Cadmium ion exchange in zeolite Y by chemical vapour deposition and reaction

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Cadmium ions have been introduced in extra-framework positions of zeolite Y by vapour deposition of cadmium metal in HY and subsequent redox reaction. The samples so-obtained have been investigated with carbon monoxide and xenon adsorption as well as with ^{129}Xe NMR spectroscopy. Unusual distributions of the Cd^{2+} ions with preference for the low oxygen-coordinated S III sites in the supercages were detected. A subsequent rehydration/dehydration cycle leaves the sample with a Cd^{2+} distribution similar to zeolites obtained by conventional aqueous ion exchange.

Placing transition-metal cations in extra-framework positions of zeolites is conventionally performed by various techniques like ion exchange from aqueous transition-metal solutions (wet exchange),[1,2] impregnation,[3] or contact of the hydrogen or ammonia form with the crystalline solids (solid-state exchange).[4] An interesting alternative procedure that works completely under anhydrous conditions, is the chemical vapour deposition and reaction (CVDR) technique,[5] by which metals of appropriate reduction potential are deposited and reacted with the zeolites in their hydrogen form.

In a previous paper we have demonstrated that the CVDR of zinc metal in zeolite HY produces transition-metal ion concentrations and distributions much different from samples prepared conventionally.[6]

In this contribution, we report the results of CVDR experiments with cadmium and HY, and compare the cation distribution of the so-obtained materials with wet-exchanged zeolites.

Experimental

Zeolite NH_4NaY (Y 64, UOP; Si/Al = 2.4) was repeatedly ion-exchanged with an aqueous 1 M NH_4Cl solution under reflux conditions and subsequently thoroughly washed with doubly distilled water. The obtained zeolite NH_4Y ($\leqslant 3\%$ residual Na^+) was placed in an all-glass assembly with an attached reservoir[6] containing 99.999% cadmium metal (STREM Chem., Kehl, Germany). Under high vacuum the zeolite was dehydrated and deammoniated at 420 °C for 24 h. Subsequently, the zeolite and the metal were held for 26 h at 330 °C where the equilibrium vapour pressure of cadmium is 0.2 hPa.[7] After removal of the container with the residual cadmium metal, the sample, still under high vacuum, was heated at 350 °C (200 h) and, finally, at 420 °C (16 h) by which procedure surplus cadmium was observed to be expelled from the sample. At ambient temperature, this sample, designated CdY(1), exhibited a faint yellow coloration. It was found that the coloration was reduced, but not completely removed even after a further heating period of 70 h at 490 °C.

The proton content of CdY(1) was determined by ^{1}H NMR spectroscopy to be $20 \pm 10\%$ of the value in HY indicating incomplete reduction of H^+ by the deposited cadmium metal. On the other hand, energy dispersive X-ray fluorescence spectroscopy (EDX) and wet chemical analysis yielded cadmium contents corresponding to $92 \pm 10\%$ and $99 \pm 5\%$ reduction, respectively.

The zeolite CdY(1) was rehydrated at ambient temperature for three months over saturated NH_4Cl solution and subsequently heated for 12 h at 420 °C under high-vacuum conditions. The so-obtained sample is designated CdY(2). For comparison purposes, experimental data will be shown of zeolite Cd(68)Y which was prepared from zeolite NaY by the wet exchange technique (68% exchange) using aqueous 0.1 M $Cd(NO_3)_2$ solution.[8]

Adsorption isotherms of xenon and carbon monoxide were measured volumetrically at 25.0 ± 0.2 °C. Ambient temperature ^{129}Xe NMR spectra were obtained with a Bruker CXP 100 spectrometer operating at the resonance $\omega_0/2\pi = 21.4$ MHz. For each sample a single resonance line was observed and its chemical shift δ determined relative to xenon gas at vanishing pressure according to $\delta = 10^6\ (v - v_{\mathrm{ref}})/v_{\mathrm{ref}}$.

