Cadmium solid state NMR studies of cadmium-exchanged zeolites

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Received 6 November 2001; accepted 18 January 2002

Cadmium-113 NMR spectra of several hydrated and dehydrated ion-exchanged zeolites are reported. The spectra are nearly featureless and have linewidths dominated by chemical shift dispersion, chemical shift anisotropy and/or dipolar coupling to other ions. Dehydration produces increased broadening. In two zeolites, however, a second ^{113}Cd peak is observed upon dehydration, which is deshielded relative to the original peak. Cadmium–aluminum dipolar recoupling experiments show that the new peak is sited closer to the zeolite framework. The appearance of this new peak is accompanied by a change in sample color; in one case this was monitored quantitatively *via* optical absorption spectroscopy. The color changes, closer proximity to the zeolite lattice, and the magnitude of the deshielding are consistent with dehydration producing low-lying electronic states deriving from overlap of metal 5s electrons and the oxygen π orbitals.

KEY WORDS: NMR studies; zeolites; cadmium NMR.

1. Introduction

Zeolites consist primarily of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra linked at their corners to form channels and cages of discrete sizes. The charge difference between the various tetrahedra is compensated by cations that determine the catalytic and sorptive properties of zeolites [1,2]. Zeolites containing cadmium ions hae been used in applications such as stabilization of CdS and CdTe semiconducting clusters that exhibit third-order nonlinearity [3,4]. Cadmium-exchanged zeolite A has been reported to have unusual dehydration properties, retaining water even after evacuation for 2 days at temperatures above 500 °C [5]. Zeolite RHO containing cadmium ions has been found to entrap xenon [6] and store hydrogen [7].

To date little is known about the local dynamics and coordination of Cd cations in zeolites. In particular, a specification of the siting of Cd ions in the hydrated and dehydrated states would define the nature of activity more completely. Crystal structures are available for zeolites LTA [8] and ZK-5 containing cadmium ions [5], and a description of Cd dynamics and spatial location of $Cd(CH_3)_2$ and its reaction products in zeolite Y upon dehydration have been reported [9]. NMR spectroscopy is an excellent technique for probing local chemical and spatial environments of cations in zeolites [10]. The NMR properties of the cadmium nucleus make it especially attractive for studying cadmium-containing zeolites [11].

In this paper we report on the ^{113}Cd NMR spectroscopy of a series of cadmium-containing zeolites. Prompted by observed changes in the NMR spectra upon dehydration, we performed optical absorption spectroscopy on one of the zeolites in both the hydrated and dehydrated state, as well as cadmium–aluminum dipolar recoupling experiments. The data suggest that a portion of the cadmium ions exhibit low-lying electronic states upon dehydration as a result of Cd ions being in closer proximity to the framework; these states account for visible light absorption and increased paramagnetic shifts of the Cd ions.

2. Experimental

Zeolites A (Aldrich), X (Alfa), Y (Alfa), mordenite (Chemie Uetikon, FM-8/Na), and ZSM-5 (Conteka, CBV-3020) were obtained commercially. Zeolites rho [12], ZK-5 [13], and chabazite [14] were prepared using modifications of the literature methods. Cadmium-exchanged forms of these zeolites were prepared by conventional ion-exchange techniques. The fractional exchange in each case was estimated from the elemental analysis (*via* ICP), as given in table 1. As can be seen from these data, the incorporation of Cd ranges from complete replacement down to roughly 40%. At low fractional exchange (*e.g.* Cd-chabazite and Cd-ZK-5) there may be multiple cadmium sites at nominally identical positions, provided the local environment is influenced by adjacent ions.

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1011-372X/02/0500-0019/0

Table 1
Fractional exchange of Na by Cd in the zeolites

Zeolite	Fraction of ions exchanged
Cd-A	1.03 ± 0.03
Cd-X	0.91 ± 0.01
Cd-RHO	0.86 ± 0.09
Cd-Y	0.82 ± 0.02
Cd-mordenite	0.80 ± 0.08
Cd-chabazite	0.60 ± 0.07
Cd-ZK-5	0.38 ± 0.03
Cd-ZSM-5	0.38 ± 0.03

