 2.5×10^8 Pa in the form of pellets 13 mm in diameter and 1.2 mm in thickness, the compactness being 0.87. Electric contacts were deposited by sputtering a platinum film on the surface of the pellet. In order to measure the polarization conductivity, a measuring cell was used allowing measurement under vacuum. The set-up is equivalent to an electrical circuit represented by a resistance and a capacitance in parallel [18].

The sample was equilibrated at a relative humidity of 48%. It was heated under vacuum (1 Pa) at different outgassing temperatures (TT) varying from 100°C up to 400°C in steps of 50°C, and maintained at the chosen temperature for 24 h.

The conductivity measurements were made under vacuum as a function of frequency at different temperatures, which obviously cannot exceed TT. The application of a sinusoidal electrical field allows the measurement of the real and imaginary parts of the electrical permittivity. The pellets were evaluated by measuring, respectively, the components in phase and the components shifted by 0.5π with regard to the voltage imposed. This is achieved using an analyzer (HP 4192 A) in the frequency range from 10 Hz to 10 MHz. The input impedance of the analyzer is greater than 10 M Ω and its sensitivity of 1.2 pF allows an accuracy of $\pm 3.5\%$ to be obtained [19].

TSC experiments were also performed on the same samples. These experiments were carried out under He with a TSC/RMA spectrometer (Solomat type 91000+) covering the temperature range from -170°C to 400°C . This method has been described in detail elsewhere [20–22]. We give here some indications of the principle of the thermally stimulated depolarization (TSDC) current method.

The TSDC method consists of determining, following a strictly controlled temperature program, the current created by the return to an equilibrium state of a dielectric sample which has been previously polarized. The following steps of polarization and depolarization are generally required when the relaxation spectrum of a material is desired in a temperature range from T_p to T_0 :

1. heating to the polarization temperature T_p ;
2. application of a d.c. electric field E_p for a time t_p long enough to saturate the various polarization processes involved;
3. rapid cooling in the field to the temperature T_0 ;
4. cutting off the external field and linear heating of the short-circuited sample.

The TSDC spectrum (i.e. the current induced by depolarization of the sample during heating) is measured during this last step.

In practice, unless otherwise specified, we have adopted T_p values lower than T_T so that the water content of the sample was not significantly affected during the TSDC run. Other experimental parameters were as follows: $t_p = 2$ min; $T_0 = -160^{\circ}\text{C}$; $E_p = 3 \times 10^5 \text{ V m}^{-1}$; heating rate $b = 10 \text{ K min}^{-1}$.

The method of thermally stimulated polarization current (TSPC) is the natural complement of the TSDC technique. It is based on the opposite process, i.e. measuring the currents generated by the build-up of a polarized state in a dielectric (external field applied during heating). It has been used to check the intrinsic nature of the relaxations observed.

These TSDC and TSPC methods are ‘global’ techniques allowing a complete picture of the temperature-dependent relaxations to be observed in one experiment. Their performances can further be markedly increased when used in a fractional

analytical mode (relaxation map analysis, RMA), allowing progressive isolation of a series of sub-relaxations corresponding to quasi-elementary motions [20,21]. For that purpose, only a fragment of the TSDC spectrum of relaxation is polarized by a windowing effect which allows the isolation of a single relaxation mode. The repetition of this process and the variation of the polarization temperature allow the isolation of the corresponding elementary relaxation modes one by one. Each elementary relaxation curve can be transformed into its Arrhenius representation (not given here) which expresses the variation of the relaxation time with temperature [20,23]. The slope of each straight line gives the activation energy of the process.

In order to analyze specific regions of the TSDC spectrum, all these methods were used to some extent, namely TSDC and TSPC global experiments as well as thermal windowing experiments for RMA analysis. Blocking electrodes ($10 \mu\text{m}$ thick Teflon® foils) were used to prevent electrode polarization and injection effects.

It has already been shown that the techniques of polarization conductivity and of TSDC are complementary [24,25].

