ELECTRICAL INVESTIGATION OF THE MECHANISM OF WATER ADSORPTION/DESORPTION BY NATURAL CLINOPTILOLITE DESICCANT USED IN FOOD PRESERVATION

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ZEOLITE DESICCANTS

Zeolites are microporous silico-alluminate compounds with a regular arrangement of channels. Such microporosity makes zeolites able to adsorb small molecules like water, ethanol, formaldehyde, acetic acid, etc.

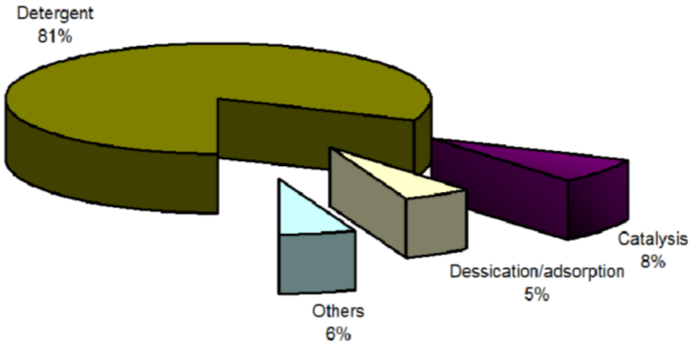
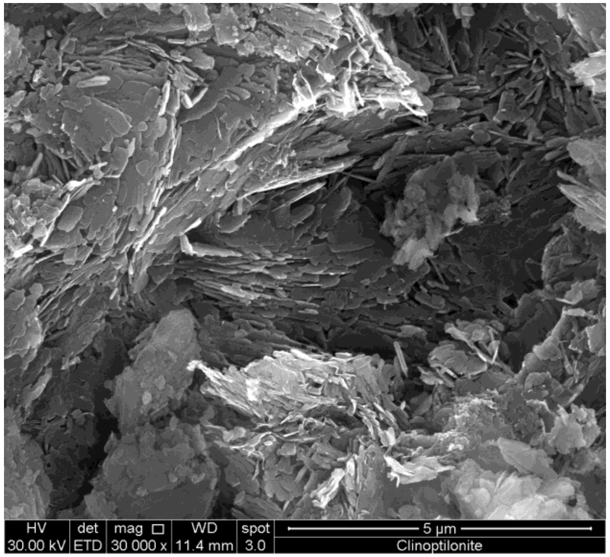
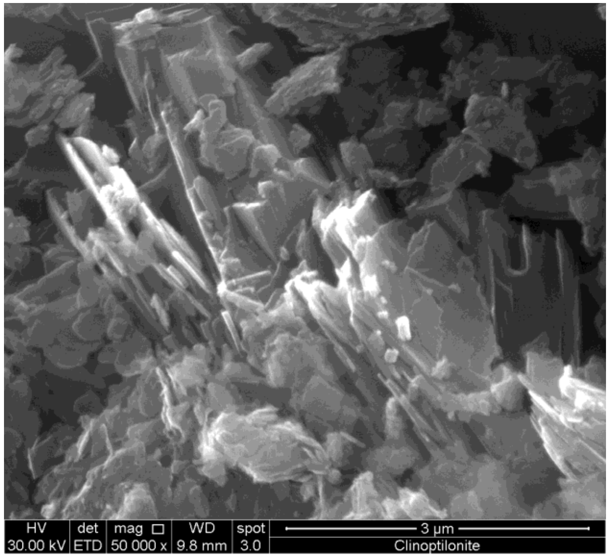
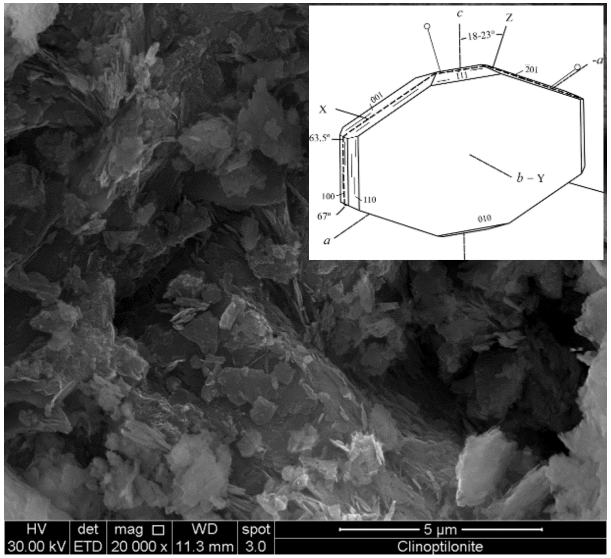


