Application of the Electronegativity Equalization Method to the Interpretation of TSDC Results: Case of a Mordenite Exchanged by Na⁺ and Li⁺ Cations

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The work presented here proposes a new interpretative method for thermally stimulated depolarization current (TSDC) measurements. By applying the concept of electronegativity equalization to TSDC results, we show that it is possible to obtain an experimental evaluation of the chemical potential of the electrons of the exchanged cation and of the host site in zeolites. This step leads to an evaluation of the fundamental parameters, such as the effective hardness and electronegativity of the sites of zeolites. Such an approach gives an evaluation of the heterogeneity of the aluminosilicate surface and is applied, for the first time, to an exchanged hydrogen mordenite containing various amounts of substituted lithium ions or sodium ions. A relation betwen electronegativity and hardness and the acid–base properties of the zeolite is made possible.

I. Introduction

When an aluminosilicate sample containing cations is subjected to an electric field, a polarization is observed. This phenomenon is usually ascribed to the hopping of these ions, initially trapped in sites located on the surface of the crystal lattice of the solid.[1–3] We recently showed that the study of such a process, more commonly called dielectric relaxation, leads to the evaluation of the energy associated with the detrapping of the exchangeable ions.[4] This energy, in the case of zeolites or clays exchanged with monovalent cations, can be associated with the following chemical dissociation:

$$(\text{Site}^{\delta-}\cdots\text{M}^{\delta+}) \leftrightarrow \text{Site}^- + \text{M}^+ \tag{1}$$
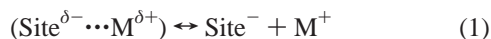
where M⁺ indicates the exchangeable cation, Site⁻ is the site, and (Site$^{\delta-}\cdots$M$^{\delta+}$) represents the chemical bond formed by the cation trapped in the zeolite site, which has a high degree of ionicity, indicated by the "*partial exchanged charge*" δ ($\delta \leq$ 1). This type of charge transfer was originally studied by Mulliken[5] and later by Parr and Pearson.[6] They have demonstrated that the corresponding electron transfer can be determined from the electronic chemical potential of the compound in the final state of eq 1. The determination of this chemical potential provides a quantitative measure of the ease with which the electrons leave one chemical species for another, to reach global equilibrium in the site–cation bound system. The purpose of this study is to show that the dielectric relaxation phenomenon, probed by means of thermally stimulated depolarization current (TSDC) measurements, and modeled by using the electrone-

gativity equalization criteria or charge sensitivity analysis methods (EEM),[7–10] can provide information about the chemical potential of the localized ion acceptor sites of the solid network.

II. Thermally Stimulated Depolarization Current Spectroscopy (TSDC)

II.1. Experimental Procedure. TSDC experiments were carried out under helium with a TSC/relaxation map analysis spectrometer (Solomat type 91000⁺), covering the temperature range −170 to 400 °C.

The TSDC method determines the current created by the return to the equilibrium state of a dielectric, which has been previously polarized, under a strictly controlled temperature program.[11,12] The experimental method used, detailed elsewhere,[11–13] can be briefly described as follows. The polarization and depolarization steps are generally required when the relaxation spectrum of a material has to be recorded within the temperature range $T_p - T_0$: (i) heating to the polarization temperature T_p; (ii) application of a dc electric field E_p for a time t_p of sufficient duration to obtain saturation of all the polarization processes involved; (iii) rapid cooling in the field to the temperature T_0; (iv) cutting off the external field and linear heating of the short-circuited sample. The TSDC spectrum reflects the current induced by depolarization of the sample during this step.

II.2. TSDC Analysis. Let us start with a summary of the essential elements of the TSDC method, which has been described in detail elsewhere.[4] Under isothermal conditions, one can consider that the elementary polarization $P(t)$ of an ideal system, characterized by a single relaxation time τ, follows a Debye-type behavior. The depolarization current density J_d is then expressed by[12–14]

$$J_d = -\frac{dP(t)}{dt} = \frac{P_0}{\tau}\exp\left[-\int_0^t \frac{1}{\tau}\,dt\right] \tag{2}$$

where P_0 represents the initial polarization.

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The relaxation time τ depends on temperature and the orientation energy of the dipoles ΔE, which represents the potential barrier to be crossed during the hopping process, according to the relation:

$$\tau = \tau_0 \exp\left[\frac{\Delta E}{kT}\right] \quad (3)$$

In this equation, k represents the Boltzmann constant and τ_0, the preexponential factor, is assumed to be a constant that depends on the nature of the studied dipole. It is the inverse of the vibration frequency of the particle trapped in its site. It can be shown,[4] by using a statistical thermodynamic calculation,[15] that its value depends on the mass of the ion, which relaxes, and on the environment in which it moves.

