

Microporous Stilbite single crystals for alcohol sensing

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Abstract The possibility of shape-selective resistive gas sensors for polar molecules using the microporous aluminosilicate Stilbite is investigated. The electrical impedance of natural Stilbite single crystals at 80°C decreases in presence of methanol, 2-propanol and 3-pentanol, but increases with increasing water and neo-pentanol vapour pressure. The interaction can be described by a Langmuir-type adsorption equation. The conductivity effects are interpreted mainly by mobility effects, due to sterical interactions in the zeolite channels.

Keywords Adsorption · Impedance spectroscopy · Electrical conductivity · Alcohols

Introduction

Zeolites are natural aluminosilicates with a relatively low framework density: tetrahedral building units of aluminum and silicon form a three-dimensional lattice with structure-inherent channels and cages. [1] An $[\text{AlO}_4]^{5-}$ -tetrahedron, present in the $[\text{SiO}_4]^{4-}$ framework, carries an excess negative charge, which has to be compensated by cations present in the channels and cages together with water molecules forming hydration spheres for the charge compensating cations [2, 3], depending on the synthesis conditions [4–6]. The water molecules are bound in a characteristic way: channel and cage size, framework charge, type and distribution of ions within the cavity system are factors affecting the conditions of zeolitic water bonding. The structure of the zeolite Stilbite

(STI) with chemical formula $\text{NaCa}_4[\text{Al}_9\text{Si}_{27}\text{O}_{72}] \times 30\text{H}_2\text{O}$ is shown in Fig. 1. One recognizes in this particular case a two-dimensional channel system along the [100] and the [101] directions.

Zeolites are known to have specific catalytic, ion exchange and sorption properties. While ion exchange takes place in aqueous solutions at temperatures mostly below 100°C, the zeolite lattice is “activated” for sorption purposes by heat treatment at temperatures above 250°C, where the maximum catalytic activity is observed. At elevated temperatures, the zeolitic water is gradually desorbed, depending on the respective crystallographic position. In almost all zeolite structure types known today, above 250°C the zeolitic water of all crystallographic positions is desorbed and, therefore, the distribution of the charge compensating cations is to a great extent rearranged, leaving additional space for gas molecules to enter the channel system. However, irreversible changes of the zeolite framework lattice often occur under these conditions [7, 8].

The idea of the sensor application is that molecules can enter the zeolite micropores (pore size below 2 nm) only up to a certain diameter and that the interactions with the zeolite depend on the polarity and shape of the molecules. This can be the opportunity to design sensor systems in gas and liquid phases with a much enhanced selectivity in comparison to conventional ones. Table 1 [9] shows the molecular dimensions of different alcohols in relation to the size of interconnected channels in STI ($0.5 \times 0.47 \text{ nm}^2$ in (100) direction and $0.27 \times 0.56 \text{ nm}^2$ in (001) direction [2]). Water and methanol fit easily into the channels, but 2-propanol and 3-pentanol only in one orientation and the largest molecule, 2,2-dimethyl-1-propanol (neo-pentanol) has dimensions comparable to the channel size. In the resistive mode, the question is how the conduction properties of single crystalline zeolites are changed by polar molecules, while a dynamic

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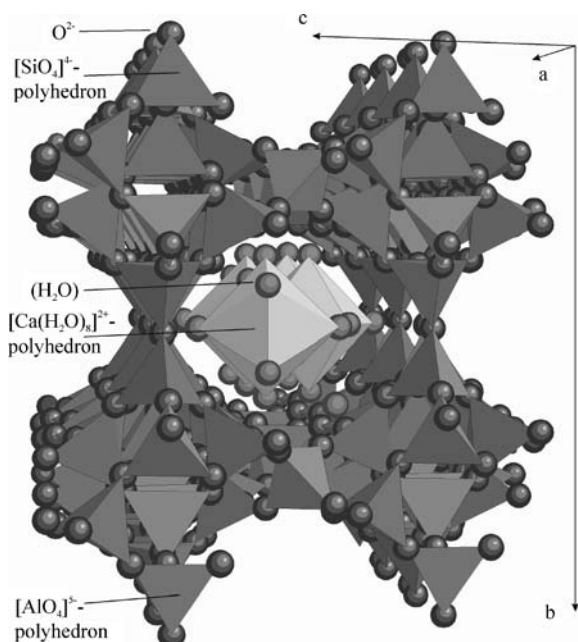