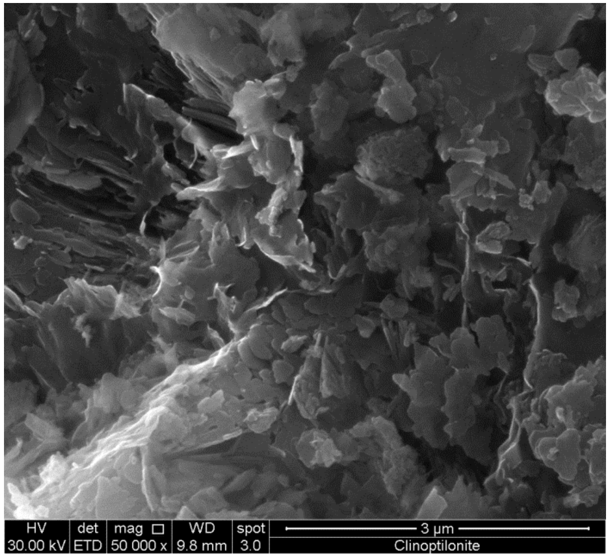
Chart showing the utilization percentage of synthetic zeolites in 2008

MICROSTRUCTURE OF POWDERED NATURAL CLINOPTILOLITE



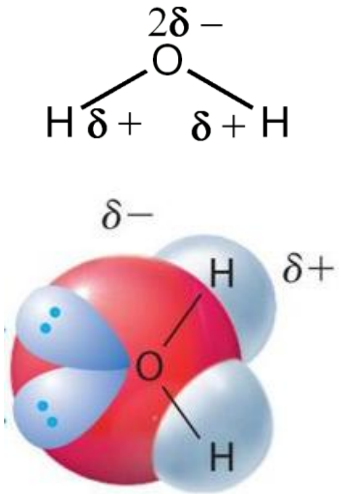




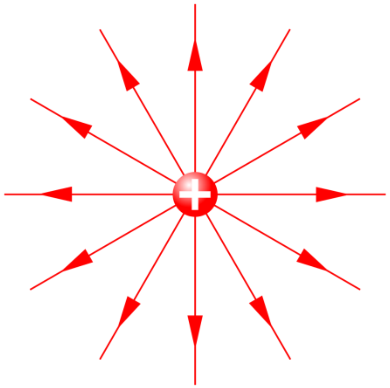


AIM OF THIS STUDY

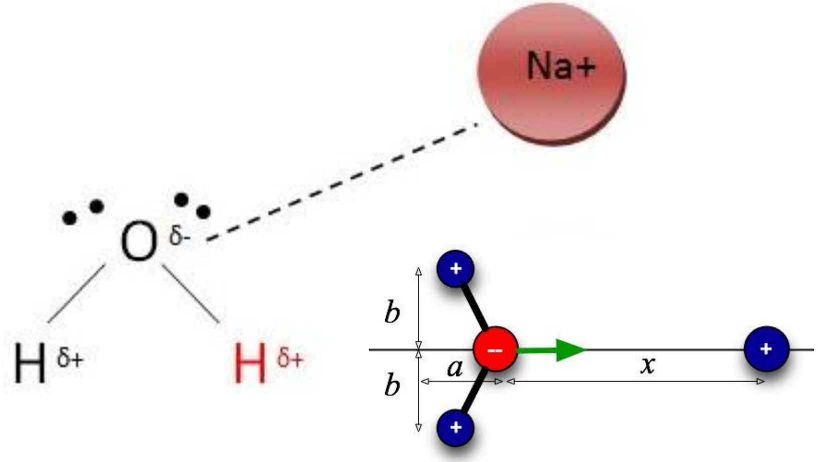
Extra-framework charge balancing cations should be involved in the mechanism of gas-phase molecular adsorption in zeolites because long-range electrostatic interactions are possible between the electric field of cations and the total dipole-moment of the adsorbate molecules. Such attractive cation effect should act with both polarizable and high polar molecules like, for example, water. However, it is still not clear the exact structure of the hydrated cationic sites and the molecular pathway involved in the hydration process. Such information can be obtained only by a kinetic analysis of the water adsorption/desorption process, and this aspect has not been deeply investigated yet.