If the sample is heated at a constant rate q, the variable temperature T is related to the time t by the relation $T = T_0 + qt$. Finally, we can determine the depolarization current of an ideal system, characterized by a single relaxation time, as follows:

$$J_d(T) = \frac{P_0}{\tau_0} \exp\left[-\frac{\Delta E}{kT}\right] \exp\left[-\frac{1}{q\tau_0} \int_{T_0}^{T} \exp\left[-\frac{\Delta E}{kT}\right] dT\right] \quad (4)$$

In real systems, a distribution of relaxation times must be considered. It corresponds to a distribution of energies $G(\Delta E_i)$ so that the total depolarization current J_D is finally written as the sum of the contribution of each dipole i:

$$J_D(T) = \frac{P_0}{\tau_0} \sum_i G(\Delta E_i) \exp\left[-\frac{\Delta E_i}{kT}\right] \exp\left[-\frac{1}{q\tau_0} \int_{T_0}^{T} \exp\left[-\frac{\Delta E_i}{kT}\right] dT\right] \quad (5)$$

It is possible, by fitting the experimental curve to eq 5, to determine the distribution law $G(\Delta E)$ that characterizes the studied system. The results thus obtained provide an evaluation of the values of the most probable orientation energy.[4] To determine the physical significance of the parameters obtained from dielectric relaxation measurements, it is then necessary to propose a microscopic model of the polarization phenomenon due to the hopping process of an ion in the solid. As long as the ion remains located in its site, it is comparable to a particle maintained in a single potential well. Such a trapped charge carrier performs, under the effect of thermal motions, oscillating movements whose amplitude depends on the thermal fluctuations and the configuration of its environment. It is generally considered that these oscillations are harmonic as long as the charge carrier remains embedded in its potential well. Occasionally, due to thermal fluctuations, the particle can be expelled from its site. The cation can proceed to hop, if it reaches an activated energy state higher than that characterizing the state in which it remains trapped.[16] If this hop remains localized, it creates a polarization current and the experimental values ΔE are a measure of the energy required for each hop. This hopping mechanism is illustrated in Figure 1. Because of the thermal fluctuations, the distribution function $G(\Delta E)$ appears as a summation of Gaussian functions,[16] with the number of these functions being related to the nature of the studied compound.

II.3. Experimental Results Obtained on a Series of Hydrogen Mordenites, Exchanged by Sodium and Lithium Ions to Various Degrees. The examined samples consist of powders of protonated mordenite-type zeolites (symbolized by MOR−H), of general formula $H_{7.38}Al_{7.38}Si_{40.61}O_{96}\cdot27H_2O$. They
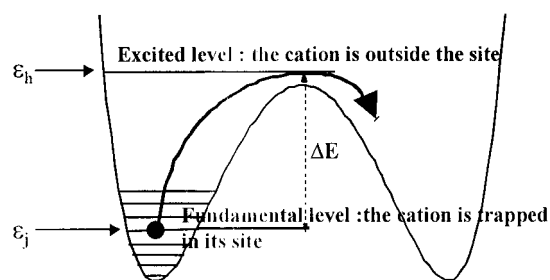
Figure 1. Schematic representation of the hopping process. ϵ_h and ϵ_j correspond to the excited and the fundamental levels, respectively.
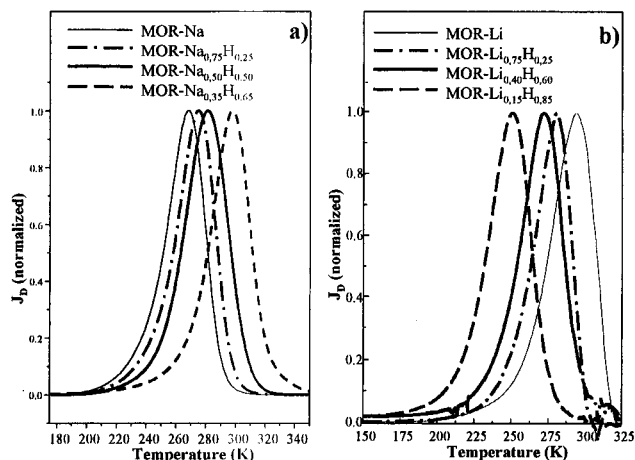

Figure 2. Evolution of the normalized depolarization current density $J_D(T)$ as a function of the sodium (a) and the lithium (b) exchanged degree.

were exchanged in water to various degrees with lithium ions[17] (MOR−Li_xH_{1-x}, where $x = 1$, 0.75, 0.4, and 0.15) and sodium ions (MOR−Na_xH_{1-x}, where $x = 1$, 0.75, 0.5, and 0.35). Disc-shaped pellets of 133 mm² diameter area and approximately 1 mm thickness were obtained by compressing up to 4×10^8 Pa. They were then heated at 200 °C under vacuum for 24 h. This heat treatment makes it possible to analyze samples, whose hydration rate, evaluated by thermogravimetric analysis, is equal to two water molecules per unit cell. We verified experimentally that the effect of the water molecules on dielectric relaxation from the exchangeable cations was shown to be negligible, i.e., the dielectric response is not modified by treatment temperatures higher that 200 °C.