Results

Fig. 1 shows the results obtained by diffuse reflectance spectroscopy (DRS) in the UV–VIS region, applied as described elsewhere[9] to the rehydrated samples CdY(1), Cd(87)Y,[10] and HY. The spectra of the cadmium-loaded samples exhibit a strong absorption below 215 nm which is not very significant since it can be usually observed due to a charge transfer from 2p orbitals of framework oxygen to empty orbitals (5s in the case of Cd^{2+}) of the introduced metal ions.[11] It is observed that the rehydrated sample CdY(1) [Fig. 1(c)] reveals an onset of the absorption around 500 nm, explaining the pale yellow colour, and two well developed absorption bands at 229 and 287 nm which were not detectable in a sample prepared *via* the conventional wet cadmium exchange. The onset as well as the wavelengths of the bands are close to values (218 and

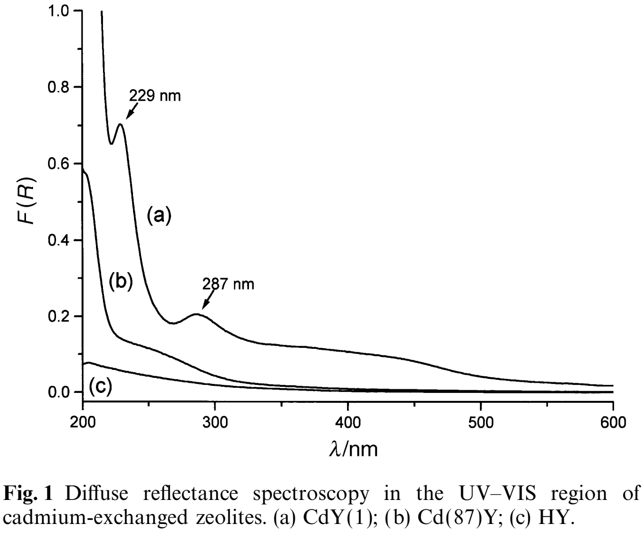

Fig. 1 Diffuse reflectance spectroscopy in the UV–VIS region of cadmium-exchanged zeolites. (a) CdY(1); (b) Cd(87)Y; (c) HY.

289 nm) observed for melts of cadmium metal in $Cd(AlCl_4)_2$ which have been assigned to diamagnetic $Cd_2{}^{2+}$ species.[12,13] These findings indicate that under the applied preparation conditions dicadmium species are tenaciously held in the zeolite matrix.

Fig. 2 shows the adsorption isotherms (298 K) of carbon monoxide in the cadmium-exchanged zeolites CdY(1) and CdY(2) prepared from HY by the CVDR technique in comparison to previous results for zeolite Cd(68)Y obtained from NaY by the wet-exchange procedure.[8] In addition, the figure shows adsorption isotherms of CO in the respective parent zeolites HY and NaY. In contrast to the linear curves observed for the latter zeolites, each of the cadmium-exchanged samples exhibits an initial steep increase of adsorption which is followed by virtually constant and linearly increasing ($p > 30$ hPa) isotherm sections in the cases of the CVDR and wet-exchanged samples, respectively (1 hPa $= 10^2$ Pa).

Fig. 3 shows the adsorption isotherms of xenon in the CVDR cadmium-exchanged zeolites in comparison to Cd(68)Y,[8] HY and NaY. As in the case of CO, the transition-metal exchanged samples exhibit strong initial adsorption and subsequent almost linear courses up to the highest pressures investigated. Here, the saturation behaviour is not observed. The straight line slopes of the CVDR samples are distinctly smaller than for Cd(68)Y, HY, and NaY.

Fig. 4 shows the ^{129}Xe NMR chemical shifts of xenon in the zeolites CdY(1) and CdY(2) in comparison to Cd(68)Y,[8] HY, and NaY as function of the concentration of sorbed xenon. In contrast to the parent zeolites with linearly increasing curves, the cadmium-exchanged samples show high initial shift values and shallow minima at intermediate xenon concentrations. Interestingly, the values of the chemical shifts at low concentrations are in the same sequence as the adsorbed amounts of both CO and Xe at low equilibrium pressures.