Water molecule permanent dipole



Cation electric field

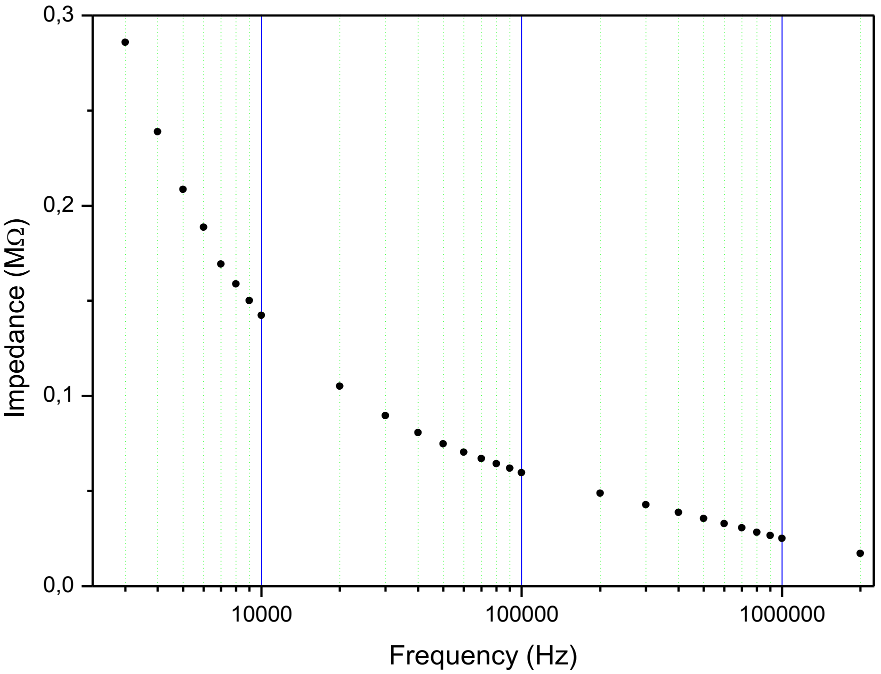


Cation-dipole moment interaction

KINETIC ANALYSIS METHOD (1)

The presence of cations in zeolites allows electrical conduction. Therefore, cations have at same time a leading role in physical adsorption of polar/polarizable molecules and electrical transport, and consequently it is possible to investigate the adsorption process (for example, for water) by a simple electrical technique.

When a D.C. electric field, E, is applied to a zeolite sample, two different phenomena take place: (i) electrical transport and (ii) electrode polarization. In these conditions, the current intensity, I, is not directly proportional to the charge carrier density, since during the conduction process, cations progressively accumulate at electrode surface and the number of charge carriers decreases.

