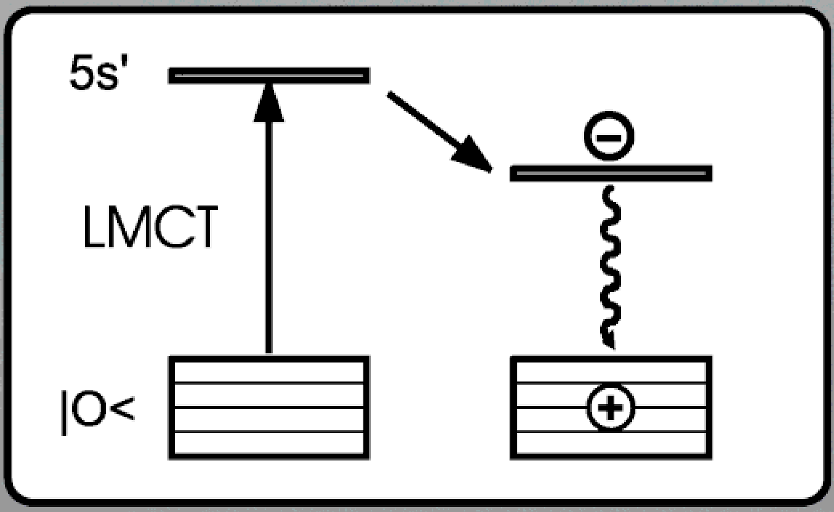
The cause of the yellow color of activated silver-containing zeolite A

Colorless in the hydrated state, silver-containing zeolite A turns yellow to brick-red upon activation. This color change is reversible with respect to desorption/adsorption of water. The reason for this phenomenon, which has been known since 1962, was unclear until now. It is now shown that a charge-transfer transition from the oxygen atoms of the zeolite lattice to the empty 5s orbital of the silver ions is responsible for the yellow coloring.



The Yellow Color of Silver-Containing Zeolite A**

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Zeolites are crystalline alumosilicates with a cavity structure. Their lattices are enormous polyanions which contain cations for charge compensation. In the nonactivated state, the cavities are filled with water. As a rule, these structures absorb light neither in the visible nor in the near ultraviolet range. Zeolite A has a three-dimensional network of cavities,[1] and the composition of its $\mathrm{Na^+}$ form is $\mathrm{Na^+_{12}[(SiO_2)_{12}(AlO_2)_{12}]}$. The $\mathrm{Na^+}$ cations can be partially or fully exchanged with $\mathrm{Ag^+}$ ions.

$\mathrm{Ag^+_xNa^+_{12-x}A}$, colorless in the hydrated state becomes a yellow to brick-red color upon activation. Rálek et al. observed this property for the first time after thermal activation under vacuum.[2] Later it was discussed by various authors in connection with the formation of silver clusters.[3] An autoreduction mechanism which involves formation of $\mathrm{Ag^0}$ and release of $\mathrm{O_2}$ from the zeolite framework was assumed. We show here that upon activation under high vacuum $\mathrm{Ag^+_xNa^+_{12-x}A}$ turns yellow already at room temperature and that all absorption bands appearing in the UV/Vis region only depend on the hydration of the $\mathrm{Ag^+}$ ions. We explain this coloring as electronic transitions from the lone pairs of the oxygen atoms of the zeolite lattice to the empty 5s orbital of the $\mathrm{Ag^+}$ ions (ligand-to-metal charge transfer, LMCT).

Figure 1 shows the colors which occur after activation of the zeolites under high vacuum in gas-tight glass ampoules. Ampoules 1–3 contain $\mathrm{Ag^+_xNa^+_{12-x}A}$ ($x = 0$, 1/8, and 6, respectively) after activation at room temperature. In ampoule 4, zeolite activated at 200 °C with six $\mathrm{Ag^+}$ ions per pseudo unit cell is shown. The optical properties depend on the quality of the zeolite as well as the conditions during the activation.[4] For this reason, we measured spectra of chemically pure and highly crystalline $\mathrm{Na^+_{12}A}$ which was partially and fully exchanged with $\mathrm{Ag^+}$ ions. It was activated under defined conditions which were as mild as possible.