Fig. 1 Stilbite crystal structure

equilibrium between water in the gas phase and water in the cavity system is established and how to extend these investigations to zeolites in contact with liquid water. This is the base for developing zeolite-type sensors in aqueous solution, which could be applied in the biomedical sector, given their non-toxicity and biocompatibility.

Experimental

To study this application, natural single crystals of Stilbite STI (maximum $2 \times 5 \times 10 \text{ mm}^3$) were cut with a diamond saw. Sputtered Au electrodes of ca. 120 nm thickness were deposited and the 0.1–0.5 mm thick contacted crystal was placed in a spring loaded ceramic sample holder with Au contacts. The electrical properties were determined along *c* axis by impedance spectroscopy (EG&G) in the frequency range 47 mHz–150 kHz with a signal amplitude of 15 mV. The sensor effect was investigated using methanol, 2-propanol, 3-pentanol and 2,2-dimethyl-1-propanol as polar organic molecules with different size and dipole

Table 1 Size and dipole moment of different polar molecules [9]

Molecule	Width (nm)	Length (nm)	Depth (nm)	Dipole moment/D
H ₂ O	0.33	0.38	0.30	1.80
Methanol	0.37	0.42	0.42	1.71
2-propanol	0.56	0.60	0.49	1.65
3-pentanol	0.59	0.88	0.56	1.65
2,2 dimethyl-1-propanol	0.60	0.62	0.43	Unknown

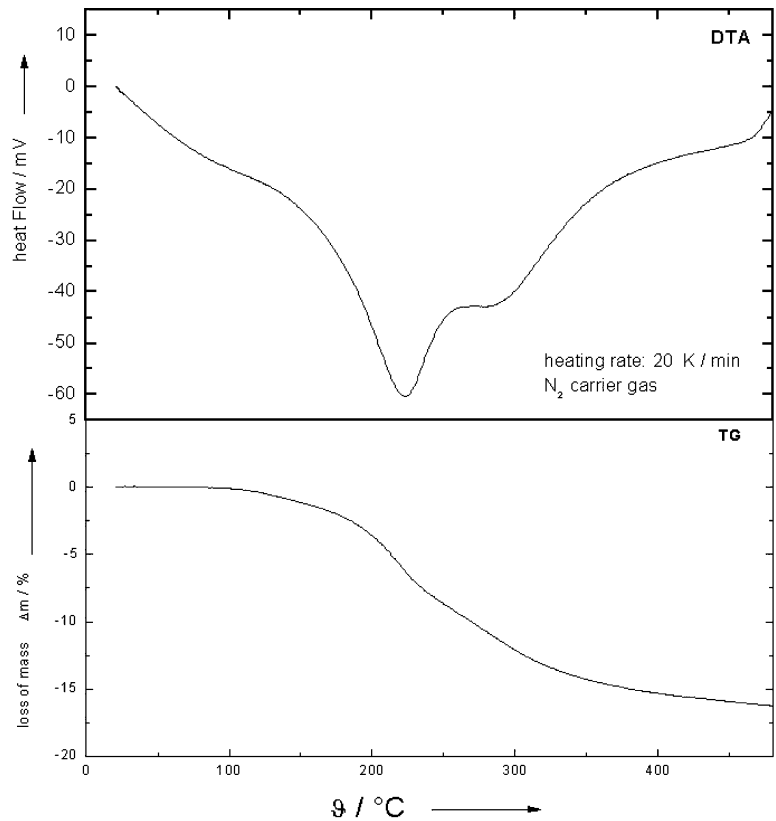
moment. For this purpose, the carrier gas stream was split into two equal parts of 60 SCCM (standard cubic centimeters) flow, led through two different thermostated bottles for independent saturation with water and the respective alcohol. The partial pressures of water and liquid alcohol were fixed by the thermostat temperature [10]. Water proof was investigated with dummy cells, using quartz crystals instead of zeolites [11]. The time-dependence of impedance spectra in presence of water vapor showed that drift-free measurements are possible up to 110°C [12]. Furthermore, the conductivity of Stilbite single crystals was also studied between 0 and 30°C in bi-distilled water inside a thermostat. Only the (100) face was exposed to the liquid.