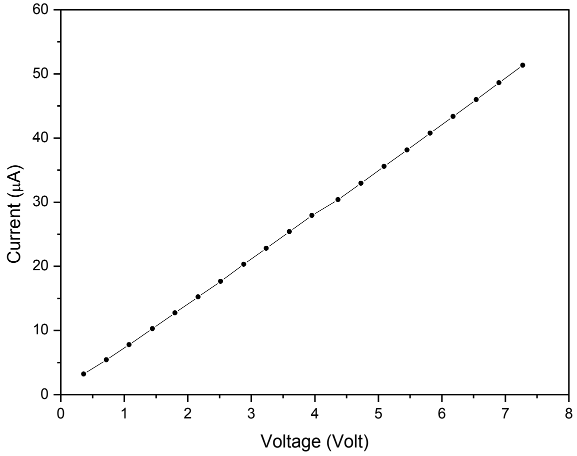


Impedance spectrum of a natural clinoptilolite sample

KINETIC ANALYSIS METHOD (2)

When a sinusoidal electric field is applied to the natural clinoptilolite sample, the amount of cations that stops at the electrode surface decreases significantly as much as higher is the frequency.

If the frequency of the sinusoidal electric field is higher than 1kHz, the amount of cations stopped at electrode surface is almost negligible.



I-V characteristic of the natural clinoptilolite sample at a frequency of 5kHz

For a sample biased by a high-frequency A.C. electric field (e.g., 5kHz), the current density, J, moving in the sample is directly proportional to the charge carrier density, n:

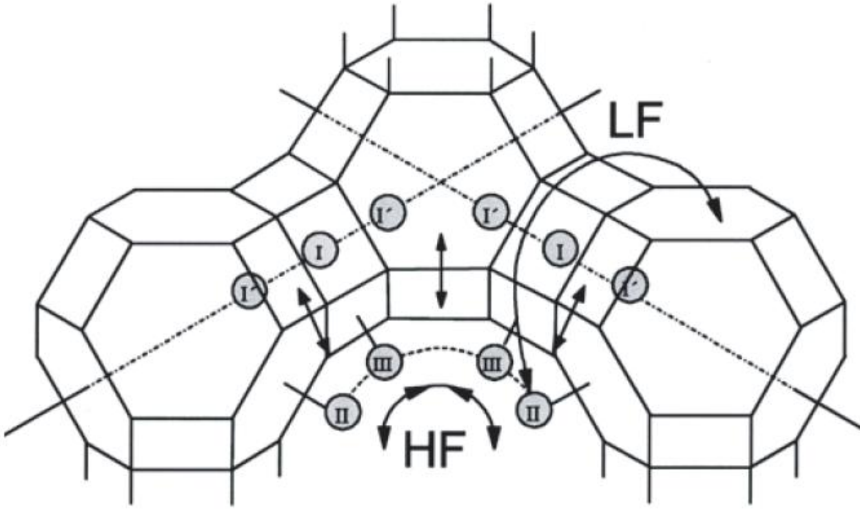
$$\boxed{J = I/A = z \cdot e \cdot n \cdot \mu \cdot E}$$

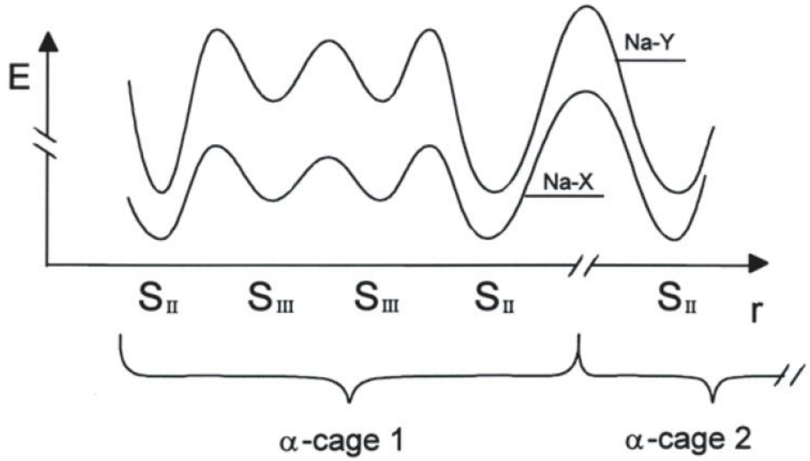
$$\boxed{\sigma = J/E = z \cdot e \cdot n \cdot \mu}$$

where:
z: cation valence,
e: elemental charge,
n: charge carrier density,
μ: cation mobility,
A: cross-section area,
E: applied local electric field.