3. Results and discussions

3.1. D.c. conductivity

Fig. 1 shows the typical evolution of the total conductivity measured as a function of frequency f . Measurements at several temperatures are reported for the same outgassing temperature ($T_T = 400^{\circ}\text{C}$) on zeolites X and Y. For clarity, only some of the curves are presented. They show that the total conductivity measured with an a.c. current can be expressed by

$$\sigma_{ac}(\omega) = \sigma_0 + \sigma'(\omega), \quad (1)$$

where $\omega = 2\pi f$ is the circular frequency of the applied field. This decomposition into two terms is very clear in the case of NaX, and for measurements performed at relatively high temperatures. Eq. (1) is mathematically justified, if σ_0 and $\sigma'(\omega)$ are strictly independent contributions.

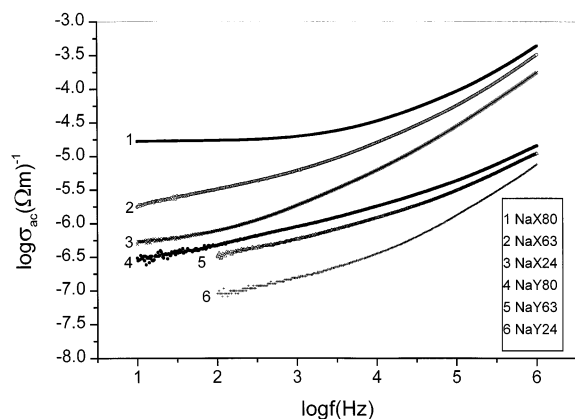


Fig. 1. Evolution of the total conductivity, σ_{ac} , as a function of frequency for NaX and NaY (TT=400°C), for different temperatures (the suffix to the zeolite indicates the temperature of measurement in °C).

The component σ_0 is the diffusive part of conductivity due to displacements of charge carriers over relatively large distances. It corresponds to the limit of σ_{ac} when ω tends towards 0. $\sigma'(\omega) = A\omega^s$ is the dispersive part of the conductivity. The exponent s is a function of temperature and frequency, and generally varies between 0 and 1. Parameter A depends on temperature [1]. The complex impedance diagrams can show the influence of the electrodes on the electrical measurements. For dehydrated zeolites the complex diagram does not show any particular features. However, for the hydrated solids, the low frequency part of the diagram is modified due to the diffusive component of the conductivity. The high frequency domain was limited to 10^6 Hz to avoid electrode effects, but they cannot be completely eliminated.

Compared with other ionic crystalline solids, zeolites have a high electric conductivity [3,26]. This conductivity results from the great mobility of the exchangeable cations. Thus zeolites can be regarded as weak electrolytes. Their conductivity is of an ionic nature and stems from the migration of the cations between close sites. For all treatment temperatures, we found that NaX zeolite is more conducting than zeolite Y, which is the expected behavior, if the assumption is made that the charge carriers responsible for conductivity are the

exchangeable cations (Na^+ ions). Indeed, NaX zeolite contains more Na^+ ions than NaY (84 exchangeable cations versus 61). When the Si/Al ratio increases (passing from faujasite X to Y), there is a reduction in the number of negative charges per unit of volume and thus the distance between negative charges becomes larger. This would imply a lower probability of finding a free site at a given distance and results in a reduction in measured total conductivity. Thus, the total conductivity measured on NaX at 24°C is higher than that measured on NaY at 80°C. The latter being practically insulating at ambient temperature after a heat treatment at 400°C, the points obtained at very low frequencies have not been represented in Fig. 1.

For relatively high measuring temperatures, the value of the d.c. conductivity, σ_0 , can be determined from the low frequency part of the a.c. results, as will be shown. Usually, the evolution of σ_0 with temperature follows the Arrhenius law (in fact, the theory of Nernst and Einstein [27]), showing that σ_0 depends both on the number of charge carriers and the activation energy E_{dc} :

$$\sigma_0 = \frac{B}{T} \exp\left(-\frac{E_{dc}}{kT}\right), \quad (2)$$

where B is the pre-exponential factor which contains the number of charge carriers and the hopping distance [27], and k is the Boltzmann constant. Parameter B is sometimes developed following very well known models. The number of charge carriers can be evaluated if the hopping distance and the phonon frequency (for example) are chosen. In this work we prefer to avoid assumptions concerning these parameters and discuss the activation energy.

