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Photochemical and Photophysical Properties of Ag^+ -Zeolite Monograin Layers on a Substrate

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Abstract

The desorption of water from zeolite monograin layers is very fast under evacuation. Based on this, we have reinvestigated the colour changes observed upon dehydration-hydration of Ag^+ -A-zeolites, and we have found that the yellow colour can be obtained by evacuation at room temperature within a few minutes. After adding a little of degassed water via the vacuum system, the colour of the samples turned to white again within a fraction of a second. The evacuated Ag^+ -A- and the $(\text{Ag}^+)_6(\text{Cl}^-)_2$ -A-zeolite layers show red luminescence after irradiation at 355 nm which decays within 20 to 140 μs . Appropriately prepared layers evolve oxygen on illumination in the presence of water and small amounts of Cl^- up to a critical concentration above which the oxygen evolution stops abruptly. The Ag^+ -A-zeolite monograin layers deposited on glassy carbon electrodes show a remarkable electrochemical behaviour which is explained by an intrazeolite electron transport mechanism.

Introduction

Zeolite monograin layers on a substrate are very suitable to study properties of modified zeolites, which have been a matter of controversy over many years in some cases. The advantage of monograin layers is that transport processes at the zeolite microcrystal/gas (ZM/g), the ZM/liquid or the ZM/electrode phase boundaries are directly accessible and not hidden by the slow and sometimes not well defined intergrain transport or by adsorption/desorption steps. We report on hydration-dehydration, luminescence, photochemical and electrochemical ex-

periments of Ag^+ -A-zeolite and of $(\text{Ag}^+)_n(\text{Cl}^-)_x$ -A-zeolite monograin layers deposited on different substrates.

Dehydration-hydration of Ag^+ -A zeolites

The desorption of water from zeolite monograin layers is astonishingly fast under evacuation at room temperature.¹ Based on this finding we have reinvestigated the colour changes observed upon dehydration-hydration of Ag^+ -A-zeolites. Rálek et al. reported in 1962 that Ag^+ -A-zeolites turn from white over yellow to full yellow-red under dehydration at 473 K and also at 623 K and back to grey-white under rehydration.² These colour changes were discussed by a number of authors and the explanations for their occurrence range from charge transfer interactions between the Ag^+ ions and the zeolite framework oxygen, responsible for the yellow colour, to multistep autoreductive processes involving framework oxygen and formation of partially reduced silver clusters. This discussion has recently been reviewed by Sun and Seff.³ EHMO calculations of $[\text{Ag}_3(\text{H}_2\text{O})_3]^{3+}$ in a β -cage showed that such colour changes correlate with charge transfer transitions from framework oxygen to the silver ions and that orbital interactions between the Ag^+ are important.⁴ Band structure calculations of silver zeolite models lead to a similar result.⁵

We have observed that the yellow colour can be obtained by evacuating thin Ag^+ -A-zeolite layers at room temperature. Very pure zeolite A prepared in our laboratory was used. Evacuation in a vacuum of $6 \cdot 10^{-5}$ mbar at about 25°C for 25 minutes is enough to turn the white samples into yellow ones. The colour became more intense and turned to full, deep yellow upon prolonged

evacuation. After adding a little of degassed water via the vacuum system, the samples turned to white again within a fraction of a second. This was reproduced several times over 3 days, and no permanent changes could be observed. Addition of dry oxygen to the yellow samples did not have any visible effect. Samples dehydrated at room temperature under vacuum ($1.8 \cdot 10^{-5}$ mbar) for more than 1 h showed a red luminescence upon excitation with a 10 ns Nd-YAG laser pulse at 355 nm. After heating the Ag^+ -A-zeolite layers under vacuum to 100°C they became brown-yellow. Addition of degassed water turned their colour to light yellow.

Luminescence spectra of fully exchanged Ag^+ -A-zeolite layers on a quartz plate measured from 1 to 21 μs , 21 to 41 μs , 41 to 61 μs , 101 to 121 μs , and 141 to 161 μs after a Nd-YAG laser pulse of 10 ns at 355 nm are illustrated in Figure 1. Main parts of the apparatus used to carry out these measurements have been described before.⁶ The shape of the spectra does not change with time and the peak maximum is at 660 nm. The decay of this luminescence can be described by two exponentials of about the same weight and lifetimes in the order of 24 and 140 μs .