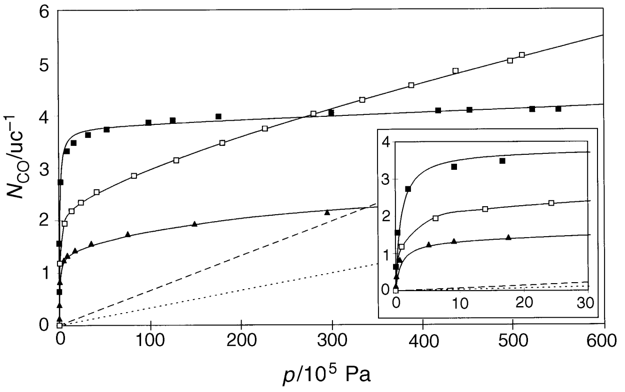

Fig. 2 Adsorption isotherms of carbon monoxide at 298 K in cadmium-exchanged zeolites. (■) CdY(1); (▲) CdY(2); (□) Cd(68)Y; (---) NaY; (···) HY.

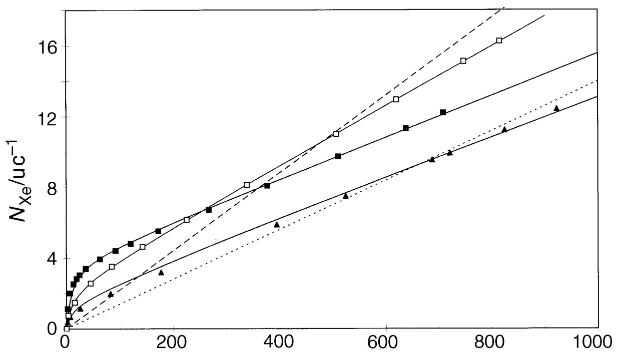

Fig. 3 Adsorption isotherms of xenon at 298 K in cadmium-exchanged zeolites. (■) CdY(1); (▲) CdY(2); (□) Cd(68)Y; (---) NaY; (···) HY.

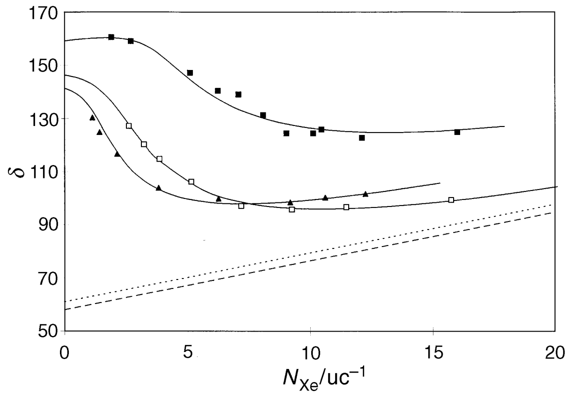

Fig. 4 ^{129}Xe NMR chemical shifts of xenon at ambient temperature in cadmium-exchanged zeolites. (■) CdY(1); (▲) CdY(2); (□) Cd(68)Y; (---) NaY; (···) HY.

Discussion

In previous papers the adsorption isotherms of carbon monoxide and xenon as well as the ^{129}Xe NMR chemical shifts of xenon sorbed in conventionally ion-exchanged zeolites Cd(x)Y ($x = 46$, 68, 87%) where x is the degree of exchange were analysed quantitatively in terms of a model that considers localized adsorption of both probe molecules on two types of cadmium ion sites (site 1 and 2), and non-localized adsorption on the remaining cage wall (region 3).[8,10] Both CO and Xe are assumed to form 1 : 1 cation–molecule complexes in the supercages. Actually, such coordination has recently been proven valid for CO in cadmium-exchanged zeolite X.[14] The two ion sites were tentatively identified with Cd^{2+} cations residing at the crystallographic four-ring (S III) and six-ring (S II) positions at the walls of the supercages of the faujasite structure, respectively.