Fig. 2 represents the evolution of the measured d.c. conductivity at 150°C for various treatment temperatures (TT). Indeed, near this temperature of measurement, the d.c. component is always present for all treatment temperatures of the two zeolites. It can be noted that, at each treatment temperature, the conductivity, σ_0 , obtained on NaX is higher than that obtained on NaY, as mentioned above. The difference in conductivity is

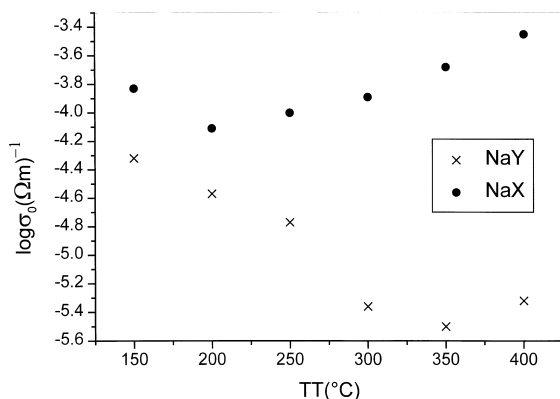


Fig. 2. Evolution of d.c. conductivity measured at 150°C as a function of TT for NaX and NaY (the measurement error is represented within the boundaries of each data point).

smaller for the lowest temperatures of dehydration, and increases considerably with TT.

Indeed, during dehydration, the conductivity of NaY strongly decreases whereas, in the case of NaX, only a weak variation is observed. This different behavior can be related to a different displacement of cations during dehydration [28–31]. The extra-framework sites III and III' in the supercage are coordinated to fewer lattice oxygen atoms and more water molecules than the sites I or II. As a consequence, the occupation of sites III and III' becomes energetically less favored when hydration decreases. Na⁺ cations in these positions tend to move to the more stable sites II in the six-membered rings between the supercages and the sodalite cages. In the case of zeolite X, sites II are already completely occupied by Na⁺ cations, and dehydration scarcely affects the number of cations in sites II, III and III' [30,31]. In the case of zeolite Y, occupation of site II is 35% in the hydrated form, and dehydration brings about a massive displacement of cations from sites III and III' to the available sites II [32]. In dehydrated Y, sites II are 97% occupied and only five Na⁺ cations per cage can still be localized in the supercage.

Thus, the differences in the conductivity behavior are explained by the fact that in NaX the number of charge carriers hardly changes, and only the electrostatic interactions with the oxygen atoms of the network are modified. Conductivity

strongly decreases in faujasite Y because there are very few charge carriers left in the dehydrated zeolite. Whatever the cation position, the average number of water molecules coordinated to each cation evolves in a different way for zeolites X and Y. At TT lower than 150°C more water molecules per cation are present in zeolite Y than in zeolite X, as shown in Fig. 3. Around 150°C, both zeolites retain one water molecule per cation, and at higher TT zeolite Y is dehydrated more easily than zeolite X. Implications of this trend can be observed in the activation energy of conduction.

If we suppose that the activation energy is independent of temperature, as it is usually the case, then Eq. (2) implies that the function $\ln(\sigma_0 T) = f(T^{-1})$ leads to a linear dependence, the slope of which is E_{dc}/k . Experimentally, we found this approximation valid for all the samples at all dehydration temperatures. For each TT, the activation energy, E_{dc} , is determined. The variations of the activation energies with the outgassing temperature are presented in Fig. 4. They vary from 0.61 to 0.85 eV for NaY and from 0.58 to 0.90 eV for NaX. It is the energy necessary for an ion to move from its site towards another vacant site.

In the case of NaX, the activation energy increases when TT varies from 100 to 150°C, then strongly decreases when TT passes from 150 to 400°C. NaY presents a practically opposite evolution. Although NaX is more conducting than NaY (see Figs. 1 and 2), the activation energy obtained on NaX is not always lower than that obtained on NaY. In fact, in this process, activation energies

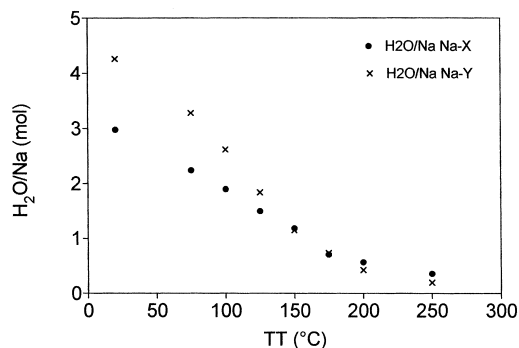


Fig. 3. Number of water molecules coordinated to each sodium atom as a function of TT.