The onset of water loss in Stilbite single crystals under dynamic conditions was studied by differential thermal analysis and thermogravimetry (SETARAM) using a heating rate of 20 K/min under nitrogen flow. The gas atmosphere was analyzed after contact with zeolite by Fourier-transform infrared spectroscopy (FTIR, Biorad).

Results

Conductivity measurements using single crystalline aluminosilicate materials are quite difficult because of the possible water loss. Figure 2 shows desorption of water in natural STI single crystals, which starts around 110°C under dynamic conditions. Irreversible structural alteration of STI begins at about 180°C [13]. The impedance of STI single crystals depends strongly on water partial pressure. Figure 3 shows a typical complex plane impedance plot obtained with Stilbite single crystals contacted with gold electrodes. The equivalent circuit used for interpretation is also shown. The electrodes show capacitive (blocking) behavior. The single crystal can be adequately described by a parallel resistance-capacitance circuit (Constant Phase Element with $n > 0.9$). The resistance is determined as usual from the real axis intercept. An Arrhenius plot of conductivity covering the temperature domain between 0 and 110°C is presented in Fig. 4. The points up to 30°C were measured in liquid water, the others in air with a defined water partial pressure ($P = 0.03 \text{ bar}$). The activation energy is slightly higher in the gas phase than in the presence of liquid water. Extrapolating the low temperature data, the two straight lines intersect around 80°C, which is the temperature of our measurements. At 80°C, the impedance of the zeolite sample increases with increasing $P(\text{H}_2\text{O})$ (Fig. 5(a)). This shows that it is not simply water adsorption on the external zeolite surfaces which takes place, because in that case the resistance should decrease with increasing water pressure. Under constant water partial pressure, the STI single crystal impedance is not only sensitive to water but also to other polar and non polar molecules. Figure 5(b) shows the effect of different alcohol molecules

Fig. 2 Temperature dependent water desorption in Stilbite single crystals studied by differential thermal analysis and thermogravimetry



in the gas phase: all lead to a decrease of impedance, except neo-pentanol. The time constant is about 60 min (corresponding to 90% of final signal); optimization is certainly possible by using powdered samples.

Gas phase analysis by FTIR after contact with powdered STI at 100°C confirmed that the conductivity modification is based on adsorptive interaction, as only the IR spectrum of pure methanol is observed and no CO₂ (Fig. 6). Catalytic oxidation takes place only above 300°C, although the

irreversible alteration of the zeolite crystal lattice already starts before.

Discussion

The conductivity of STI single crystals is not only dependent on the concentration of polar substances, but also on the molecular dimensions with respect to the zeolite channel size. The results of our investigations give insight into the processes taking place within the zeolite cavity system. The mechanism of the conduction process itself is still under investigation, but first hints could be obtained based on these results, showing that the population of the channel system plays an important role, and also the polarity and size of substances involved in the process.