Each exchanged mordenite was examined by TSDC. The corresponding spectra, showing the degree of exchange of lithium and sodium ions, are represented in Figure 2. Since the temperature domains of dielectric relaxation characterizing each reference system, MOR−H, MOR−Na, and MOR−Li (cf Figure 3), are sufficiently separate, we can state that the position of the maximum of the peak of the dielectric relaxation associated with each partially exchanged zeolite MOR−Na_xH_{1-x} and MOR−Li_xH_{1-x} is representative of the specific relaxation of the Na^+ and Li^+ ions, respectively.

By supposing that the dipole/dipole interactions are negligible, we consider that the energy levels ϵ_i, on which the charge carriers are in equilibrium, are distributed according to a function $g(\Delta E)$ of Gaussian type.[16] In the specific case of mordenites exchanged with lithium and sodium ions, the global distribution function $G(\Delta E)$, used to account for the experimental behavior of the relaxing dipoles, appears as the sum of three Gaussian functions $g(\Delta E)$.[17] For each Gaussian function, each specific parameter, such as the central value or the half-height width, is characteristic of the studied material.

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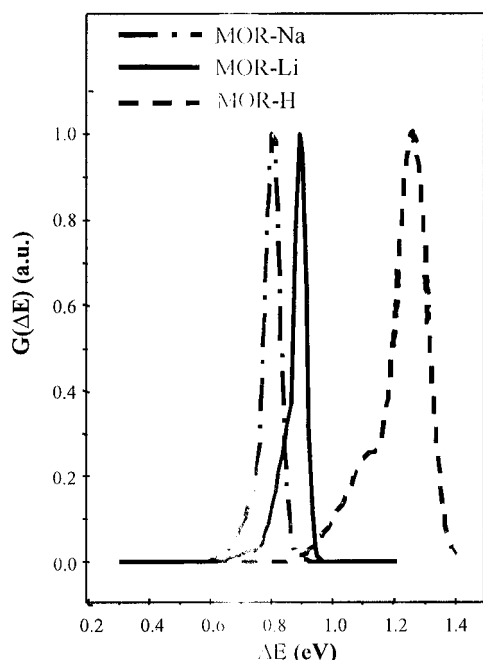
Figure 3. Comparison between the distribution functions of the energies, according to the nature of the extraframework cation.
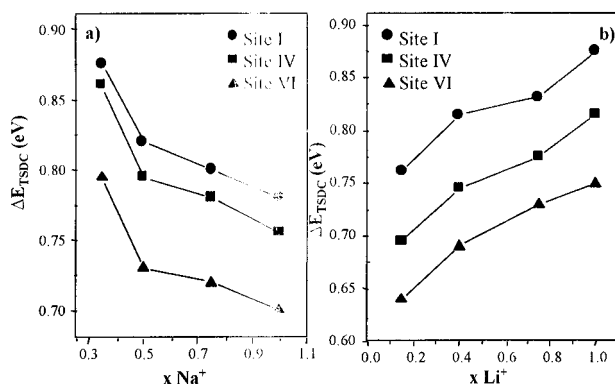
Figure 4. Evolutions of the energy obtained by the analysis of the TSDC spectra as a function of the sodium (a) and the lithium (b) exchanged degree, for the three occupied sites (($\bullet$) site I; ($\blacksquare$) site IV; ($\blacktriangle$) site VI).

We have shown previously that each one of these three central values, for each type of studied compound, is associated with the specific interaction of the considered ion with each type of occupied site of the zeolite.[17] Indeed, the environment of the occupied site modifies its characteristic energies and consequently the Gaussian function, which describes the density of the energy levels. A study of the coordination, geometry and bonding distances from the oxygen atoms constituting the site and the cation suggested the adoption of the following sequence of energies for MOR–Na or MOR–Li, since in each case, the lithium and sodium ions are localized in the same sites.[18-21]

$$\Delta E_{siteI} > \Delta E_{siteIV} > \Delta E_{siteVI}$$

The evolution of the energies thus obtained as a function of the Na$^+$ and Li$^+$ contents is represented in Figure 4. It may be noted that they differ according to the nature of the exchangeable cation. To explain this difference, it is necessary to evaluate the extent of the interaction between the exchangeable cation and the oxygenated network constituting the host site, according

to the nature of the cation and the zeolitic network. Since, in a general way, this type of interaction is related to the specific characteristics of the electron cloud of both interacting species, it is straightforward to introduce the concepts of electronegativity and hardness in the theoretical interpretation of these TSDC results.