KINETIC ANALYSIS METHOD (3)

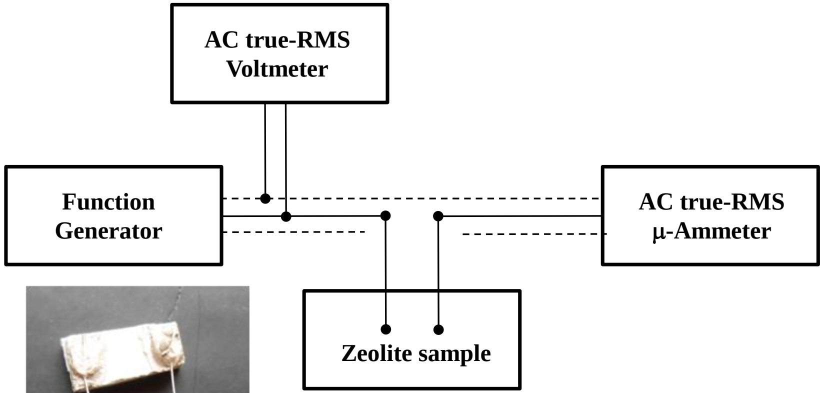
A kinetic analysis of the adsorption/desorption can be performed by simple current intensity measurements. In particular, owing to the strong electrostatic interaction between cations and framework nucleophilic areas, dehydrated cations could be considered as not mobile ($\mu=0$), while they become mobile after adsorption of one water molecule.

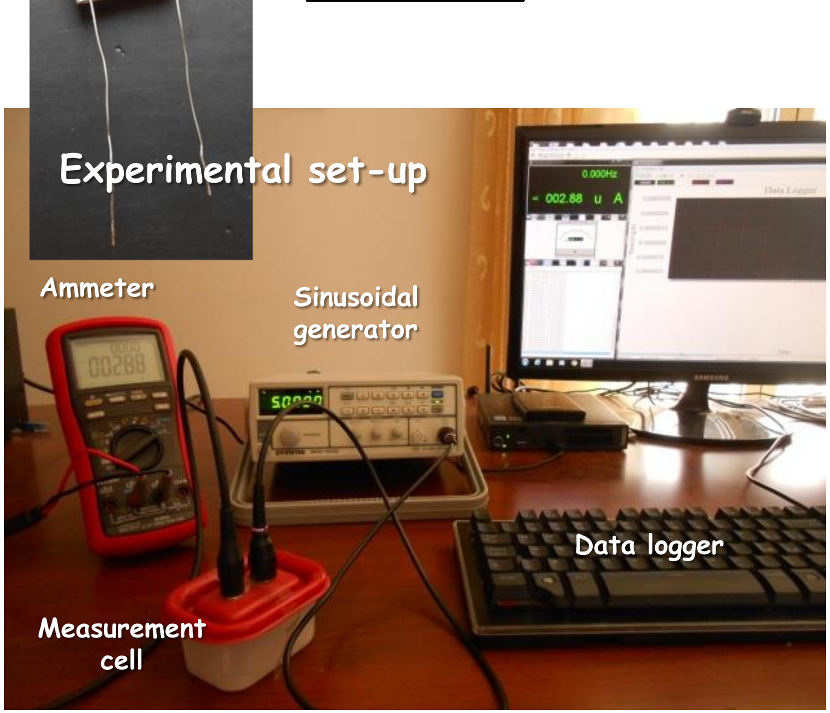




The temporal evolution of the normalized current intensity, I/I_0, could be used to establish the relative cation concentration increase/decrease, during the process of adsorption/desorption, respectively. Based on this type of investigation, the kinetic order of the water adsorption/desorption process can be established and the kinetic rates measured too.

