TRANSMISSION SPECTRA OF SINGLE CRYSTAL ZEOLITES CONTAINING Ni^{2+}-IONS

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Transmission spectra of nickel-exchanged single crystal zeolites are recorded on a single beam microscope-spectrophotometer driven by microcomputer. This digital method yields an improved spectral resolution. Receiving the absorption spectra of transition metal ions present in the zeolite-lattice, both the sodium- and the exchanged forms of zeolites were on-line computed and evaluated. In relation to absorption-maxima of complexed ions in aqueous solutions, the spectra of transition metal complexes surrounded with zeolite network show bathochromic band-shift as well as -broadening and -splitting, respectively. With regard to possible coordination spheres of transition metal ions in the zeolite framework, the spectra are interpreted in terms of ligand field theory. The method presented will also allow an analysis of the sites of hydrocarbons in exchanged zeolites by comparing these spectra with those, which are not loaded with organic compounds, and the spectra of the free organic molecules, respectively.

Introduction

For understanding the role of transition metal ions in zeolite catalysis and for setting up defined starting conditions in reactions of organic compounds in zeolites it is necessary to study, how these ions are incorporated into the zeolite lattice. In addition to EPR-investigations, which are accomplished in cooperation with the Bulgarian Academy of Sciences, the method of electronic excitation spectroscopy in combination with ligand field theory is useful to determine cation positions in zeolites.

Employing large single crystals of defined structure and measuring their absorption spectra in transmitted light, more detailed information can be obtained about particular crystallites eliminating undesired outer-surface effects. Furthermore, compared with the frequently used reflectance technique, in transmission spectroscopic investigations almost no scattering effects are to be found.

Method and apparatus

The transmission spectra of nickel containing single crystal zeolites were carried out with a microscope-spectrophotometer (Leitz) between 220 and 800 nm using mirror objectives (Ealing/Beck) of magnification-factor 74.

The lapse of measurement is driven by microcomputer. Using a stepping motor to push the monochromator, the range of wavelengths can be scanned in 25 000 different steps. At each scanning point an optional number of single values according to the actual intensity of transmitted light is transferred to a calculator (Hewlett Packard 9830A). One to ten data per measuring position are chosen to be recorded and averaged by calculator. Moreover, higher accuracy is received by scanning the whole measuring range repeatedly and by adding and averaging the resulting spectra at each point (cumulative method).

Independently of recording, absorption spectra are evaluated by subtraction of sample- and reference-curves, respectively. Small differences are recognized in comparing sodium zeolites with those containing transition metal ions in small amount.

Preparation of Samples

Synthesis and growth of single crystals were carried out by a method for preparation large crystals of sodium X zeolite (particle sizes 30 to 50 µm in diameter) described by J. F. CHARNELL [1]. The structure of the faujasite type zeolite was confirmed by X-ray diffraction. A Si/Al-ratio of 1.15 was determined by X-ray fluorescence analysis.

Ni^{2+}-ions were introduced into the prepared single crystal zeolites by ion exchange from aqueous solutions of nickel acetate (conc. 0.01—0.5 mol/l, pH 7, T = 80 °C, degree of exchange 10 to 80%) [2]. The degree of exchange was calculated on the basis of Ni- and Al-contents in the zeolite, which was determined by atomic absorption spectroscopy.

Adsorption of benzene on sodium and nickel exchanged X zeolites was accomplished by stirring small amounts of zeolites in anhydrous benzene at 50 °C for 10 hrs.

Results

Fig. 1 shows the spectrum of a nickel exchanged zeolite (deg. of exchange 75%) compared to the spectra of nickel acetate crystal and an aqueous solution of nickel acetate. The spectra of the nickel acetate crystal and the nickel exchanged zeolite show in addition to the known maxima at 390 to 400 nm and 650 to 730 nm another band in the near UV-region. This maximum has also been observed in the spectrum of aqueous nickel perchlorate solution as a shoulder [3].