The equations expressing this concept in quantitative forms are as follows.[10]

$$N_J=\frac{n_1k_1(J)p}{1+k_1(J)p}+\frac{n_2k_2(J)p}{1+k_2(J)p}+K_3(J)p \qquad (J=CO,\ Xe) \quad (1)$$

is the adsorption isotherm which relates the concentration of the adsorbed species N_J with the equilibrium pressure p of the respective adsorptive. The two Langmuir type terms describe the localized adsorption at the sites $i = 1$ and 2 with concentration n_i and adsorption constant k_i(J), and the Henry type term accounts for non-localized adsorption with Henry constant K_3(J). The chemical shift δ of xenon as a function of the equilibrium pressure p and the xenon concentration N_{Xe} is given by

$$\delta=\frac{1}{N_{Xe}}\left[\frac{n_1k_1(J)p}{1+k_1(J)p}\delta_1+\frac{n_2k_2(J)p}{1+k_2(J)p}\delta_2+K_3(J)p\delta_3\right]+N_{Xe}F \qquad (2)$$

N_{Xe} and p are related through the adsorption isotherm, eqn. (1). The first term of this equation is the weighted average of the chemical shifts δ_i experienced by the xenon atoms at the sites $i = 1$ and 2 and in region 3. The weighting factors are the fractional occupancies of xenon at these places according to eqn. (1). The basis for this formulation is the rapid exchange of the xenon atoms among the various sites available. The second term of eqn. (2) accounts for the magnetic interactions between the xenon atoms to first order of approximation.[15,16]

The parameters occurring in eqn. (1) and (2) may be considered, to a first order of approximation, to be characteristic either for the structure of the zeolite under study (F), for the sites accessible to both CO and Xe [k_i(J), δ_i ($i = 1$, 2)], or for the investigated sample [n_i, K_3(J), δ_3]. The values of the former two types of parameters obtained from the analysis of the previously mentioned conventionally wet-exchanged zeolites Cd(x)Y,[10] are collected in Table 1. The cited value $F=1.84$ ppm uc (uc = unit cell) has been shown to be valid for a series of transition-metal exchanged zeolites Y as well as for HY and NaY,[17] and therefore appears to be characteristic for the faujasite structure. Actually, zeolites of other structure types exhibit much different values of this parameter.[18] The solid curves through the experimental adsorption isotherm and chemical shift data of zeolite Cd(68)Y (Fig. 2–4) are the best fits with the parameter values of Table 1, and the individual parameters of this sample collected in Table 2. Obviously, the experimental data are very well reproduced.

The interesting question arises whether the adsorption isotherm data of CO and Xe as well as the ^{129}Xe NMR chemical shifts of xenon in the cadmium-exchanged zeolites obtained by the CVDR technique can likewise be reproduced on the basis of eqn. (1) and (2) as well as the structure and site characteristic parameters of Table 1. Actually, the solid lines drawn in Fig. 2–4 show the result of the fittings with these parameters, and the further parameter data (Table 2) which are characteristic for the samples under consideration. The experimental data can, in fact, be rather well reproduced. As is seen from Table 1, the value of δ_1 for sample CdY(1) had to be modified slightly to obtain the good agreement with the experimentally determined chemical shifts.

The data collected in Table 2 allow several interesting conclusions to be drawn. We consider first the concentrations of the adsorption sites, n_1 and n_2, which have to be associated with Cd^{2+} ions residing on the supercage positions S III and S II, respectively.[8] The sum of both concentrations is rather low in any case amounting to less than one cadmium ion per two supercages. These findings reflect the known preference of multivalent cations for places within the small β-cages and the hexagonal prisms.[19]

The highest concentration of supercage Cd^{2+} ions is found for the zeolite CdY(1), prepared under anhydrous conditions. Moreover, these cations are found to populate exclusively the S III positions. Interestingly, a much different situation is prevailing for zinc-exchanged zeolite Y prepared under similar conditions.[6] In that case, both types of sites were found to be populated to a roughly equal extent, namely $n_1=4.4$ Zn^{2+} uc^{-1} and $n_2=4.1$ Zn^{2+} uc^{-1}.

