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Ion-exchange with Pd/Pt and Fe and their reduction to metallic state in zeolites: positron annihilation and Mössbauer studies

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ABSTRACT

Positron annihilation and Mössbauer-effect measurements were performed on fajaussite X-, Y- and ZSM-5 zeolites in as-produced and also in ion-exchanged (with Fe and Pd or Pt) and subsequently reduced states. A correlation of the positron data with the filling-up of the cages of the zeolites due to the formation of metallic particles was found. The Mössbauer results revealed that the metallic particles are bimetallic.

INTRODUCTION

Zeolites represent a class of materials with steadily increasing importance. Their use as host matrices for high dispersion metallic particles is of special interest, as they might be preferably applied as catalysts. Their preparation starts with ion exchange in aqueous slurries. These ions are reduced to metallic state by introducing ions of an easily reducible second element (usually from the Pt-group). To follow this process investigations were focussed to the study of the local properties of the metallic particles inside the cages, e.g. by EXAFS /1/ or TEM /2/. Various types of zeolites were studied by positron annihilation (PA), too, showing a correlation of the annihilation parameters with e.g. the cage size, the metallic ions present, the water content, etc. /3-8/.

In the present study the filling-up of the cages is followed by positron lifetime measurements on PdFe-X, PdFe-ZSM-5 and PtFe-Y systems. ^{57}Fe Mössbauer-effect (ME) measurements of the corresponding systems were performed for identification of the metallic states of ions involved.

EXPERIMENTAL

The X-, Y and ZSM-5 zeolite samples were obtained in as-received and ion-exchanged (with Pd/Pt and Fe ions) as well as in H_2 reduced states as described in /9, 10/: no other accompanying chemical changes were induced. The Si:Al ratios were 1.2, 2.4 and 20.9 for the X, Y and ZSM-5 zeolites, respectively.

Positron lifetime measurements were carried out on samples equilibrated in ambient atmosphere (i.e. the samples contained adsorbed water in the amount of ca. one adsorbed water molecule per lattice-aluminium ion - as was determined from gravimetric measurements. This amount of water does not change significantly the free pore volumes of zeolite.) The samples for the PA measurements were prepared by pressing the powder-form zeolite into disks of about 1.5 mm thickness. A sandwich arrangement of the samples was used with a ^{22}Na positron source of about 20 MBq activity (embodied by thin Ni foils) in-between. A high data statistics of over 10^7 counts in the spectra was collected. (Time-resolution: 290 ps, determined by a ^{60}Co source and also by evaluation of a ^{207}Bi spectrum). The lifetime distributions were evaluated with the PATFIT programme package /11/ with appropriate source correction.

The Mössbauer measurements on calcined and H₂-reduced samples were performed in an in-situ cell (i.e. the water content of samples was negligible during these measurements). A conventional (KFKI-made) spectrometer was applied in constant acceleration mode, employing a ⁵⁷Co/Pd source of 1 GBq. The registered isomer shift values were related to metallic α -iron.

RESULTS AND DISCUSSION

For the interpretation of data it is worth to mention that the treatments applied do not significantly change the state of samples. One might expect some removal of Al from the lattice as a consequence of Fe³⁺ \leftrightarrow Fe²⁺ (auto)reduction processes /12/. In contrast, XRD measurements on the samples revealed that neither the ion exchange nor the H₂-reduction resulted in noticeable lattice destruction taking place during these treatments /13/.

Positron annihilation measurements

The PA lifetime distributions were evaluated with the assumption of two, three and four lifetime components. The best fit was achieved for four components. The hard task of evaluating very short and rather long lifetimes simultaneously was circumvented partly performing the measurements not in vacuum but in ambient temperature where the long lifetimes were found much shorter (several ns instead of several 10 ns). The annihilation of the positrons takes place through several competitive annihilation channels not present in conventional solids. One may interpret the four components as: a) τ_1, I_1 : p-Ps, zeolite bulk material, metal atoms; b) τ_2, I_2 : extended free volumes in the zeolite; c) τ_3, I_3 : surface states in cages/channels of the zeolite; d) τ_4, I_4 : pick-off of o-Ps.

Zeolite sample	τ_1 /ps	τ_2 /ps	τ_3 /ps	τ_4 /ps	I_1 /%	I_2 /%	I_3 /%	I_4 /%
X	182	392	1215	1880	16.63	61.65	10.54	11.18
error (+/-)	6	5	103	67	1.17	0.79	1.90	2.33
PdFe-X	166	368	943	2067	15.53	75.64	5.97	2.86
error (+/-)	5	3	58	62	0.97	0.57	0.30	0.29
Y	172	402	1096	2237	15.41	62.60	7.75	14.24
error (+/-)	6	5	76	23	0.97	0.54	0.31	0.55
PtFe-Y	195	442	1534	3221	21.26	63.42	6.43	8.89
error (+/-)	4	4	87	50	0.93	0.71	0.26	0.45
ZSM-5	249	500	1577	3981	22.08	73.27	3.66	0.99
error (+/-)	4	4	88	258	1.01	0.82	0.13	0.16
PdFe-ZSM-5	178	404	1200	2253	22.71	59.58	12.61	5.10
error (+/-)	3	4	40	64	0.81	0.53	0.32	0.59

Table 1. PA lifetime parameters for the as-received and ion-exchanged sample pairs.