In our gas phase investigations, small deviations from complete filling of the zeolite channel systems with water molecules can be assumed. In the natural state, charge compensating Ca²⁺ ions occupy all possible sites and are coordinated with 8 water molecules forming a hydration sphere; only about 20% of Na⁺ sites are occupied for charge compensation and the sodium ions do not possess a complete hydration sphere. Na⁺ ions do not take part in the ion exchange process and it can be concluded that they are rather immobile [11]. Kelemen et al. [14] stated that relatively immobile hydrated complexes are present in hydrated zeolites,

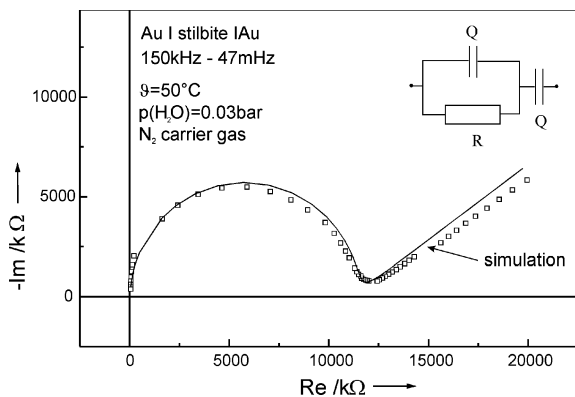
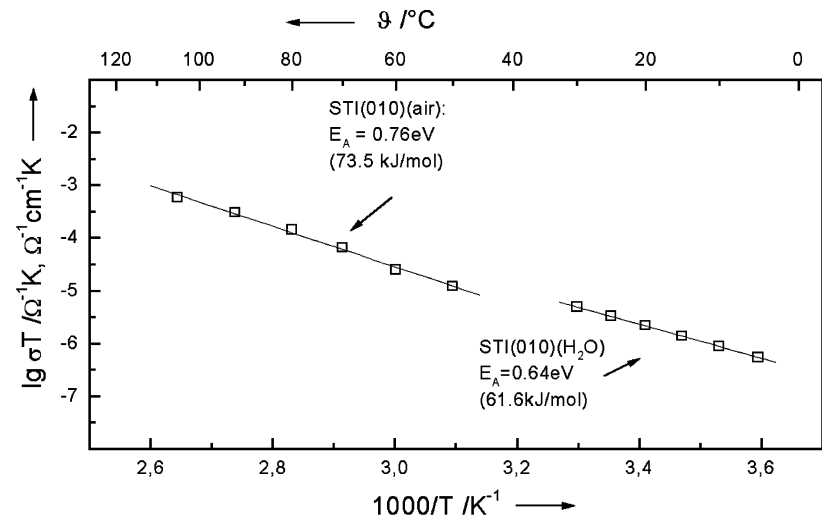


Fig. 3 Typical complex plane impedance diagram of a Stilbite single crystal with sputtered gold electrodes. The squares are the experimental data and the full line represents the simulated spectrum using the given equivalent circuit

Fig. 4 Temperature dependence of the conductivity of Stilbite single crystals in the gas phase and in pure water



and showed a relation between cation size, channel size and activation energy of conductivity. From literature and our experiments, it can be concluded that the presence of water molecules causes a steric hindrance for cationic motion in hydrated zeolites. One point which still needs to be elucidated is the transference number of protons and other cations in STI.

The conduction process is influenced by gaseous molecules accessing the zeolite channel system. Effects of surface conduction are overcompensated by effects of the inner surface (channels and cages). The isothermal conductivity of a solid can be written as the sum of several contributions, ionic and electronic. Each contribution is the product of the carrier charge, the carrier concentration and the carrier

mobility. If only protons linked to water molecules contribute to the ionic conduction process, the water content of the channel system strongly influences the mobility and the number of charge carriers. The fact that an increase of water vapor pressure leads to an increase of STI resistivity indicates that the conductivity effect is mobility related, probably due to steric hindrance inside the limited channel space (Fig. 1). A maximum concentration of H₂O molecules can be assumed under channel saturation conditions, which is however not achieved during experiments in the gas phase, but only in the liquid phase.