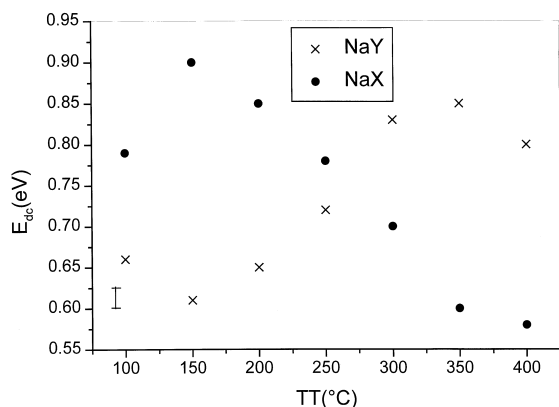


Fig. 4. Variation of the activation energy, E_{de} , as a function of TT for NaX and NaY (the bar represents the mean error for the data set).

alone do not account directly for the conducting character of a sample. The values obtained on the fully dehydrated solids (TT=400°C) are in excellent agreement with those already reported and justified by considerations based on the cation–framework interaction [2]. However these values (especially that of NaY) are different from those reported by Haidar and Jonscher [5].

As mentioned above, because of the Si/Al ratios of the two zeolites, NaX and NaY show a different behavior of σ_0 . The number of negative charges of the network to be compensated is low in the case of the faujasite Y, compared with that of faujasite X. This mainly concerns sites III' which are particularly involved in the electrical transport process. As a consequence, there is a decrease in the number of the exchangeable cations when passing from faujasite X to Y. This reduces the probability of the hopping process at a given distance. Therefore, during dehydration, not only is a correlative decrease of σ_0 expected, but also an increase in the potential barrier (represented by the activation energy) to be crossed by the cation during its diffusive phenomenon.

3.2. Relaxation

In Fig. 1, it can be seen that starting from a given frequency, the polarization component is more important than the d.c. component. It

changes as a function of frequency according to the law $\sigma(\omega, T) = A\omega^s$ [33], and s is a function of T and ω . The factor A , commonly used as an adjustable parameter to fit the law $A\omega^s$, leads to very dispersed values for zeolites. We therefore chose to work in terms of domain of relaxation and TSDC.

The shape of the curves obtained on zeolites X and Y suggests the presence of more than one relaxation process. Fig. 5 shows, as an example, for various outgassing temperatures, the conductivity measured on zeolite Y at 63°C. Two processes of relaxation are observed. One which appears at low frequency and another at relatively high frequency as shown in Fig. 5 (the arrows indicate, as examples, the limit of the two domains of relaxation for particularly favorable cases, easy to visualize. For high TT only the high frequency component is visible).

It should be noted that these phenomena correspond to the localized movement of charge carriers and can be considered as hopping of exchangeable cations around their equilibrium position. Several interpretations have been proposed to account for this double process. According to the authors, the two relaxations do not arise from the same species. In the analysis presented it is assumed that the cation movements are not correlated. This implies that the discussion does not take into account the notion of energy distribution assigned to possible cooperative motion of the ions.

Based on structural considerations, we ascribed

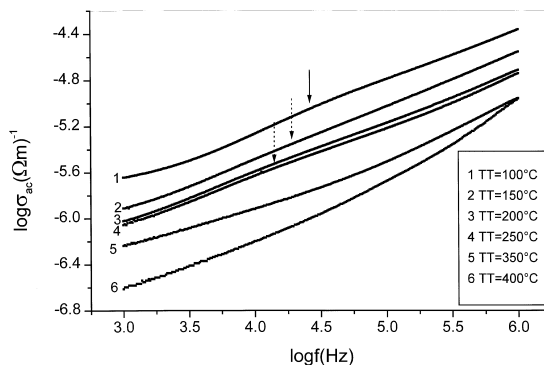


Fig. 5. Plots of $\sigma_{ac} = f(\text{frequency})$ showing two relaxation domains for NaY; the measuring temperature is 63°C (the arrow indicates the peak separating the domains of relaxation).