EXPERIMENTAL DETAILS





A natural clinoptilolite sample (T.I.P., Germany), in form of slab, was biased by a sinusoidal voltage of $20V_{pp}$ (5kHz), provided by a DDS function generator (GW Instek, SFG-1013) and the effective current intensity (I_{eff}) was measured by a true-RMS ammeter contained in a 100kHz bandwidth digital multimeter (Brymen, BM869s).
Time-resolved data were recorded on a PC by using the DMM datalogging system.
During the hydration/dehydration process, the applied voltage resulted practically a constant because of the very low clinoptilolite sample conductivity.
To achieve an atmosphere with constant humidity (75% by weight), the saturated salt method was used (wet-NaCl, 25°C).

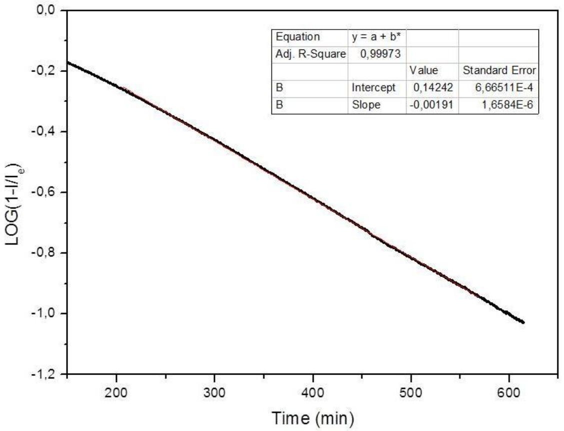
EXPERIMENTAL RESULTS

The kinetics of H_2O adsorption on natural clinoptilolite, studied in isothermal conditions (25°C), and in presence of constant humidity (75%), has been found to follow a pseudo-first order behavior (irreversible Lagergren model):

$$\boxed{\text{Log}(1-Q_t/Q_e)=-k\cdot t/2.303}$$

Where:
Q_t = adsorbed H_2O amount at t time;
Q_e = adsorbed H_2O amount at equilibrium;

The Q_t/Q_e ratio numerically corresponds to the I_t/I_e ratio



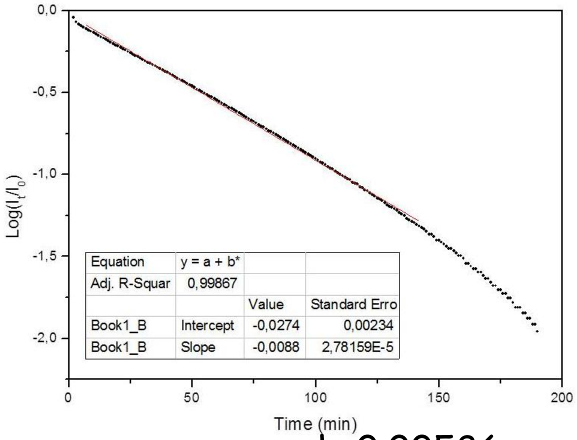
Equation	y = a + b*		
Adj. R-Square	0,99973		
		Value	Standard Error
B	Intercept	0,14242	6,66511E-4
B	Slope	-0,00191	1,6584E-6

Differently, a first-order kinetic behavior has been found to control H_2O desorption from clinoptilolite in dry air.

$$\boxed{\text{Log}(Q_t/Q_0)=-k'\cdot t/2.303}$$

Where:
Q_t = adsorbed H_2O amount at t time;
Q_0 = initial adsorbed H_2O amount;

The Q_t/Q_0 ratio numerically corresponds to I_t/I_0



Equation	y = a + b*		
Adj. R-Squar	0,99867		
		Value	Standard Erro
Book1_B	Intercept	-0,0274	0,00234
Book1_B	Slope	-0,0088	2,78159E-5

A correlation factor, R^2, very close to one was found in the best-fittings of data based on these two models, thus indicating the validity of each of them.