The I_3 and I_4 data on the as-received samples show that the most space for the formation of the long-living components is available in the Y and X zeolites, having cages, compared to the channel-rich ZSM-5 structure. The faujasite zeolites (X, Y) have higher ion exchange capacity than the ZSM-5 structure, which is mirrored in the PA data. The filling-up of the free volumes of the zeolites is mainly noticeable from the changes of the long-living components and from that of their relative intensities. The reversed feature found for the ZSM-5 zeolites might be correlated not only with the probable breaking-up of channels into a cage-like structure, but also with the possibility that in the as-received state a substantial amount of o-Ps might be formed, being lost from registration due to the

three- annihilation. These changes might be correlated with the appearance of "dispersed" and "localised" metallic components in the zeolite structure but no further information is revealed on the state of metallic ions by PA.

Mössbauer spectroscopy

Mössbauer spectra of (2wt% Pd + 0.2wt% Fe)-X, (2wt% Pd + 0.2wt% Fe)-ZSM-5 and (4wt% Pt + 1wt% Fe)-Y zeolite (recorded at 300 K in situ after appropriate ion exchange, calcination, and reduction in H₂ at 720 K) are shown in Fig. 1 a-c, respectively. The ME spectrum of 0.07 wt% Fe-X zeolite system recorded after the same treatments is also shown in Fig. 1 d, demonstrating that under the conditions applied single iron ions cannot be reduced to metallic state. The spectrum is composed of the doublets of high-coordination ("octahedral", Fe²⁺_{oct}) and low-coordination ("tetrahedral", Fe²⁺_{tetr}) components /9/. Spectra of samples containing Pd or Pt are significantly different - a metallic component is clearly present in them.

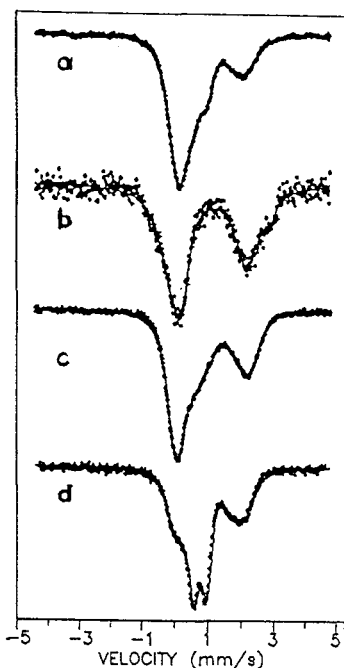


Figure 1. 300 K Mössbauer spectra obtained after hydrogen reduction of various zeolite samples with appropriate ion exchange [a - (2wt% Pd + 0.2wt% Fe)-X: b - (2wt% Pd + 0.2wt% Fe)-ZSM-5: c - (4wt% Pt + 1wt% Fe)-Y: d - 0.07 wt% Fe - X zeolite systems].

In the case of 2wt% Pd + 0.2wt% samples the line at 0.14 - 0.17mm/s points to the presence of a bimetallic PdFe component /10/ (spectral areas of 36% and 15% for X and ZSM-5 zeolites, respectively). In the 4wt% Pt + 1wt% Fe sample 27% spectral area can be attributed to a metallic PdFe component. (The observed isomer shift value, 0.07mm/s, is a typical metallic isomer shift and is very close e.g. to the values found on PtFe/SiO₂ systems /14/). Our data do not support the interpretation of studies on (3wt% Fe + 11wt% Pt)-NaY system, in which one component with 0.31mm/s isomer shift value is attributed to (Pt_x-Fe)ⁿ⁺ entities /15/. In case of PdFe systems, no magnetic splitting was detected even in the Mössbauer spectrum at 80 K /16/ - which is a strong indication of small particle sizes. Taking into consideration that i/ silica supported systems display a magnetic sextet, while the zeolite hosted systems with the same Pd and Fe content do not exhibit this feature, and ii/ the bimetallic Pd_xFe component is formed from the low-coordination Fe²⁺_{tetr} component located in the cages of zeolite - it might be proposed that the metallic particle formation proceeds inside the cages of zeolite.

The Mössbauer results unambiguously reveal the formation of bimetallic PdFe particles in X-zeolite. The formation of PtFe in Y-zeolites takes place in a significantly lower amount and the lowest portion of bimetallic particles was found in the ZSM-5 zeolite.

There are still many open questions in zeolites, well suited for further studies by PA and Mössbauer spectroscopy, i. e. with respect to the size distribution and localization of the metallic particles, thought to have preference at the inner "wall" of channels/cages. Further work is in progress along these lines.

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