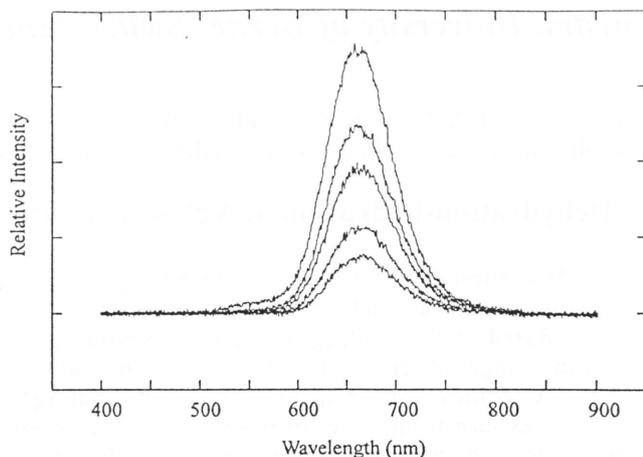


Figure 1. Time resolved luminescence spectra of fully exchanged Ag^+ -A-zeolite at -171°C and $1.8 \cdot 10^{-5}$ mbar.

The yellow colour of the evacuated Ag^+ -A-zeolites can be attributed to a charge transfer transition from zeolite framework oxygen to the silver ions. The Ag^+ -framework oxygen distances become shorter upon dehydration.⁷ The luminescence originates from a relaxed excited state which we have denoted as $(|O|<)^{\oplus}(5s')^1_{\text{relaxed}}$.⁸ This colour change is reversible up to temperatures of at least 80°C and it is definitely not due to an autoreduction process of any kind.

Photochemical Behaviour

Appropriately prepared Ag^+ -A-zeolites evolve oxygen on illumination in the presence of water. Cl^- occluded in the cavities of zeolite A forms $(\text{Ag}^+)_n(\text{Cl}^-)_x$ -A-complexes. n and x refer to a unit cell of the zeolite A. At approximately neutral pH, addition of small amounts of

Cl^- to the Ag^+ -A-zeolites leads to enhanced O_2 evolution up to a critical concentration above which the oxygen evolution drops abruptly.⁹ The critical concentration is reached when free Cl^- is present in the solution. Up to this limit the $(\text{Ag}^+)_n(\text{Cl}^-)_x$ -A-zeolite samples show the same type of self-sensitization as reported previously.¹⁰ We assume that the O_2 evolution occurs at the surface of the particles. Silver chloride present at this surface seems to be essential for the photochemical behaviour of the system. Cyclic voltammograms of $(\text{Ag}^+)_6(\text{Cl}^-)_2$ -A-zeolite monograin layers on glassy carbon electrodes in the dark and under irradiation show nearly reversible behaviour. Studying the luminescence of $(\text{Ag}^+)_6(\text{Cl}^-)_2$ -A-zeolite monograin layers on a quartz plate in the same way as described in the previous section, we have observed the time resolved spectra illustrated in Figure 2.

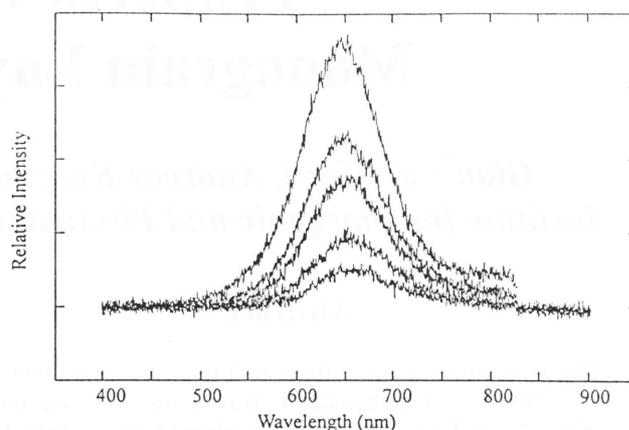


Figure 2. Time resolved luminescence spectrum of $(\text{Ag}^+)_6(\text{Cl}^-)_2$ -A-zeolite monograin layers at -171°C and $1.8 \cdot 10^{-5}$ mbar.