III. General Analysis

The empirical concept of electronegativity was introduced to interpret the chemical properties of the elements of the periodic classification. The electronegativity measures the capacity of an atom engaged within a molecule to attract negative charges. Different scales exist. Pauling,[32] the first to introduce this concept, assigned a single value of electronegativity to each atom. Later, Sanderson[7] proposed another way of interpreting this parameter, postulating that when two atoms combine to form a molecule their respective electronegativities tend to be equalized via a charge transfer. This fundamental principle, improved by Parr and Pearson,[6] and finally extended by Mortier et al.,[9,10] allows for the qualitative and quantitative prediction of the intrinsic properties of the material studied,[8] starting from the estimated partial charge localized on the atoms of the molecule. Thereafter, Pearson[23] introduced another fundamental parameter, termed the chemical hardness η. It accounts for the capacity of the electron cloud to be modified. The issue is the determination, for any considered atom, of its aptitude to "resist" a modification of its electron cloud. Since the mechanism of dipolar reorientation can be viewed as a modification of charge distribution, we thus propose to apply here the electronegativity equalization method (EEM), initially developed by Nalewajski,[24,25] to the TSDC results, to evaluate the hardness and the electronegativity of the exchanged cations of the mordenite. Therefore, we need to extend the mathematical formalism, describing the electronegativity and the hardness of any chemical species forming an isolated entity, to the case of an ion introduced in a network.

III.1. Formation of a Single and Isolated Bond. The formation of a bond of the type of the chemical pseudoreaction, i.e., between two isolated ions, is done by means of a charge transfer ΔN:

$$\text{Site}^- + \text{M}^+ \leftrightarrow (\text{Site}^{\delta-} \cdots \text{M}^{\delta+})$$
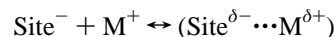
The energy of the electron cloud of both species is always related to the electron density. By making a second-order expansion near the reference state, for which the atom is isolated (its electronic population being equal to N_0 and its energy E_0), the electron cloud energy of the considered atom according to its electron population N, can be described by the following equation:[8]

$$E(\Delta N) = E_0 + \frac{\partial E}{\partial N}(\Delta N) + \frac{1}{2}\frac{\partial^2 E}{\partial N^2}(\Delta N)^2$$

$$\text{with } \Delta N = N - N_0 \quad (6)$$

The chemical potential $\mu = \partial E/\partial N$ and the hardness $\eta = \partial^2 E/2\partial N^2$ are respectively, the first and second derivatives of the energy according to the electronic charge localized on an atom (see Figure 5a). From the definition of the electronegativity χ given by Mulliken,[5] we note that this quantity is opposite to the chemical potential μ of the electrons.[26,27] μ_0 and η_0 are the chemical potential and the hardness of the species under consideration, in its reference state (for which the number of
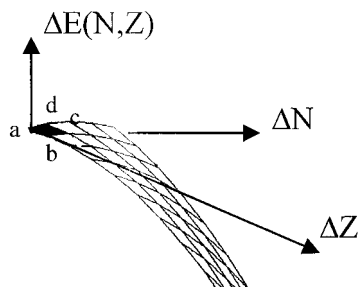
Figure 5. Evolution of the absolute value of the atomic energy as a function of the charge transfer and ΔN and the effective charge ΔZ perceived by an chemical species inserted in a network.

electrons of the electron cloud is equal to N_0 with $\Delta N = 0$), then eq 6 becomes:

$$E(\Delta N) = E_0 + \mu_0(\Delta N) + \eta_0(\Delta N)^2 \qquad (7)$$

Each state of the considered atom different from the reference state is thus characterized by a variation of the charge ΔN, representing the population of its electron cloud, and consequently by an energy $E(\Delta N)$. The chemical potential of the electrons is therefore:[6]

$$\mu = \frac{\partial E}{\partial N} = \mu_0 + 2\eta_0 \Delta N \qquad (8)$$

III.2. Case of the Interaction of an Atom (or a Group of Atoms) with the Network. We have shown previously that the exchangeable ions are trapped in sites, with which they interact.[17] To analyze this interaction more precisely, we consider that the chemical species cation + site is inserted in the zeolitic network, mainly composed of oxygen, aluminum, and silicon atoms. The site can be considered as a chemical species, which would have the geometrical characteristics, such as the position or the volume, of the cavity that receives the cation. It is supposed that the valence electrons of the oxygen atoms, located at the inner side of this cavity, constitute a cloud that is able to exchange a part of its charge with the cation. Since the partial charge, ΔN, received by the cation is identical to that given by the site, the electronic charge of the latter then varies by the quantity $-\Delta N$.