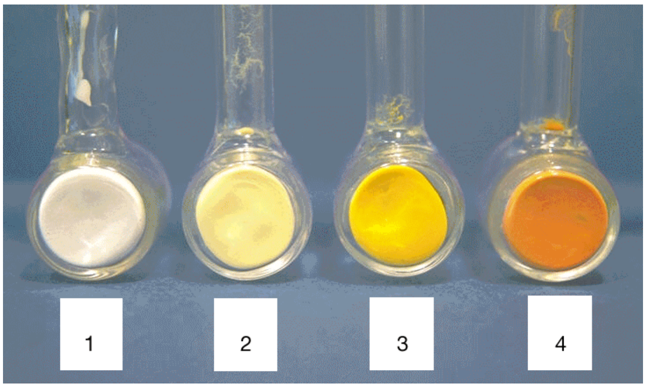

Figure 1. Upon activation, colorless zeolite A containing $\mathrm{Ag^+}$ ions turns yellow to brick-red, depending on the conditions. Samples of $\mathrm{Na^+_{12}A}$ (1), $\mathrm{Ag^+_{0.13}Na^+_{11.87}A}$ (2), and $\mathrm{Ag^+_6Na^+_6A}$ (3), activated under high vacuum at room temperature, are shown. Ampoule 4 contains $\mathrm{Ag^+_6Na^+_6A}$, which was treated at 200 °C under high vacuum.

Figure 2 shows UV/Vis spectra of $\mathrm{Ag^+_xNa^+_{12-x}A}$ after activation under high vacuum (2×10^{-7} mbar) and at room temperature. The spectra of samples with a degree of exchange of up to one $\mathrm{Ag^+}$ ion per pseudo unit cell show a band at 420 nm with a shoulder at 450 nm. At a higher degree of exchange, the shoulder dominates, and with six or more $\mathrm{Ag^+}$ ions per pseudo unit cell upwards it is the only band in the visible range. Higher loading thus leads to a slight bathochromic shift of the long wavelength absorption band maximium. However, regardless of the degree of exchange, the coloring remains yellow.

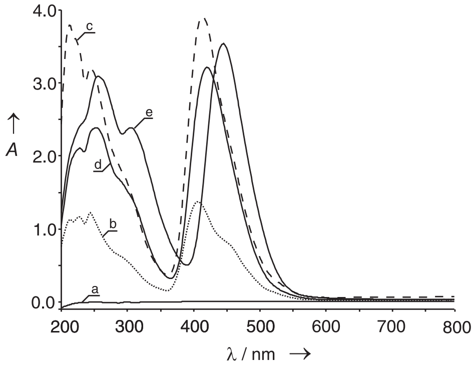

Figure 2. Dependency of the UV/Vis absorptions on the degree of exchange of the zeolite activated under high vacuum at room temperature: a) $\mathrm{Na^+_{12}A}$, b) $\mathrm{Ag^+_{0.5}Na^+_{11.5}A}$, c) $\mathrm{Ag^+_1Na^+_{11}A}$, d) $\mathrm{Ag^+_{1.5}Na^+_{10.5}A}$, e) $\mathrm{Ag^+_6Na^+_6A}$.

Figure 3 shows the statistical distribution of $\mathrm{Ag^+}$ ions in the unit cells as a function of the mean degree of exchange. It was calculated on the simplifying assumption that no coordination site is occupied with preference. With this we can qualitatively understand the dependency of the spectra on the degree of

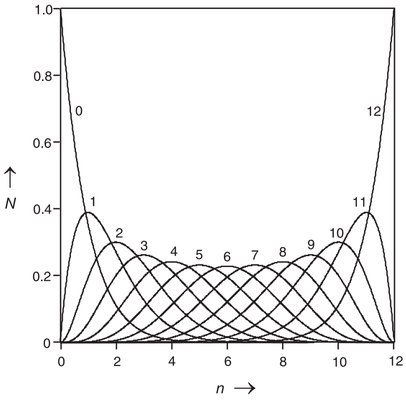

Figure 3. Calculated distribution of the $\mathrm{Ag^+}$ ion in an $\mathrm{Ag^+_xNa^+_{12-x}A}$ model with 12 equivalent sites per cage. The graph shows which share (N) of the cages contains 0,1,2,...12 $\mathrm{Ag^+}$ ions at a chosen average degree (n) of exchange.

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exchange. The absorption band at 420 nm is caused by the presence of an individual Ag^+ ion in a cage. An emerging bathochromic shift indicates the occurrance of interactions with further Ag^+ ions entering the cage. The distribution shows that the share of unit cells with one Ag^+ ion increases until an average content of one Ag^+ ion per unit is reached. With an average degree of exchange as low as 1.5 Ag^+ ions per unit cell, the share of cells with only one Ag^+ ion is already substantially smaller and roughly corresponds to the sum of the shares with more than one Ag^+ ion. The spectra thus demonstrate an increase and decrease in the intensity of the band at 420 nm and a bathochromic shift which starts at a degree of exchange as low as 1.5 Ag^+ ions per cage.