The kinetic constants measured for the adsorption and desorption processes are: k=0.00586 min^{-1} and k'=0.0203 min^{-1} (at 25°C), respectively.

PROPOSED WATER ADSORPTION MECHANISM

Such experimentally found kinetic orders suggest an adsorption mechanism based on a direct water-cation electrostatic interaction, with formation of a dipole-cation bond as rate-limiting elemental step:

$$F^{-}Me^{+} + \mathbf{H_2O} \rightarrow F^{-}Me(\mathbf{OH_2})^{+} \qquad \text{Slow}$$

where F^{-} represents the framework nucleophilic area.

However, the significant change of cation mobility, as a consequence of the adsorption process, would suggest the existence of a second, faster elemental step, based on the transfer of the adsorbed water molecule at the framework-cation interface to maximize hydrogen-bond interactions

$$F^{-}Me(\mathbf{OH_2})^{+} \rightarrow F^{-}\mathbf{H_2O}Me^{+} \qquad \text{Fast}$$

In fact, the separation of the cation from the negative charge in the framework, as a consequence of the H_2O molecule interposition, decreases the intensity of the Coulomb's force, making possible cation movement by hopping.

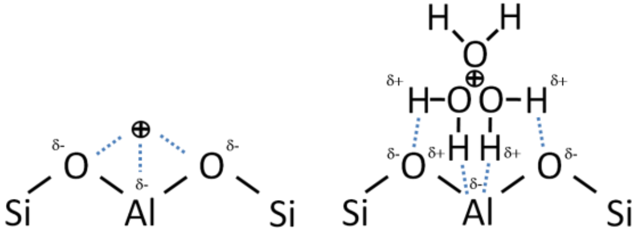
CONCLUSIONS

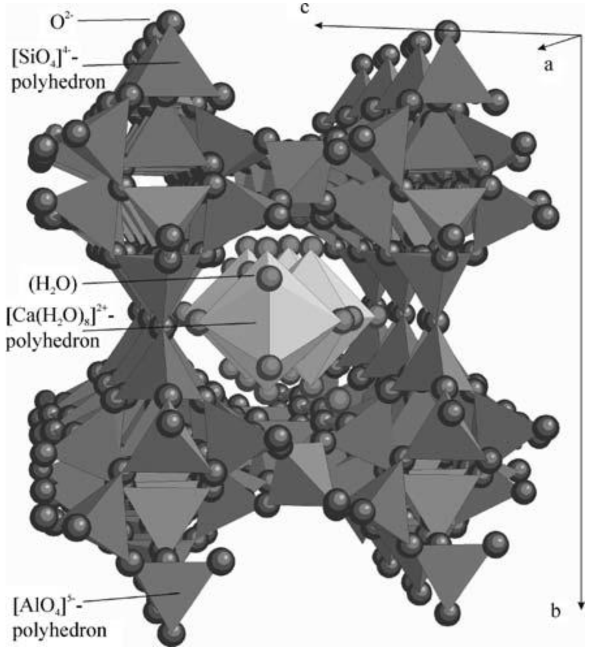
A kinetic analysis of the physical adsorption/desorption process of water on natural clinoptilolite has been performed by monitoring the temporal evolution of the relative current intensity in a biased sample (sinusoidal voltage of $20V_{pp}$, 5kHz), exposed to a constant humidity environment (75%) at 25°C. According to the performed kinetic analysis the adsorption mechanism involves two-steps:

1) slow water-cation electrostatic association,

2) fast water transfer at framework-cation interface.

This second faster step decreases the intensity of the Coulomb interaction between cation and framework, making possible transport in the zeolite sample.





Zeolite crystal structure