Contrary to the case where the system is isolated, the energy of the electron cloud of the cation, when it is trapped in its site, depends at the same time on the transfer of charge ΔN and on the external potential created by the nuclear charge due to the zeolitic network. According to the AIM model[24] (atom in a molecule), elaborated by Nalewajski, one can describe this situation by the following relation:[7,8,10,25]

$$dE = \left(\frac{\partial E}{\partial N}\right)_V dN + \int \left(\frac{\partial E}{\partial V(\vec{r})}\right)_N dV(\vec{r}) \, d\vec{r} \qquad (9)$$

where $V(\vec{r})$ is the external potential acting on the studied interaction cation–site and $\vec{r}$ represents the distance between the charges. The best current evaluation of the second term of eq 9 is obtained by ab initio calculations,[28–31] which require a knowledge of the number of electrons on each atom, the internuclear distances, the nuclear charges, and the distribution functions of these nuclear charges.

In our case, we did not attempt to determine this density function but to find its influence on the value of the electronic energy of both the exchangeable cation and its site. In a first approximation, this corresponds to describing the perturbations

caused by the electric field of the environment on the studied chemical species by means of an effective charge ΔZ.

Initially proposed by Nalewajski,[24,25] these considerations allow us to describe the evolution of the energy of the electron cloud of the studied species according to both variables, ΔN and ΔZ. This is obtained by a second-order expansion near the reference state already described.[10,25]

$$E(\Delta N, \Delta Z) = E_0 + \frac{\partial E}{\partial N}\Delta N + \frac{\partial E}{\partial Z}\Delta Z + \frac{1}{2}\frac{\partial^2 E}{\partial N^2}(\Delta N)^2 +$$
$$\frac{1}{2}\frac{\partial^2 E}{\partial Z^2}(\Delta Z)^2 + \frac{\partial^2 E}{\partial N \partial Z}\Delta N \Delta Z \quad (10)$$

By defining:

$$\nu = \frac{\partial E}{\partial Z}, \quad \alpha = \frac{1}{2}\frac{\partial^2 E}{\partial Z \partial N} = \frac{1}{2}\frac{\partial \mu}{\partial Z}, \quad \text{and} \quad \beta = \frac{1}{2}\frac{\partial^2 E}{\partial Z^2}$$

eq 10 becomes:

$$E(\Delta N, \Delta Z) =$$
$$E_0 + \mu_0 \Delta N + \nu_0 \Delta Z + \eta(\Delta N)^2 + 2\alpha \Delta N \Delta Z + \beta(\Delta Z)^2 \quad (11)$$

Nalewajski[32–34] showed that the parameters η, α, and β are similar to thermodynamic coefficients, connected to each other by Maxwell's relations. We approximate these coefficients by setting them to a constant value. In fact, this approach consists of approximating the evolution of $E = f(\Delta N, \Delta Z)$ within a small domain of variation by a parabolic function. The error thus introduced is likely to be smaller than the experimental error. More precisely, our problem consists of connecting the energy variations, evaluated by TSDC, with those that can be calculated by eq 11. The energy values obtained by TSDC, lower or slightly higher than 1 eV, are such that the experimentally explored domain is limited to the surface *abcd* (Figure 5). In this reduced energetic explored domain, the constant chemical hardness is called $\tilde{\eta}$.

III.2.1. Case of the Cation Trapped in a Zeolite Site. According to eqs 7 and 11, when the cation is in interaction with its host site, its energy E_c can be written[9,10,29] as:

$$E_c = E_{0c}^* + \mu_{0c}^* \Delta N + \tilde{\eta}_c \Delta N^2 \qquad (12)$$

In this expression, E_{0c}^* corresponds to the electronic energy of the cation, in its new reference state.[29] It corresponds to that of the untrapped cation, while remaining under the influence of the electric field of its surroundings, represented by the effective charge ΔZ_{0c}. Thus, E_{0c}^* represents the energy of the new reference state, due to the perturbation introduced by ΔZ_{0c} on E_{0c}, the electronic energy of the isolated cation. Therefore, eq 12 is similar to eq 7 but takes into account the surrounding system. Let us now consider the following expressions, obtained by comparison between eqs 11 and 12:

$$E_{0c}^* = E_{0c} + \nu_{0c}\Delta Z_{0c} + \beta_c \Delta Z_{0c}^2$$

$$\mu_{0c}^* = \mu_{0c} + 2\alpha_c \Delta Z_{0c}$$

$$\textit{and } \tilde{\eta}_c = \text{constant} \qquad (13)$$

Note that E_{0c}^*, μ_{0c}^*, and $\tilde{\eta}_c$ are independent of ΔN in these equations.

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The terms can be interpreted as follows:

(i) ΔZ_c and ΔZ_{0c} represent the surroundings effective charge influencing the energy of the trapped and untrapped cation, respectively. These parameters can be described by:

$$\Delta Z_c = f(\Delta Z_{(L/c)}, \Delta Z_{(s/c)}) \quad \text{and} \quad \Delta Z_{0c} = f(\Delta Z_{0(L/c)}, \Delta Z_{0(s/c)}) \tag{14}$$

where $\Delta Z_{(L/c)}$ and $\Delta Z_{(s/c)}$ (or by analogy $\Delta Z_{0(L/c)}$ and $\Delta Z_{0(s/c)}$) represent the effective charge perceived by the cation, which accounts for the influence of the zeolitic lattice and the site, respectively.