The counterpart of the activation process is the readsorption of water. The reversibility of the activation was examined. The results for $Ag_6^+Na_6^+A$ activated at room temperature are shown in Figure 4. All absorption bands occurring during the activation (spectrum b) disappear after the adsorption of pure water vapor (spectrum c). This reaction clearly contradicts an autoreduction in which Ag^0 is produced and O_2 is released. It clearly corresponds to a dehydration/hydration of the Ag^+ ions.

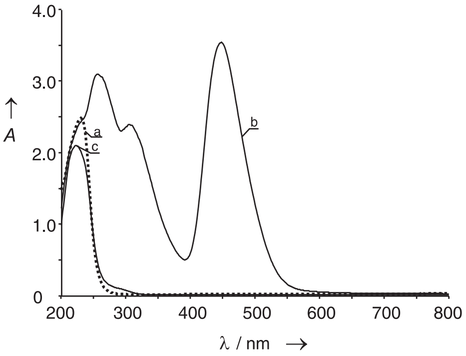

Figure 4. UV/Vis spectra of silver-containing zeolite A. The absorptions occurring because of the activation are reversible with respect to the readsorption of water. a) Freshly exchanged, nonactivated $Ag_6^+Na_6^+A$; b) $Ag_6^+Na_6^+A$ activated under high vacuum at room temperature; c) like b) but exposed to pure water vapor after activation. A = absorption.

If zeolite activated at room temperature is heated with six Ag^+ ions per pseudo unit cell under high vacuum, new bands are formed at 360 and 510 nm, and the sample becomes brick-red. Figure 5 shows the spectra of $Ag_6^+Na_6^+A$ which was activated between room temperature and 250 °C. For these samples with additional thermal activation, the reversibility with respect to the desorption and adsorption of water is restricted to the visible range. Between 300 and 400 nm, bands with decreased intensity remain.

To better classify the occurrence of the reversible yellow coloring and to understand the electronic structure of the system, quantum-chemical EHMO-EDiT calculations (EHMO = extended Hückel molecular orbital, EDiT = electronic dipole induced transitions) were carried out at an α cage with alternating Al and Si atoms.[5] In place of the neighboring cell, the free valencies were saturated with OH groups, creating a situation similar that in zeolite A. Charge neutrality was achieved by adding protons. The model thus consisted of 240 atoms. The examination of possible sites for Ag^+ ions in the model cage leads to the result shown in Figure 6, which corresponds to the data available from X-ray experiments. In the present case the energy levels and the oscillator strengths are significant for the electronic transitions in the HOMO/LUMO region. In Figure 7 we show these for the important situation in which an Ag^+ ion is coordinated over the six-ring in a completely dry zeolite. The calculated spectrum can be compared with the long-wavelength part of spectrum b ($\lambda > 300$nm) in Figure 2. The other coordination

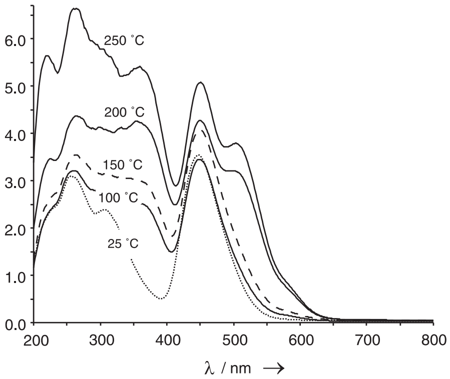

Figure 5. UV/Vis spectra of $Ag_6^+Na_6^+A$ zeolies activated under high vacuum at different temperatures. Between 150 and 200 °C, the zeolite begins to color brick-red. A = absorption.

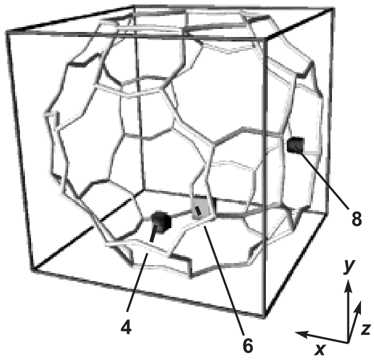

Figure 6. A model cage framed by a cube, which was used for the EHMO calculations. A calculated coordination site for Ag^+ ions over the four-, six-, and eight-rings is shown.