[28–32] the low frequency relaxation to the cations of sites II, and the high frequency relaxation to the cations of sites III'. It should be noted that in NaX, which is highly conducting, low frequency relaxation is often masked by the d.c. conductivity, unless the measurements are carried out at low temperature (for higher temperatures, high impedance electrodes can be used [34]). For a given TT, and at low measuring temperature, two relaxations are observable for NaX, whereas for NaY the high frequency relaxation only is visible. When the measuring temperature increases, the low frequency relaxation can also be detected. The two dehydrated zeolites (outgassed at $TT=400^{\circ}\text{C}$), show only one process of relaxation at ambient temperature. This relaxation assigned to the cations of sites III' is characterized by an activation energy of 0.38 and 0.40 eV for NaX and NaY, respectively. This is obtained from plots of $\sigma'(\omega)=f(T^{-1})$ at constant frequency. These results are in agreement with the interpretation of Jansen and Schoonheydt [8] who attributed the relaxation of faujasite zeolites, at ambient temperature, to the relaxation of cations of sites III' with activation energies ranging from 0.31 to 0.44 eV. These results are also consistent with those of Matron et al. [13], who characterized the high frequency relaxation by an activation energy of 0.42 eV.

The values obtained for dehydrated NaX and NaY, and the shape of the experimental curves, enable us to conclude that, in the dehydrated state, the two zeolites have comparable mechanisms of conduction. The transport properties are due to short distance hopping of exchangeable cations from sites III' and II. The acceptor sites could be sites of comparable character.

Our assumptions were confirmed by the results of the TSC/RMA measurements. Fig. 6(a) reports the spectra obtained on two outgassed zeolites ($TT=150^{\circ}\text{C}$). They represent in fact the current generated by depolarization of the sample according to the temperature (see Section 2). It may be seen from this figure that the spectrum corresponding to NaY is significantly moved towards higher temperatures, i.e. high energies compared with the spectrum of NaX. In the case of samples outgassed at 250°C (Fig. 6(b)), this displacement is more pronounced. The TSC/RMA technique shows that

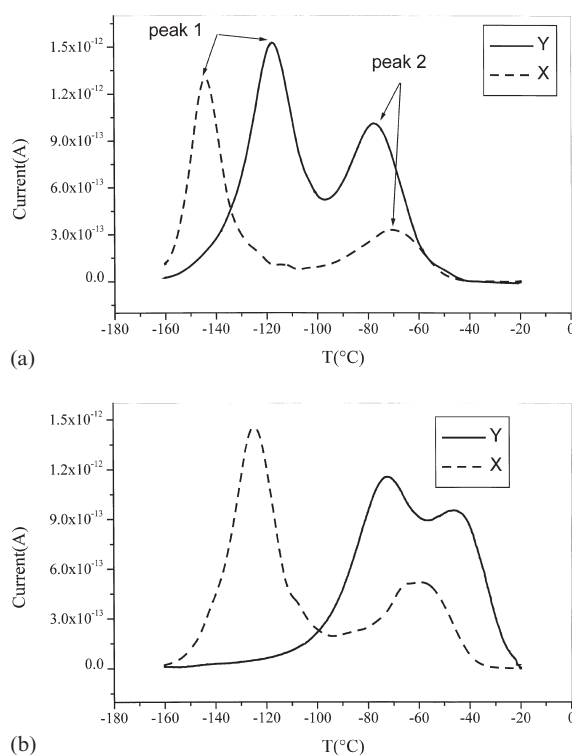


Fig. 6. (a) TSDC spectra at $TT=150^{\circ}\text{C}$ for NaX and NaY ($E_p=3 \times 10^5 \text{ V m}^{-1}$, $T_p=-20^{\circ}\text{C}$, $t_p=2 \text{ min}$, $T_0=-160^{\circ}\text{C}$, $b=10 \text{ K min}^{-1}$). (b) TSDC spectra at $TT=250^{\circ}\text{C}$ for NaX and NaY ($E_p=3 \times 10^5 \text{ V m}^{-1}$, $T_p=-20^{\circ}\text{C}$, $t_p=2 \text{ min}$, $T_0=-160^{\circ}\text{C}$, $b=10 \text{ K min}^{-1}$).

the peaks obtained are strictly of a dipolar nature. Such a technique also makes possible the determination of the energies associated with the various peaks. The activation energies found on NaX and NaY are reported in Table 1, where the values of the activation energies for three representative TT values are also given.