(ii) E_{0c}^*, μ_{0c}^*, and $\tilde{\eta}_c$ effectively account for the influence of the surroundings of the cation on the energy, the chemical potential, and the chemical hardness, respectively. For this reason, they can be called "*conditional variables*". They implicitly represent the perturbation introduced by the electric field of the zeolitic lattice and of the site on the behavior of the electron cloud of the cation.

(iii) E_{0c}^* and μ_{0c}^* represent the energy and the chemical potential of the electrons of the cation, taken in its reference state, when it is under the influence of the surroundings but not trapped in the host site. That means that no charge is exchanged between the cation and its site ($\Delta N = 0$).

According to eq 13, it is then possible to express the chemical potential of the cation, when it is trapped in its site, with which it exchanges a charge transfer ΔN, as:

$$\mu_c = \mu_{0c}^* + 2\tilde{\eta}_c \Delta N \tag{15}$$

III.2.2. Case of the Cation Acceptor Site. The behavior of the electron cloud of the host site is determined by the oxygenated network, located at the edges of the cavity. This means that it is under the influence of the electric field created by the surrounding charges induced by both the zeolitic network and the cation. This is now represented by the effective charge ΔZ_s, when the cation is trapped in the site, and ΔZ_{0s}, when the cation is detrapped from the site. The same approach as that used in the case of the cation can thus be proposed in the case of the site. By analogy with expressions 12−15, it is then possible to describe the electronic energy of the site by:

$$E_s = E_{0c}^* - \mu_{0c}^* \Delta N + \tilde{\eta}_s (\Delta N)^2 \tag{16}$$

with

$$E_{0c}^* = E_{0s} + \nu_{0s} \Delta Z_{0s} + \beta_s \Delta Z_{0s}^2$$

$$\mu_{0c}^* = \mu_{0s} + 2\alpha_s \Delta Z_{0s}$$

$$\tilde{\eta}_s = \text{constant} \tag{17}$$

and

$$\Delta Z_s = f(\Delta Z_{(L/s)}, \Delta Z_{(c/s)}) \quad \text{and} \quad \Delta Z_{0s} = f(\Delta Z_{0(L/s)}, \Delta Z_{0(c/s)}) \tag{18}$$

In these expressions, E_{0c}^*, μ_{0c}^*, and $\tilde{\eta}_s$ have the same meaning as in the preceding equations related to the cation, but assigned to the host site. ΔZ_s and ΔZ_c have different values.

Then, the chemical potential of the site, when it traps the cation, with which it exchanges a charge transfer equal to $-\Delta N$, is defined as:

$$\mu_s = \mu_{0c}^* - 2\tilde{\eta}_s \Delta N \tag{19}$$

III.2.3. Case of the Interaction Cation/Host Site. According to the EEM method, equilibrium is reached when the chemical potentials of the cation and the site with which it interacts are equal:

$$\mu_s = \mu_c \tag{20}$$

By replacing μ_s and μ_c by their respective expressions (eqs 15 and 19), the charge exchanged during the transfer of the cation from its reference state to its equilibrium state, i.e., the charge transfer, which occurs when the cation falls into the site, is written as:

$$\Delta N = \frac{\mu_{0s}^* - \mu_{0c}^*}{2(\tilde{\eta}_s + \tilde{\eta}_c)} \tag{21}$$

III.3. Interpretation of the TSDC Results. We have described the dielectric relaxation phenomenon, measured by TSDC, by the existence of hops of the exchangeable ions from one site to another.[1−3] It is considered that this hop corresponds to the transition that occurs between the initial state (for which the cation, localized in its site, has the electronic energy previously given equal to E_c), and the final state, where the cation is considered out of its site, but always under the effect of the electric field of the zeolitic network and the site. This final state is characterized by electronic energy E_{0c}^*. Similarly, it is supposed, by analogy, that the electronic energy associated with the host site when it releases the cation, changes from E_s, to E_{0s}^*.

As a consequence, the variation of energy determined in TSDC, ΔE_{TSDC}, corresponding to the cation hopping process, is the sum of two contributions:

$$\Delta E_{TSDC} = (E_{0c}^* - E_c) + (E_{0s}^* - E_s) \tag{22}$$

By replacing E_c and E_s of eq 22 by their respective expressions (eqs 12 and 16), the following relation is obtained:

$$\Delta E_{TSDC} = (\mu_{0s}^* - \mu_{0c}^*)\Delta N - (\tilde{\eta}_s + \tilde{\eta}_c)(\Delta N)^2 \tag{23}$$

If we consider an expression for the charge transfer between the site and the exchangeable cation, according to eq 21, one finds a relation similar to that initially derived by Parr and Pearson:[6]

$$\Delta E_{TSDC} = \frac{1}{4} \frac{(\mu_{0s}^* - \mu_{0c}^*)^2}{(\tilde{\eta}_s + \tilde{\eta}_c)} \tag{24}$$

With the aim of simplifying this expression, Nalewajski noted that, whatever the considered element (that it is an atom or a group of atoms) and its oxidation state, it can be assumed, in a first approximation, that:[25]

$$\frac{\mu^*}{\tilde{\eta}} = -C_N \tag{25}$$

where C_N is a constant. From the values reported by Nalewajski,[35] we fixed C_N equal to 1.24.