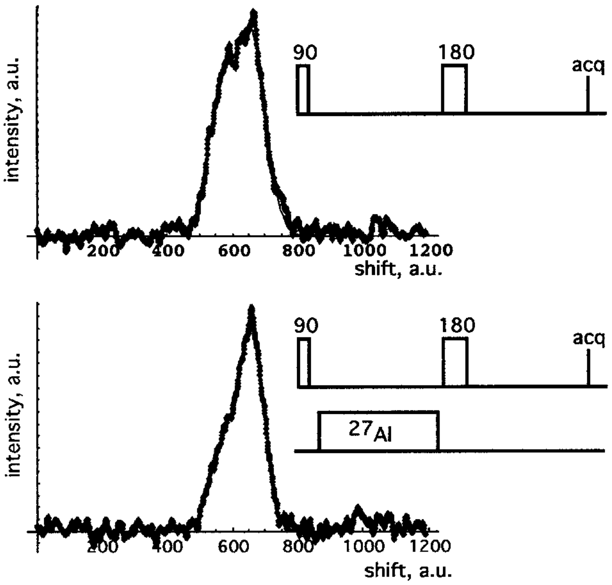

Figure 1. (a) Spin–echo spectrum of Cd-A; (b) dipole-recoupled spectrum of Cd-A. The dipole-recoupling experiment for determining differences in dipolar strengths at various cadmium sites is shown in the inset.

Samples were initially in a hydrated state and were examined as prepared. Dehydrated samples were prepared by holding the sample at 400 °C for 4 h under a pumped pressure of 0.1 Pa. The dehydrated samples were kept in sealed glass tubes under molecular oxygen. The presence of molecular oxygen was required to shorten the cadmium NMR spin–lattice relaxation time to expedite the collection of NMR data. Samples were stored at room conditions until they were examined. No noticeable changes in the spectroscopic parameters resulted from prolonged storage of the materials.

NMR experiments on nonspinning samples were performed on a Tecmag spectrometer with a probe specially built in this laboratory at a nominal ^{113}Cd NMR frequency of 79.93 MHz. To minimize the effects of acoustic ringing, the data were collected with a spin–echo sequence, using spin–temperature alternation. The $\pi/2$ pulse width was set at 2 ms and the echo time was set at 30 ms in all experiments. With the shortened relaxation times of 2–3 s in these samples, we used a recycle delay for both hydrated and dehydrated samples of 10 s, which allows quantitative recovery of the magnetization. We also performed magic-angle-spinning (MAS) experiments on the hydrated samples with a Chemagnetics CMX-2 spectrometer, also at 79.93 MHz. The samples were packed in 5 mm Chemagnetics spinners and examined with a commercially available Chemagnetics probe while spinning the sample at 10 kHz. In this spectrometer, the $\pi/2$ pulse width was 4 ms. For these experiments, the recycle delay was set to 10 s and the spin–echo delay was set at 30 ms. Chemical shifts were referenced to that of solid cadmium acetate dihydrate, which is assigned a shift of -14 ppm [15].

NMR dipole-recoupling experiments were implemented using the cadmium–aluminum double resonance experiment shown in figure 1. The experiment was carried out at 88.73 MHz on a Tecmag spectrometer with a Varian triple-resonance {X, Y, H} MAS probe with a 7.5 mm rotor. (The sample, however, was not spinning.) Figure 1 shows that the experiment consists of a spin–echo pulse sequence on cadmium, with detection of the second half of the echo. Irradiation of the aluminum resonance during the first part of the experiment spoils the spin–echo refocusing of the heteronuclear dipolar coupling between the cadmium and aluminum nuclei. The effect of the aluminum pulse, then, is to attenuate the Cd echo amplitude in proportion to the magnitude of the cadmium–aluminum dipolar coupling (spatial proximity). Pertinent experimental parameters were: $\pi/2$, pulse width of 12 ms; π, pulse width of 25 ms; τ, the delay between pulses, of 120 ms; relaxation delay of 10 s.

Visible spectra were recorded in the range from 200 to 700 nm using a Varian-Cary 4 spectrometer equipped with a Harrick diffuser–reflectance cell. Reflectance measurements were converted to absorption spectra using the Kubelka–Munk function.

