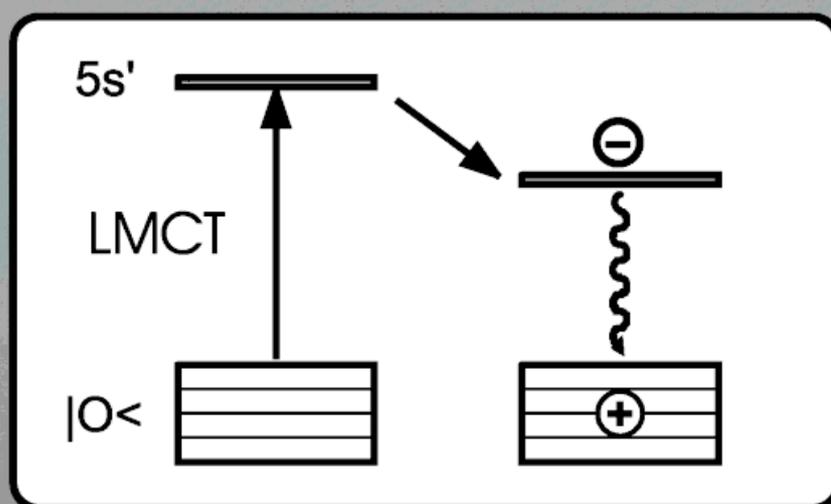


The cause of the yellow color of activated silver-containing zeolite A

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 aluminosilicates 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 Na⁺ form is Na₁₂⁺[(SiO₂)₁₂(AlO₂)₁₂]. The Na⁺ cations can be partially or fully exchanged with Ag⁺ ions.

Ag_x⁺Na_{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 Ag⁰ and release of O₂ from the zeolite framework was assumed. We show here that upon activation under high vacuum Ag_x⁺Na_{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 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 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.

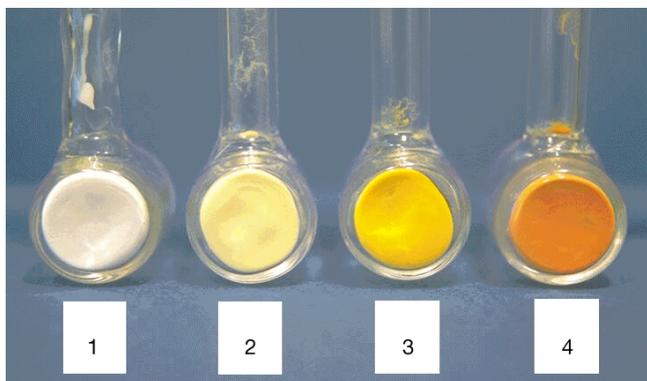


Figure 1. Upon activation, colorless zeolite A containing Ag⁺ ions turns yellow to brick-red, depending on the conditions. Samples of Na₁₂⁺A (1), Ag_{0.13}⁺Na_{11.87}⁺A (2), and Ag₆⁺Na₆⁺A (3), activated under high vacuum at room temperature, are shown. Ampoule 4 contains Ag₆⁺Na₆⁺A, which was treated at 200 °C under high vacuum.

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Ampoules 1–3 contain Ag_x⁺Na_{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 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 Na₁₂⁺A which was partially and fully exchanged with Ag⁺ ions. It was activated under defined conditions which were as mild as possible.

Figure 2 shows UV/Vis spectra of Ag_x⁺Na_{12-x}⁺A after activation under high vacuum (2 × 10⁻⁷ mbar) and at room temperature. The spectra of samples with a degree of

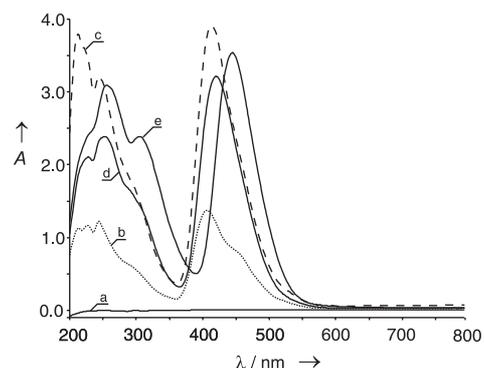


Figure 2. Dependency of the UV/Vis absorptions on the degree of exchange of the zeolite activated under high vacuum at room temperature: a) Na₁₂⁺A, b) Ag_{0.13}⁺Na_{11.87}⁺A, c) Ag₁⁺Na₁₁⁺A, d) Ag_{1.5}⁺Na_{10.5}⁺A, e) Ag₆⁺Na₆⁺A.

exchange of up to one 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 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 maximum. However, regardless of the degree of exchange, the coloring remains yellow.

Figure 3 shows the statistical distribution of 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

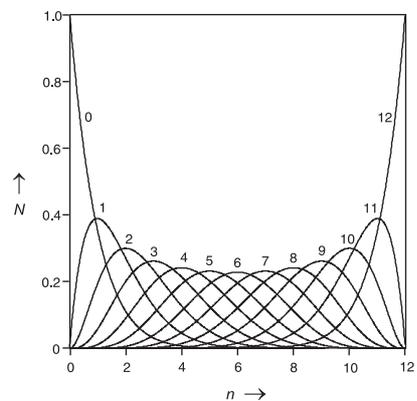


Figure 3. Calculated distribution of the Ag⁺ ion in an Ag_x⁺Na_{12-x}⁺A model with 12 equivalent sites per cage. The graph shows which share (N) of the cages contains 0,1,2,...,12 Ag⁺ ions at a chosen average degree (n) of exchange.