By associating relaxations implying stronger energies with the most attractive sites, we can ascribe peak 2 to the movements of cations on sites II (corresponding to low frequency relaxation observed in CIS) and peak 1 to the relaxation of cations located on sites III' (high frequency relaxation).

We observe in the case of NaX a weak variation of the energy of peak 1 with TT and a difference in the case of peak 2. In contrast, the energies corresponding to peaks 1 and 2 for zeolite Y

Table 1

Values of the energy corresponding to the TSDC peaks, as a function of TT (RMA determination)

Zeolite	E_{TSC} (eV) ± 0.02					
	TT = 150°C		TT = 250°C		TT = 400°C	
	peak 1	peak 2	peak 1	peak 2	peak 1	peak 2
NaX	0.41	0.47	0.43	0.54	0.43	0.53
NaY	0.42	0.48	0.50	0.58	0.46	0.54

increase as a function of TT. These energies are those associated with the displacements of the cations, which can be compared with reorientations of dipoles formed by the exchangeable cations and the oxygen atoms of the network. They correspond to an average value since not all the dipoles are identical. For low TT, the cations are in interaction with the oxygen of the network and the water molecules. As a general rule, when TT increases, the localization of Na^+ cations is modified. The higher energies observed for NaX and NaY, corresponding to peak 2, reflect the coordination of the cations on sites II. The energies of peak 1 are comparable for NaX and NaY at low TT and there is a clear difference at TT = 250°C. This evolution is characteristic of the difference in the behavior of Na^+ on sites III' in the two zeolites. These results seem to limit the importance of the water molecules involved in the mechanism of the movement of the ions. This can appear surprising, but it is emphasized that we used here an analysis based on relaxation processes. These results lead to the conclusion that, from the dehydrated state, the water molecules do not have an essential action in the phenomenon of dipolar orientation (i.e. in the hopping process) of the cation in interaction with its site. Naturally, the present work concerns a restricted view of the hydration phenomenon through two complementary techniques of relaxation.

4. Conclusion

Associating two complementary spectroscopic methods, the evolution of the dielectric properties of two faujasites according to the temperature of

dehydration has been followed. The difference in the number of exchangeable cations between zeolites X and Y is representative of the differences between these solids with regard to d.c. conductivity and activation energy E_{ac} . In the two zeolites, two relaxation processes were identified and assigned to cations in the large cages (supercages). These relaxations occur in domains depending on the dehydration temperature and according to the zeolite considered. The difference in behavior is mainly ascribed to the difference of the number of charge carriers on sites II and III' and to the cation–oxygen interactions.

References

- [1] A. Abdoulaye, S.Sh. Soulayman, G. Chabanis, J.C. Giuntini, J.V. Zanchetta, *Microporous Mater.* 8 (1997) 63.
- [2] W.J. Mortier, R.A. Schoonheydt, *Prog. Solid State Chem.* 16 (1985) 1.
- [3] D.N. Stamires, *J. Chem. Phys.* 36 (1962) 3174.
- [4] D. Vuccelic, N. Jecranic, *J. Inorg. Nucl. Chem.* 38 (1976) 2091.
- [5] A.R. Haidar, A.K. Jonscher, *J. Chem. Soc., Faraday Trans. 1* 82 (1986) 3535.
- [6] J.C. Carru, P. Tabourier, J.M. Wacrenier, *J. Chim. Phys.* 88 (1991) 307.
- [7] J.M. Wacrenier, J. Fontaine, A. Chaption, A. Lebrun, *Rev. Gener. Electr.* 76 (1967) 719.
- [8] F.J. Jansen, R.A. Schoonheydt, *J. Chem. Soc., Faraday Trans. 1* 69 (1973) 1338.
- [9] U. Lohse, H. Stach, M. Hollnagel, W. Schirmer, *Monatsber. Dtsch. Akad. Wiss. Berlin* 12 (1970) 828.
- [10] A. Abdoulaye, G. Chabanis, J.C. Giuntini, J. Vanderschueren, J.V. Zanchetta, F. Di Renzo, *J. Phys. Chem. B* 101 (1997) 1831.
- [11] U. Lohse, H. Stach, W. Schirmer, *Z. Phys. Chem.* 254 (1973) 59.