This permits the energy variation, evaluated by using the experimental measurements of the depolarization currents measured by TSDC, to be expressed in the following way:

$$\Delta E_{TSDC} = \frac{-C_N}{4} \frac{(\mu_{0s}^* - \mu_{0c}^*)^2}{(\mu_{0s}^* + \mu_{0c}^*)} \tag{26}$$

III.4. Application to a Na^+ and Li^+ Mordenite. Reference to the approach described in the previous section shows that the energy variation ΔE_{TSDC} depends on the effective potentials of the site and of the cation. However, we describe both quantities as being a function of the charge transfer ΔN between these two chemical species and of the effective charge ΔZ_c or ΔZ_s perceived by both species. In so far as it appears difficult to evaluate this last parameter without having recourse to ab initio calculations, we chose to observe its influence on the energy variation, without determining its exact value. For that purpose, we assume that ΔZ_c or ΔZ_s, which account for the electric field introduced by all the charges of the surroundings near the cation and the site, are closely related to the degree of exchange of the zeolite and thus to the nature of the exchanged cation. We then suppose, referring to the usual expression of ΔZ,[36] that for sufficiently high degrees of exchange of Na^+ and Li^+ ions, the variation of ΔZ_c, as an example, is sufficiently weak to be described by an expression of the form

$$\Delta Z_c = \Delta Z_{1c}(1 + \epsilon) \quad \text{where} \quad \epsilon = k_c(1 - x) \quad (27)$$

In this case, ΔZ_{1c} corresponds to a reference value, for which the exchange degree x is equal to 1, and k_c is a constant characterizing the evolution of ΔZ_c following the nature of the considered cation. By analogy, it is possible to obtain the same relations in the case of the site. From these relations, it is easily seen that ΔZ_c and ΔZ_s vary as the degree of exchange does.

Considering the energy evolution ΔE_{TSDC}, evaluated by TSDC and according to the degree of exchange of H^+/Na^+ on one hand and of H^+/Li^+ on the other hand, (cf Figure 4), one notes that, within the interval $0.3 \leq x \leq 1$, whatever the nature of the site under consideration, we have:

$$\frac{\Delta E_{TSDC}(x) - \Delta E_{TSDC}(x=1)}{\Delta E_{TSDC}(x=1)} \leq 0,2 \quad (28)$$

It is thus possible to use the following limited expansion:

$$\frac{\Delta E_{TSDC}(x) - \Delta E_{TSDC}(x=1)}{\Delta E_{TSDC}(x=1)} \approx \ln \frac{\Delta E_{TSDC}(x)}{\Delta E_{TSDC}(x=1)} \quad (29)$$

We then evaluate the expression 26, knowing that the energy variation ΔE_{TSDC} is described by eq 22, in which μ_{0s}^* and μ_{0c}^* are replaced by their respective mathematical expressions. Defining $y(x)$ by:

$$\frac{\Delta E_{TSDC}(x) - \Delta E_{TSDC}(x=1)}{\Delta E_{TSDC}(x=1)} - \ln \frac{C_N}{4\Delta E_{TSDC}(x=1)} = y(x) \quad (30)$$
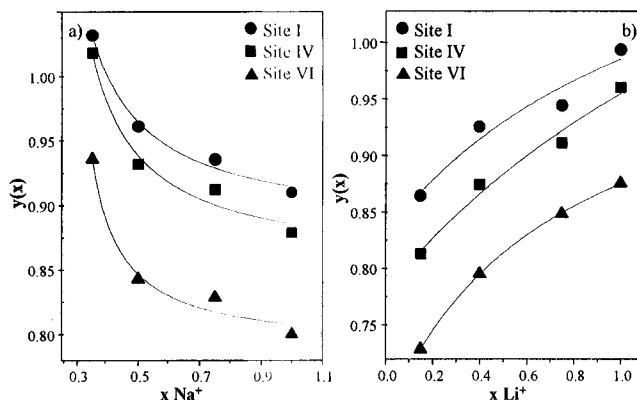
$y(x)$ can be written as:

$$y(x) = \ln\left(\frac{a + bx}{c + dx}\right) \quad (31)$$

with:

$$a + b = (\mu_{0s}^*(x=1) - \mu_{0c}^*(x=1))^2 \quad (32)$$

$$-(d + c) = \mu_{0s}^*(x=1) + \mu_{0c}^*(x=1) \quad (33)$$

The fitting of experimental results to eq 31, for $x \geq 0.3$, leads to the determination of the values of the effective electron chemical potential of the site and of the cation, for a totally exchanged mordenite sample ($x = 1$), when the cation and the

Figure 6. Evolutions of $y(x)$ calculated with $C_N = 1.24$ (eq 30) and of the corresponding fitting (eq 31) as a function of the sodium (a) and the lithium (b) exchanged degree.