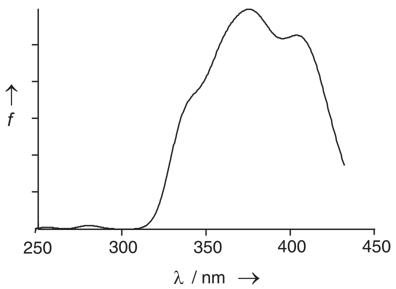

Figure 7. Result of an EHMO-EDiT calculation with a Ag^+ ion coordinated over the six-ring in the α cage. A simulated spectrum from the transitions with the highest oscillator strength f are shown.

sites lead to similar results. The HOMO region corresponds to lone pairs of the oxygen atoms bonded to the zeolite lattice. The LUMO is located on the Ag$^+$ ion and corresponds to the empty 5s orbital. On the six-ring, two transitions from the lone pairs of two oxygen atoms to the Ag$^+$ 5s orbital [Ag$^+$(5s) $\leftarrow$ O(n)] are found (340, 380 nm). The third band at 405 nm is a transition from the oxygen atoms corresponding to the connections to the neighboring α cage. If the Ag$^+$ ion is coordinated by water only, the Ag$^+$(5s) $\leftarrow$ O(n) transition is found below 250 nm. The first ionization energy of water is 12.6 eV, which means that the HOMO lies at -12.6 eV. For silicates, however, it is found at -10.7 eV, which explains the long-wavelength situation of the LMCT.[6] The coordination of only one water molecule to a Ag$^+$ ion which is coordinated to zeolite oxygen atoms leads to a destabilization or a raising of the Ag$^+$(5s) level, and therefore to a blue shift of the LMCT transitions.

We were able to show that activation at room temperature of silver-containing zeolite A with very low degrees of exchange already leads to a yellow coloring, and that the absorption of light and therefore the impression of yellow coloring are reversible with respect to the desorption/adsorption of water. The dependency of the absorption bands on the degree of exchange can be explained with a simple model of the cation distribution. Quantum-chemical calculations show that electronic transitions from the lattice oxygen atom to the silver ion are allowed, that these transitions are in the visible range, and that they experience a blue shift if coordinated with water. Hence, an observation first described 35 years ago has been quantified and explained in a noncontradictory way.

Experimental Section

Chemically pure zeolite was produced and characterized by a known procedure.[7] For the examinations, 80 mg of zeolite were freshly exchanged each time with 0.1 M AgNO$_3$ (Merck, Titrisol). At degrees of exchange up to six Ag$^+$ ions, the zeolite was placed in 5 mL of H$_2$O, and a calculated amount of AgNO$_3$ was added and suspended for 15 min. Quantitative uptake of the Ag$^+$ ions can be assumed.[8] The zeolite was washed with water twice. The zeolite stored at 92% humidity was assumed to have 27 H$_2$O molecules per formula unit.[1] To obtain samples fully exchanged with Ag$^+$ ions, the zeolite was suspended twice in 20 mL of AgNO$_3$ solution for 15 min and washed three times with 15 mL of H$_2$O. The exchanged zeolite was put into 2 mL of H$_2$O and transferred to a quartz ampoule (cylinder with a height of 2 cm and a radius of 0.75 cm) which was connected to a HV-Flansch Adapter in a gas-tight way. The ampoule was connected to the pump in a horizontal position so that the zeolite could be deposited evenly at the bottom of the ampoule. The extra water was vaporized at 10 mbar (2–3 h). For activation, the turbo pump (Alcatel) was connected until the final pressure of the apparatus was achieved (48–72 h, $1-2\times10^{-7}$ mbar). After activation at room temperature, temperature-treated samples were gradually brought to the desired temperature (±5°C) with an adjustable heat pistol. The heating rate was chosen such that the pressure within the apparatus did not exceed 5×10^{-6} mbar, to avoid irreversible brown color changes. The ampoule with the sample sufficiently adhered to the bottom was separated from the pump with a burner under gas-tight conditions and transferred to the spectrometer. UV/Vis spectra were measured as diffuse reflection spectra at room temperature with a Perkin Elmer Lambda 14 spectrometer with an integration sphere (Labshere RSA-PE-20). Before they were graphically represented, the automatically collected data were converted using the Kubelka–Munk formula.

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A Lysoganglioside/Poly-L-glutamic Acid Conjugate as a Picomolar Inhibitor of Influenza Hemagglutinin**

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Cell surfaces are often covered with oligosaccharides that play important roles in many cellular recognition events, including infection, cancer metastasis, and other intercellular adhesion processes.[1] Hemagglutinins (HAs) of influenza virus are typical examples of such receptor molecules. These trimeric proteins are capable of binding to sialylated oligosaccharides on the epithelial cell surface.[2] The minimum

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