3. Results

Spin–echo ^{113}Cd spectra of the materials examined in this study are shown in figure 2. It is clear from the MAS spectra that ^{113}Cd NMR spectroscopy detects only a single kind of cadmium in these samples; for example, all resonances of the hydrated samples have isotropic shifts in the range 0–20 ppm. These observations agree well with previously reported chemical shifts of cadmium-exchanged montmorillonite [16] and cadmium-exchanged LTA zeolite [17]. No evidence is seen from these shifts for the multiple sites detected *via* X-ray diffraction of LTA and ZK-5 zeolites [5] or in Y zeolite [9]. We surmise that the lack of observable shift differences between these sites may be the result of either fast exchange on the NMR timescale or the similarity of cadmium shifts at the various sites.

Spectra of hydrated zeolites taken without magic-angle spinning are broader than those taken with MAS; thus, Cd is subject to chemical-shift anisotropy and/or residual dipolar coupling to other ions in these materials. These anisotropies, as estimated from the widths of the spectra, do not exceed 200 ppm in the hydrated materials, and in some cases (*e.g.* X and Y zeolites) have to be less than 100 ppm. Thus the chemical-shift anisotropies of these sites are not very large compared with those of other heavy-metal ions such as lead [18–21]. Some spectra

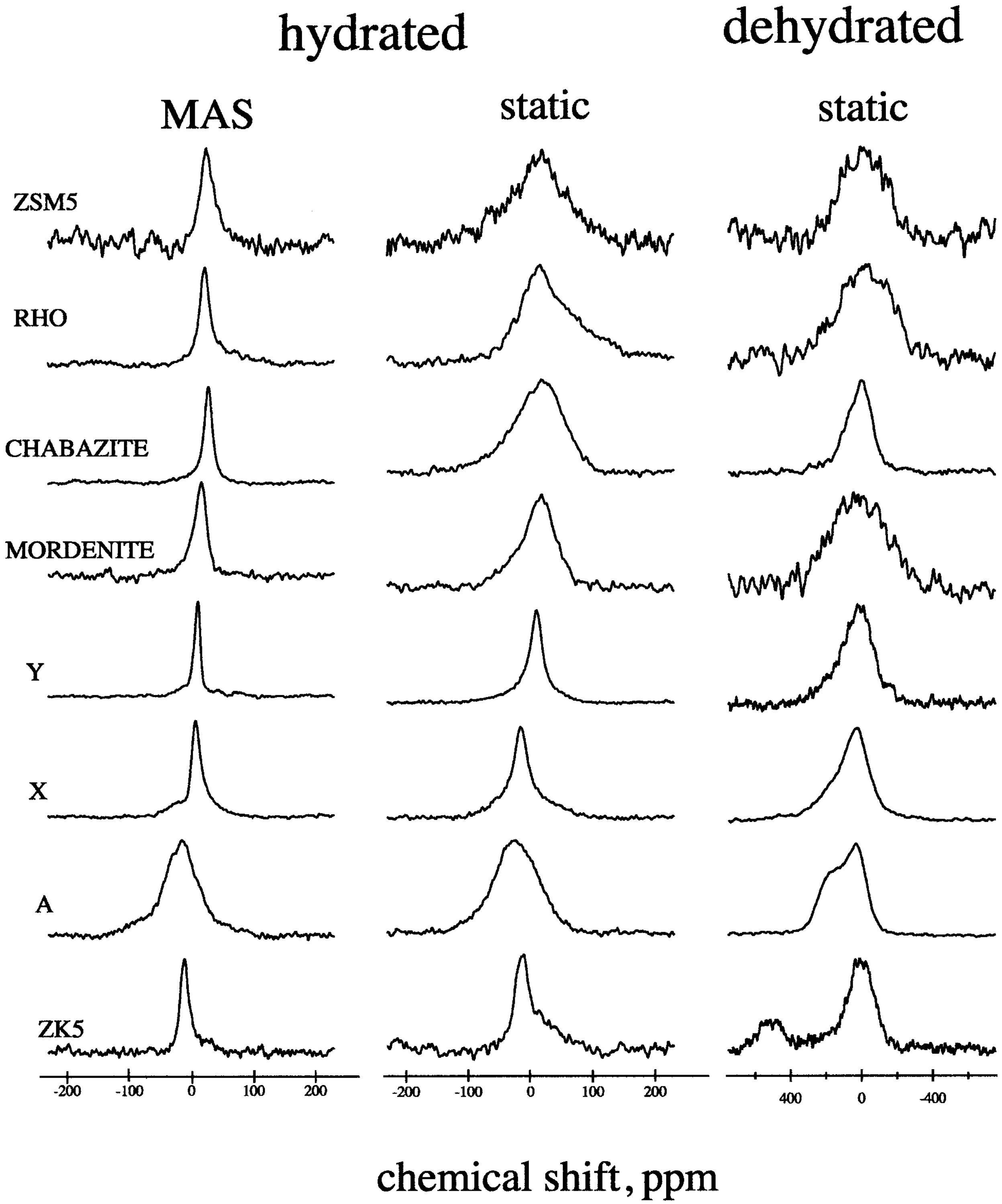

Figure 2. ^{113}Cd NMR spectra of the cadmium-exchanged zeolites: (middle) spectra of the hydrated materials under static conditions; (left) MAS spectra of the hydrated materials; (right) spectra of the dehydrated materials under static conditions. The various structures are indicated on the figure.

(*e.g.* that of Cd-RHO) show a resolvable powder pattern, while others (*e.g.* Cd-Y) show a symmetric line only slightly wider than that obtained with MAS-NMR.

Our results for Cd-A are at variance with previously published data for Cd_xNa_y-A zeolite [17], where the reported spectra contain two resonances for Cd, one at about +23 ppm and a second one at −43 ppm. The sample used in that study, however, had only about a 25% exchange of cadmium, whereas the sample we examined was essentially completely exchanged with cadmium. We surmise that, for the partially exchanged sample, the authors were detecting cadmium in a cadmium-rich environment, similar to our materials, and a minor component in a cadmium-depleted environment. Under no circumstances did we detect a resonance at large negative chemical shifts.