To rule out the contribution of the unexchanged sodium X zeolite to the spectrum due to differences in the crystal thickness between sample and reference crystal two sodium X zeolite crystals of different thickness have been measured vs. air as reference and vs. each other (Fig. 2). Curves a) and b) have a shoulder at about 240 nm. Subtraction of the spectrum of the thinner crystal (approx. 30 µm) from that of the thicker crystal (approx. 50 µm) results in a clear maximum at 240 nm, which corresponds to the absorption of the difference of the two crystals (curve c). This absorption band is due to an electronic transition of Al in the zeolite system and has always to be considered evaluating the spectra of transition metal ion exchanged zeolites.
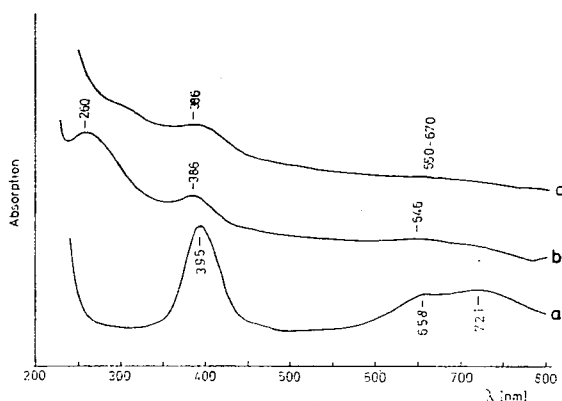
Fig. 1. Absorption spectra of: *a)* aqueous nickel acetate solution; *b)* nickel acetate crystal (ref.: air); *c)* nickel-exchanged (75 %) X zeolite crystal (ref.: sodium X zeolite).
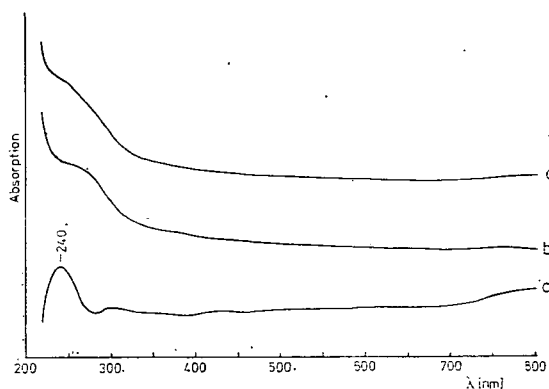

Fig. 2. Absorption spectra of sodium X zeolites: *a)* 50 μm in diameter crystal (ref.: air); *b)* 30 μm in diameter crystal (ref. air); *c)* 50 μm in diameter crystal (ref.: 30 μm in diameter crystal):

In Fig. 3 the absorption spectra of nickel exchanged zeolites in dependence on the degree of exchange are plotted. In the spectra a bathochromic shift of the two low energy bands is observed depending on the degree of exchange as compared to nickel acetate solution. The shift decreases with increasing degree of exchange. The splitting of the two bands decreases in the same direction. At high degree of exchange only one broad band remains at 650 to 660 nm, which corresponds to the low energy maximum of a nickel acetate crystal (Fig. 1).

Fig. 4 shows the spectra of sodium and nickel exchanged X zeolites after the adsorption of benzene against sodium X zeolite as reference. The vibrational spectrum

of benzene around 250 nm as measured in ethanolic solution can also be clearly observed in both zeolite spectra. No shift of the bands can be seen. Also, the nickel maxima are not significantly shifted as compared to the nickel-exchanged zeolite not loaded with benzene.
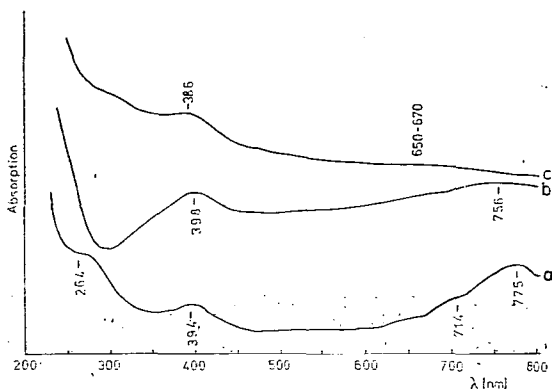

Fig. 3. Absorption spectra of nickel-exchanged zeolite crystals (ref.: sodium X zeolite): *a)* 12%; *b)* 47%; *c)* 75% degree of exchange
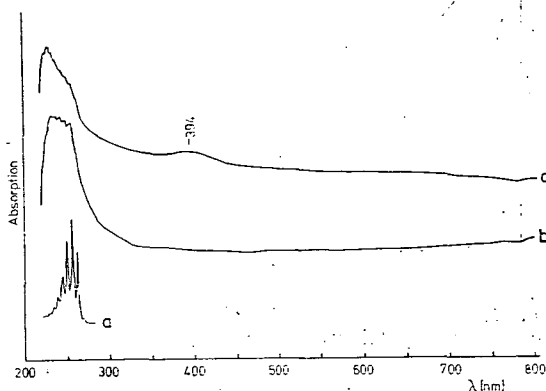

Fig. 4. Absorption spectra of: *a)* ethanolic solution of benzene; *b)* benzene loaded sodium X zeolite; *c)* benzene loaded nickel-exchanged zeolite (ref.: sodium X zeolite)

Discussion

According to [4—6] the Ni^{2+}-ions are incorporated in the zeolite lattice as octahedral $Ni(H_2O)_6^{2+}$-complexes. The maxima at 395 nm, 660 nm and 1180 nm of such nickel ions are interpreted by ligand field theory as the transitions $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (III), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (II) and $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (I) obtained for an octahedral field.