TABLE 1: Description of the Fitting Parameters a, b, c, and d, Obtained in Figure 6, and of the Corresponding Values of the Electronic Chemical Potential and the Hardness of the Cation and the Site, Where it is Trapped but with Which it Does Not Exchange any Electronic Charge[a]

site	MOR−Na			MOR−Li		
	I	IV	VI	I	IV	VI
a	−6.3	−6.6	−8.1	11.8	13.4	11.9
b	42.4	34.9	33.0	23.0	15.6	20.3
c	−3.1	−3.2	−3.9	5.3	6.2	6.1
d	17.6	14.8	15.0	7.6	4.9	7.3
μ_c (eV)	−10.2	−8.5	−8.0	−9.4	−8.2	−9.0
μ_s (eV)	−4.2	−3.2	−3.1	−3.5	−2.9	−4.4
$\bar{\eta}_c$ (eV)	8.2	6.8	6.4	7.5	6.6	7.2
$\bar{\eta}s$ (eV)	3.3	5.4	5.1	6	5.2	5.7
ΔN	0.26	0.28	0.285	0.28	0.30	0.26
ΔE (eV)	0.78	0.72	0.70	0.83	0.805	0.745

[a] These values are given for each type of site. ΔN represents the charge transfer between both chemical species.

site are localized in the reference state. Thus, these experimental evaluations permit the determination of the conditional parameters μ^*. These values account for the influence of the surroundings of the cation and the site on their ability to exchange one part of their electronic charge and their ability to deform their electron cloud.

Parts a and b of Figure 6 represent the variations of $y(x)$ as a function of the amount of exchanged cation for MOR−Li_xH_{1-x} and MOR−Na_xH_{1-x}. Table 1 reports the values of the coefficients a, b, c, and d, obtained by means of eqs 32 and 33, and the corresponding values of the derived chemical potential and chemical hardness, for both mordenites. The charge transfer between both chemical species is also reported in this table.

The method seems adequate for a realistic determination of the parameters obtained from TSDC measurements.

(i) The electron chemical potentials of the cations have values higher than those corresponding to isolated species, as predicted by the theory.[6]

(ii) The difference ($\mu_{0c}^* - \mu_{0c}$), i.e., the difference between the value of the chemical potential of the [+1] charged cation, untrapped but in interaction with the mordenite network (*reference state in the solid*), and of the isolated [+1] charged cation, is higher in the case of the lithium ion than in the case of the sodium ion. This implies that lithium ions are more influenced by their surroundings than are sodium ions. This tendency can be verified by using the Slater calculations.

(iii) The site chemical potential has the same order of magnitude as that obtained from theoretical considerations.[37]

(iv) The electron charge exchanged between the cations and the different sites also confirms the theoretical calculations.[36,39]

IV. Conclusion

We have proposed an experimental evaluation of the surface properties of zeolites by means of EEM coupled with TSDC results. To our knowledge, it is the first time that such an experimental determination has been undertaken. Taking into account the sensitivity of the TSDC technique and the importance of the parameters involved (chemical potentials and hardness of localized species on surface sites), the proposed method seems very promising. The evaluation of these parameters leads to a better understanding of the complex mechanisms responsible for the specific properties of zeolites. Indeed, the acido-basic notion thus introduced is essential for the analysis of the catalytic or the adsorption phenomena of such systems. This means that TSDC measurements, in the case of zeolite, appear as a new method for investigating the acidity of such media, depending on the particular zeolite and on the nature of the exchangeable cation.

Of course, different methods for determining zeolite acidity exist:[39] microcalorimetry, adsorption isotherm measurements,[40] NMR[41] and IR[42] spectroscopies, conductimetry,[43] and theoretical calculations.[44] In most cases, a coupling of several methods is necessary to get a complete determination of the acidity. Generally, in the more conventional methods, the results obtained strictly depend on the basicity of the adsorbed molecules, on their diffusion in the zeolitic network, and on the nature of the sites involved. Under these circumstances, it is difficult to create an acidity scale, which would not depend on the nature of the molecules used as probes. On the other hand, TSDC allows a direct determination of the considered energies since it does not need to refer to any intermediary compounds or to the adsorption mechanism. That is why our approach is, to our point of view, an original method for determining the scale of zeolitic acidity.

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