The effects of dehydration are substantial. Although the average chemical shift of resonances did not change radically upon dehydration, in every case the lines became significantly broader, and in some cases there are clear indications of asymmetry. We presume that these increased line widths are reflective of local or long-range heterogeneity of cadmium-ion environments in the dehydrated samples. In the cases of zeolite A and zeolite ZK-5, the dehydration is accompanied by the appearance of a second resonance line that is deshielded relative to the major resonance. The shifts of these new lines relative to the major peaks are 138 ppm and 489 ppm for zeolites A and ZK-5, respectively. There is also some indication in the case of zeolites X and Y of an unresolved deshielded resonance upon dehydration. The production of this new cadmium center seems to be reversible, as can be seen by the NMR spectra of Cd-A (figure 3) as it is carried through a sequence of dehydration and rehydration.

The spectra of the dehydrated zeolites Cd-A and Cd-ZK-5 are especially interesting, because they demonstrate that dehydration parses the cadmium into two distinct sites. The resonances of the new components are more deshielded than those of the major component and contribute 22% to the total intensity in the case of Cd-ZK-5 and 39% in the case of Cd-A.

Dehydration of these materials is also accompanied by a color change. Before dehydration, all materials are nominally white; upon dehydration, the color of Cd-A changes to pale yellow and that of Cd-ZK-5 to pale brick red. Other zeolites remained white upon dehydration and exhibited no discernible new NMR peaks upon dehydration. The color of the Cd-Y sample changed from white to a light gray, yet the NMR spectrum does not clearly indicate two distinct NMR-active regions; the asymmetry to the deshielded side of the main resonance may be a vestige of a second peak.

The absorption spectra of the hydrated and dehydrated Cd-A zeolites in the visible and ultraviolet regions are shown in figure 4. In the hydrated sample, the only absorption is in the ultraviolet region below 250 nm; thus, the sample appears white. The spectrum of the dehydrated Cd-A exhibits an additional band with an edge between 480 and 500 nm, in the blue region. This absorption is responsible for the pale yellow color of the dehydrated material.