At present, it seems quite difficult to find a conclusive interpretation of the observed differences of site populations between the cadmium- and zinc-exchanged zeolites prepared under anhydrous conditions (CVDR). In zeolite $Na_3H_{52}Y$ the number of protons oriented into supercages has been determined by neutron diffraction techniques[20] to be 21.1 ± 5.5 uc^{-1}. If the zeolite protons are completely reduced by zinc metal and zinc cations reside where they formed, the concentration 10.6 ± 2.8 Zn^{2+} uc^{-1} in the supercages of ZnY is expected. The experimentally determined concentration, $n_1+n_2=8.5$ Zn^{2+} uc^{-1}, is in remarkable agreement with prediction. For cadmium, the detected concentration of cations in the supercages is quite different from the corresponding proton concentration. The experimental value is 3.8 Cd^{2+} uc^{-1}. A possible explanation for this puzzling situation is the formation of stable Cd_2^{2+} ions[21,22] for which evidence comes from the UV–VIS spectra. Under these circumstances, a cadmium atom in Cd_2^{2+} carries, on the average, only one elementary charge so that such species do not act with Langmuir type adsorption but become part of region 3 with Henry type adsorption. The comparatively large value of δ_3 (76 ppm) of this sample supports this interpretation. The results of recent quantum chemical calculations on xenon–cation complexes indicate that the polarization due to the electric field of the cation plays an important role for bonding.[23]

The intermediate rehydration of sample CdY(1) leads to a population of the S II and S III sites [sample CdY(2)] which is quite similar to zeolite Cd(68)Y prepared *via* the aqueous ion exchange procedure. It seems that the Cd^{2+} ions, residing exclusively on S III after the anhydrous preparation step, are redistributed through the contact with water whereas the Cd_2^{2+} species remain uninfluenced. The latter statement follows from the observation that the value of δ_3 turns out to be almost as high as in sample CdY(1) (Table 2). Further support for this interpretation comes from the results of the previously discussed UV–VIS spectra.

Table 1 Structure and site characteristic parameters of cadmium-exchanged zeolites

	Cd(x)Y^a	CdY(1)	CdY(2)
F_1/ppm uc	1.84(2)	1.84(2)	
$k_1(X)$/hPa^{-1}	0.09(2)	0.09(2)	
k_1(CO)/hPa^{-1}	1.20(5)	1.20(5)	
k_2(Xe)/hPa^{-1}	0.0016(5)	0.0016(5)	
k_2(CO)/hPa^{-1}	0.0042(5)	0.0042(5)	
δ_1	155(3)	160(3)	152(3)
δ_2	58(2)	58(2)	

$^a x=46$, 68 or 87%.

Conclusions

The deposition and subsequent oxidation of cadmium metal vapour in zeolite HY produces cadmium-exchanged zeolites with a high concentration of cadmium ions on crystallographic S III positions. The subsequent rehydration/dehydration cycle leads to a thermodynamically more stable cation distribution similar to the dehydrated wet-exchanged sample. These findings are similar to observations for zinc-exchanged zeolite Y, and possibly are valid also for other transition-metal exchanged zeolites. It can be speculated that zeolites prepared by the CVDR technique exhibit enhanced catalytic activity towards certain reactions where cations on S III positions are involved.[24]

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Table 2 Parameters characteristic for individual properties of cadmium-exchanged zeolites

	Cd(68)Y	CdY(1)	CdY(2)	HY	NaY
n_1/uc^{-1}	2.2(1)	3.8(1)	1.4(1)	0	0
n_2/uc^{-1}	1.4(1)	0.0(1)	1.5(1)	0	0
K_3(Xe)/hPa^{-1} uc^{-1}	0.016(1)	0.012(1)	0.011(1)	0.014(1)	0.022(1)
K_3(CO)/hPa^{-1} uc^{-1}	0.0038(2)	0.0065(2)	0.0000(2)	0.0033(2)	0.0066(2)
δ_3	54(3)	76(3)	72(3)	61(2)	58(2)

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