If alcohol molecules access the channels, while H₂O molecules are still present, they change the relative H₂O concentration in the channel system. The number of protons will

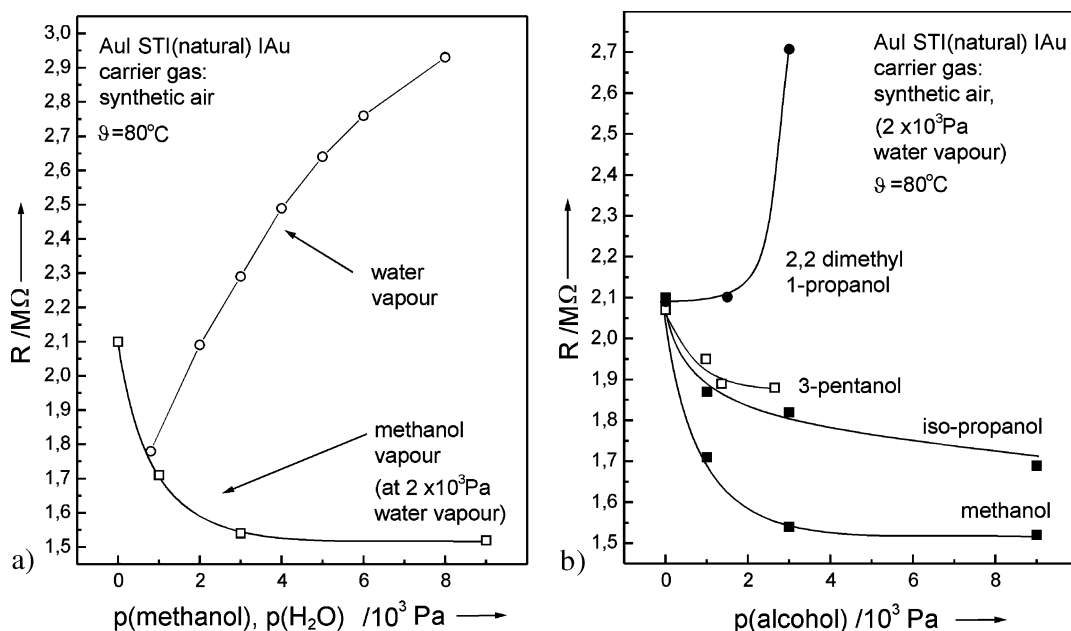
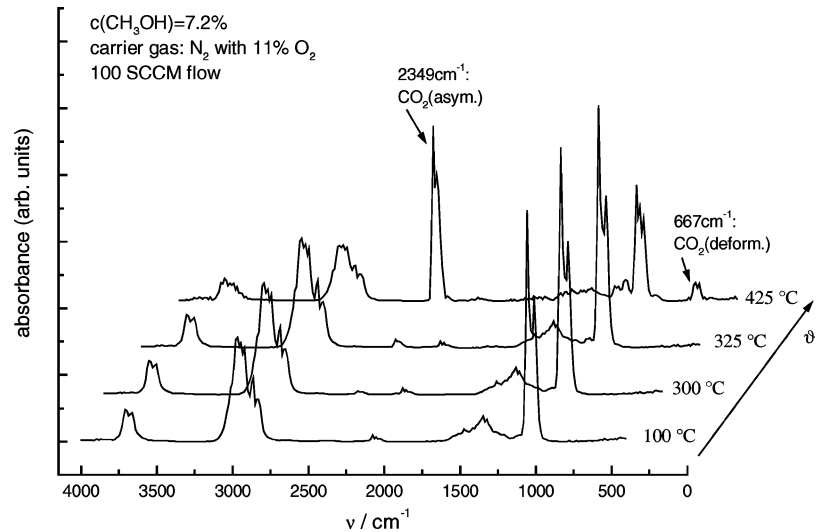


Fig. 5 (a) Water partial pressure dependence of the resistance of Stilbite single crystals compared to that of methanol; (b) partial pressure dependence of the resistance of Stilbite single crystals in presence of different alcohols

Fig. 6 Gas-phase analysis by FTIR spectroscopy. A purely adsorptive interaction with Stilbite is demonstrated below 300°C; alcohols are oxidized to CO₂ only above that temperature



be constant or decrease, given that alcohols do not contribute to a proton conduction process. The alcohol data are measured at a relatively low water partial pressure of 0.02 bar. Under these conditions, the channels are not completely filled with H₂O and the cations, especially Ca²⁺, are not fully hydrated. Small polar molecules can substitute water in the Ca²⁺ solvation sphere in the zeolite cavity system and hydrogen bridges are weakened. In sum, this would lead to a higher mobility of the charge carriers and, therefore, to a higher conductivity.