The band found in the near infrared at 1180 nm could not be measured by our method due to the limited range of the monochromator.

On the basis of the interpretation by REINEN [7] broadening and splitting of the band at 650 to 730 nm in our spectra is due to spin-orbit coupling of the $^3T_{1g}(F)$-term. This leads to an amplification of the higher energy maximum corresponding to the more energetic transition $^3A_{2g}(F) \rightarrow {}^1E_g(D)$ to the spin-forbidden $^1E_g(D)$-term of multiplicity 1.

Also, a splitting of band (III) should be seen. Using a Dq-value of 850 cm^{-1}, the Orgel-diagram for octahedral Ni^{2+}-ions [8] results in the overlap of the splitted $^3T_{1g}(P)$-term by the singlet-terms $^1T_{2g}(D)$, $^1A_{1g}(G)$ and $^1T_{1g}(G)$ leading to spin-forbidden transitions.

The base for the explanations as published by REINEN [7] is the assumption of an undistorted octahedral $Ni(H_2O)^{2+}$-complex and a value of Dq corresponding to the band between 1100 and 1200 nm.

Starting from these assumptions, we found it difficult to interpret the maxima in the near UV-region, which we observed especially for nickel acetate crystals and low degree of exchange nickel zeolites, respectively as shoulders in nickel perchlorate solution and high degree of exchange nickel zeolites. These bands as well as the shoulders are of similar intensities as compared to bands (II) and (III) (cp. [6]). Within the interpretation scheme of REINEN they have to be explained as intercombination bands $^3A_{2g}(F) \rightarrow {}^1E_g(G)$ or $^3A_{2g}(F) \rightarrow {}^1T_{2g}(G)$. However, the oscillator strengths of these intercombination bands, which result from the position of the nearest spin-allowed transition (III), should be too small to give observable intensities in the spectrum. On the other hand, the interpretation as a charge-transfer transition would result in much higher intensities of the bands than can be observed.

The D_{3h}-splitting due to the Ni^{2+}-ions discussed by KELLERMAN and KLIER [4] for thermally dehydrated nickel zeolites, where the low energy band at 260 nm is attached to the transition $^3A_{2g}(F) \rightarrow {}^3E_{1g}(P)$, can also be excluded in the case of hydrated nickel zeolites and of nickel acetate crystals, respectively.

On the other hand it seems probable to us, that the Ni^{2+}-complex incorporated in the zeolite is slightly distorted. Due to the geometry of the zeolite-lattice especially C_{2v}- or C_{4v}-symmetry should be discussed. This assertion depends essentially on the comparison of the spectra of hydrated nickel zeolite and nickel acetate, respectively, and the circumstance, that Ni^{2+}-ions in acetate crystals have a coordination sphere of D_{4h}-symmetry [9].

Assuming D_{4h}- or C_{2v}-symmetry and taking into consideration the absorption band at 260 nm, an interpretation of this band as the transition $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (III*) should be possible. This would result in correlating the band at 395 nm and the maxima between 650 and 730 nm with the transition $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (II*) and $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (I*), respectively.

In the case of nickel acetate crystal, the maximum at 646 nm would yield a Dq-value of 1548 cm^{-1}. The higher energy band (II*) should therefore appear at 406 nm and the maximum due to the transition (III*) should be at 252 nm according to the equations by SENDODA [5] and to the term-diagram for octahedral d^3- and d^8-complexes by TANABE AND SUGANO [10].

Besides spin-orbit-coupling and interaction with the neighboured $^1E_{1g}(D)$-term, the splitting of the band (I*) should be explained, within this interpretation (e.g. to D_{4h}- or C_{2v}-symmetry), by lowering of symmetry of the Ni^{2+}-complex upon in-

corporation into the zeolite lattice. On the basis of these assumptions the dependence of this band on the degree of exchange can be cleared up.

The possibility to explain the high energy maxima supports the above intepretation. On the other hand, the necessity of defining a second overtone of the complexed water for the long-wave band at about 1180 nm contradicts this assertion.

The spectra of benzene loaded zeolites indicate that benzene can be absorbed at aqueous zeolites. However, neither a remarkable alteration of the benzene structure nor a noteworthy change of the neighbourhood of Ni^{2+}-ions in the zeolite was seen.

References

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