- [12] R.A. Schoonheydt, W. De Wilde, F. Velghe, *J. Phys. Chem.* 80 (1976) 511.
- [13] W. Matron, G. Ebert, F.H. Müller, *Kolloid Z. Z. Polym.* 248 (1971) 986.
- [14] S. Devautour, H. Schaefer, J.C. Giuntini, F. Henn, J.V. Zanchetta, *Ionics* 3 (1997) 373.
- [15] D.C. Freeman, D.N. Stamires, *J. Chem. Phys.* 35 (1961) 799.
- [16] F.J. Jansen, R.A. Schoonheydt, *Adv. Chem. Ser.* 121 (1973) 96.
- [17] F. Di Renzo, F. Fajula, F. Figueras, M.A. Nicolle, T. Des Courrières, in: M.L. Occelli, H. Robson (Eds.), *Synthesis of Microporous Materials Vol. 1*, Van Nostrand-Reinhold, New York, 1992, p. 105.
- [18] J.C. Giuntini, J.V. Zanchetta, I. Brach, S. Diaby, in: H. Charcosset (Ed.), *Advanced Methodologies in Coal Characterisation*, Elsevier, Amsterdam, 1990, p. 185.
- [19] J.C. Giuntini, A. Jaboker, J.V. Zanchetta, *Clay Miner.* 20 (1985) 347.
- [20] J.P. Ibar, *Fundamentals of Thermally Stimulated Current and Relaxation Map Analysis*, SLP Press, New York, 1993.
- [21] J. Vanderschueren, J. Gasiot, in: P. Braunlich (Ed.), *Thermally Stimulated Relaxation in Solids*, Topics in Applied Physics Vol. 33, Springer, Berlin, 1979, p. 135. Chapter 4.
- [22] J. Van Turnhout, in: G.M. Sessler (Ed.), *Electrets*, Topics in Applied Physics Vol. 33, Springer, Berlin, 1980, p. 81. Chapter 3.
- [23] G. Chabanis, A. Abdoulaye, J.C. Giuntini, J.V. Zanchetta, J. Vanderschueren, I. Brach, *Ionics* 3 (1997) 23.
- [24] J.C. Giuntini, J. Vanderschueren, J.V. Zanchetta, F. Henn, *Phys. Rev. B* 50 (1994) 12489.
- [25] A. Doi, *J. Mater. Sci. Lett.* 3 (1984) 613.
- [26] G. Kelemen, G. Schön, *J. Mater. Sci.* 27 (1992) 6036.
- [27] R.C.T. Slade, H. Jinku, G.B. Hix, *Solid State Ionics* 57 (1992) 117.
- [28] G.N.D. Al-Ajdah, A.A. Al-Rished, B. Beagley, J. Dwyer, F.R. Fitch, T.K. Ibrahim, *J. Inclus. Phenom.* 3 (1985) 135.
- [29] B. Beagley, J. Dwyer, F.R. Fitch, M.A. Zanjanchi, *J. Inclus. Phenom.* 3 (1985) 143.
- [30] D.H. Olson, *Zeolites* 15 (1995) 439.
- [31] G. Calestani, G. Bacca, G.D. Andreetti, *Zeolites* 7 (1987) 54.
- [32] W.J. Mortier, E. Van den Bossche, J.B. Uytterhoeven, *Zeolites* 4 (1984) 41.
- [33] A.K. Jonscher, *Dielectric Relaxation in Solids*, Chelsea Dielectric, London, 1983.
- [34] J.C. Giuntini, J.V. Zanchetta, F. Salam, *Mater. Sci. Eng. B* 3 (1995) 75.