Assuming that the impedance change is related to alcohol adsorption on the zeolite channel walls, we can use the Langmuir adsorption equation to describe our system:

$$\Theta = \frac{KP}{1 + KP} \tag{1}$$

In this equation, *K* is the adsorption equilibrium constant, *P* is the partial pressure of the respective gas and Θ is the degree of coverage. The adsorption constant is related to the standard molar Gibbs free energy of adsorption $\Delta_{\text{ads}}G^\circ$ by the equation:

$$K = \exp\left(\frac{-\Delta_{\text{ads}}G^\circ}{RT}\right) \tag{2}$$

The degree of coverage can be expressed simply by the ratio of the measured resistance change $|\Delta R|$ under a certain vapor pressure divided by the maximum resistance change $|\Delta R^\infty|$, corresponding to formation of a monolayer of alcohol molecules:

$$\Theta = \frac{|\Delta R|}{|\Delta R^\infty|} \tag{3}$$

Using elementary arithmetics, we can rearrange these equations to get:

$$\frac{P}{|\Delta R|} = \frac{1}{K|\Delta R^\infty|} + \frac{P}{|\Delta R^\infty|} \tag{4}$$

Figure 7 shows line plots of $P/|\Delta R|$ vs. *P*; the correlation is acceptable and we can determine the maximum resistance change from the slope and the adsorption constant from the ordinate, related to the standard Gibbs free energy of adsorption at the measurement temperature. The results are summarized in Table 2; one notices that the extrapolated maximum

Table 2 Calculated data using Eqs. (2)–(4)

Molecule	$ \Delta R^\infty /M\Omega$	<i>K</i>	$-\Delta_{\text{ads}}G^\circ/\text{kJ/mol}$
Water	2.92	15	7
Methanol	0.61	230	16
2-propanol	0.46	70	13
3-pentanol	0.28	140	15

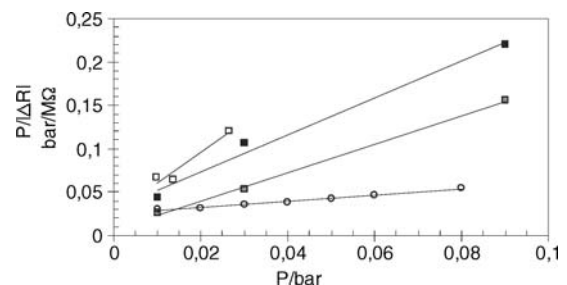


Fig. 7 Line plots according to Eq. (4) for water (○), methanol (◊), 2-propanol (■), and 3-pentanol (□)

resistance is compatible with the experiment. Within the limits of uncertainty, the three smaller alcohol molecules have comparable adsorption constants and energies and the orders of magnitude are realistic [15]. For water, adsorption constant and standard Gibbs free energy of adsorption are distinctly smaller and more compatible with physisorption, corresponding to water molecules not part of the zeolite structure. A very different behavior is observed for the largest molecule neo-pentanol. The change of resistance is negligible for small partial pressures and a sudden increase is observed at 30 mbar. In this case, one might argue that the ionic conduction is interrupted by the large neo-pentanol molecules, but more studies are necessary to conclude.

Conclusions

The impedance of STI single crystals depends on the partial pressure of polar molecules in the gas phase, including water, methanol, 2-propanol, 3-pentanol and 2,2-dimethyl-1-propanol. The change is related to the size and dipole moment of the molecules. The interaction is purely adsorptive without catalytic oxidation and can be described by a Langmuir adsorption equation. This basic principle might be applicable for development of shape-selective chemical sensors in biological environment.

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