The spectra measured from 1 to 19 μs , 21 to 39 μs , 41 to 59 μs , 101 to 119 μs and 161 to 179 μs after the laser pulse are broader than those in Figure 1, and the peak at about 650 nm moves to slightly longer wavelengths with time. The decay also of this luminescence must be described by two exponentials of about the same weight and lifetimes in the order of 22 and 120 μs . Again we assume that the luminescence originates from a relaxed charge transfer state. Up to now, however, we have no information to what extent the Cl^- is involved in this state.

Treatment of the samples with $[N(\text{ethyl})_4]^+[\text{CN}^-]$ removes residual AgCl at the zeolite-crystal surface and probably also from the cages located close to the surface. The so treated samples show weaker luminescence than those in Figures 1 and 2 with two peaks: one at about 540 nm and the other one at about 650 nm. The spectra were recorded from 1 to 11 μs , 9 to 19 μs , 17 to 27 μs , 41 to 51 μs and 73 to 83 μs after the laser pulse. The 540 nm band decays slightly faster than the 650 nm one. The decay times are in the order of 30 μs to 50 μs . Repeating the measurements on the same sample for several times results in a decrease of the 540 nm band which finally disappears. This indicates that a photochemical

reaction, the nature of which is not yet known, takes place. However, the samples treated with tetraethylammoniumcyanide did no longer evolve oxygen on illumination in the presence of water.

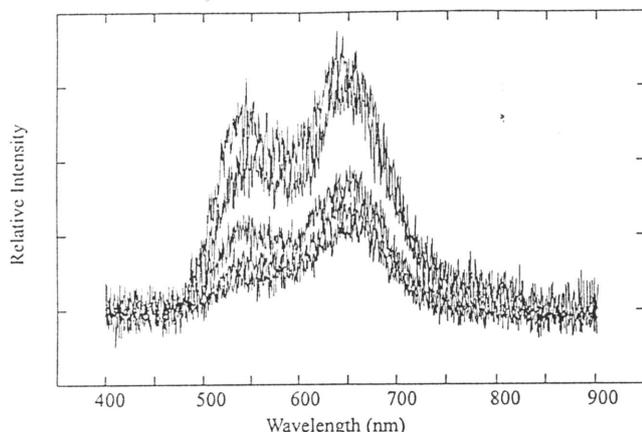


Figure 3. Time resolved luminescence spectrum of $(Ag^+)_6(Cl^-)_2$ -A-zeolite monograin layers, washed with tetraethylammoniumcyanid, at $-176^\circ C$ and $1.7 \cdot 10^{-5}$ mbar.

Electrochemical Properties

Applying a new method for preparing mechanically stable dense monograin layers on substrate electrodes, we have been able to distinguish between an intrazeolite ion transport in Cu^{2+} -Y-zeolite¹¹ and an intrazeolite electron transport mechanism in Ag^+ -A-zeolite.¹² The same method has been successful to study the question on intra- versus extrazeolite charge-transfer at MV^{2+} -Y-zeolite electrodes in different aqueous alkali electrolytes.¹³ — The Ag^+ -A-zeolite monograin layers deposited on glassy carbon electrodes show a remarkable electrochemical behaviour. The number and the position of peaks and shoulders which appear in cyclic voltammograms during the first cathodic scan depend on the Ag^+ -exchange degree, the scan rate, and the electrolyte cations. Our observations indicate the presence of eight electrochemically distinct silver species. We discuss the mechanism of the electrochemical reactions by assuming site-specific reduction potentials, site-to-site interconversion of Ag^+ ions and formation of silver clusters. Seven peaks observed in the cyclic voltammograms are related to reduction within the zeolite in an intrazeolite process. One corresponds to an extrazeolite process, namely the reduction of Ag^+ ions on the surface of the glassy carbon electrode after ion exchange of Ag^+ out of the zeolite. Four peaks out of the seven are tentatively assigned to the reduction of Ag^+ at different sites in the zeolite framework, and three to the reduction of

silver clusters formed in the α -cage during the cathodic scan. As stated above, we propose an intrazeolite electron transport mechanism.¹² Band structure calculations of silver clusters in the cages of zeolites indicate that the interactions are sufficient for such a mechanism to take place.⁵ We expect that recent advances on in situ growth of zeolites onto supports will stimulate the intersection of electrochemistry and zeolite science^{14c} and help to rapidly advance the control and the understanding of the photochemical, the photoelectrochemical and the spectroscopic properties of modified zeolites.

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