The nature of the two Cd peaks detected for dehydrated Cd-A and Cd-ZK-5 is further addressed by the dipole-recoupling experiment in which the residual dipolar coupling to framework aluminum ion probes changes in spatial proximity to the zeolite framework (figure 1). In this experiment, the Cd spin–echo amplitude has the dipolar coupling to the aluminum nucleus

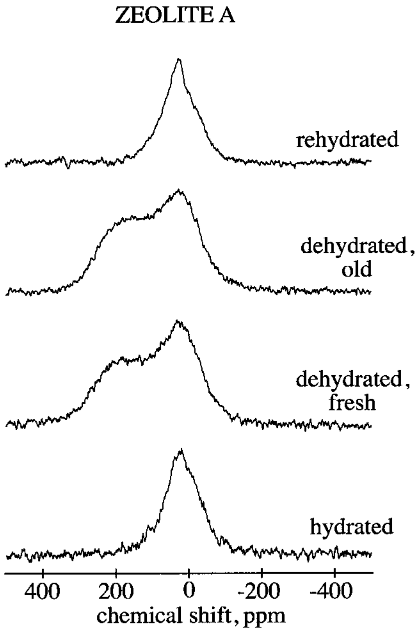

Figure 3. ^{113}Cd NMR spectra of Cd-A zeolite collected in a hydration/dehydration/rehydration cycle.

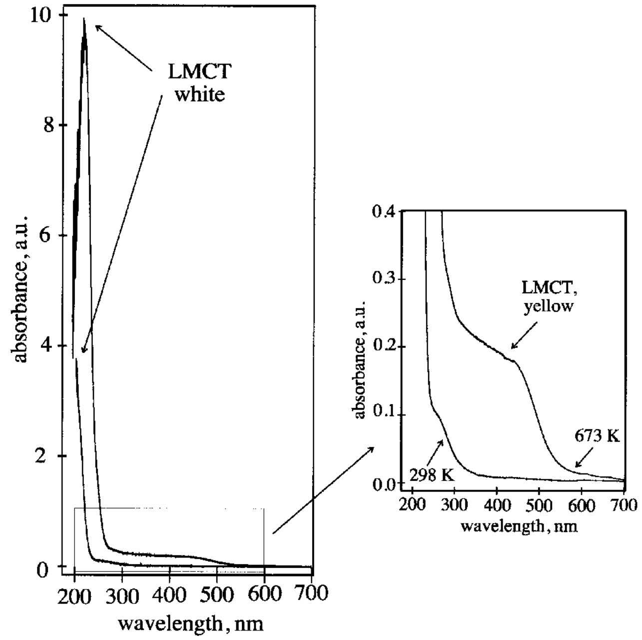

Figure 4. Spectra of hydrated and dehydrated Cd-A zeolite in the region from 200 to 700 mm.

mapped on to it, in a manner similar to the SEDOR experiment [22]. The amplitude of the deshielded resonance relative to that of the more shielded resonance is clearly reduced in the dipole-recoupled experiment, as compared with the standard spin–echo experiment. This demonstrates that the two resonances are associated with cadmium nuclear sites having different dipolar couplings to aluminum. In particular, the deshielded resonance is associated with a stronger cadmium–aluminum dipolar coupling, and therefore is more closely sited to the zeolite framework.*

4. Discussion

Color change in metal-ion-exchanged zeolites upon dehydration has been reported for silver- [23], sodium- [24], and copper-exchanged zeolites [25]. In the case of Ag-exchanged zeolites, there have been two explanations proposed to explain this change. The first [26] proposes that Ag^0 clusters form in the pore space of the zeolites, leading to color centers upon processing at the elevated temperatures associated with dehydration. Since color changes have been observed in Ag-zeolites under room-temperature evacuation,† another proposal is that color change upon dehydration results from a ligand-to-metal charge transfer [LMCT], whereby optical absorption proceeds *via* excitation of spatially proximate ligand (*i.e.* zeolite) electrons into empty metal orbitals.

The UV–visible spectrum, the NMR data and the literature X-ray data on similar samples are all consistent with the following model. The X-ray structure of the fully hydrated Cd-A zeolite shows three sites for Cd^{2+} ions [5]. In two of these sites, Cd^{2+} ions are octahedrally coordinated to three framework oxygens and *three* water oxygens. In the third site, Cd^{2+} ions are bound to three framework oxygens and *two* water oxygens, forming a trigonal bipyramidal structure. The coordination of cadmium with framework oxygen allows the possibility of transfer of electrons in the oxygen lone-pair orbital to the unfilled Cd 5s orbital by light absorption through the LMCT process, provided the Cd 5s orbitals are proximate enough for electron transfer. In the hydrated state we presume that no Cd ion is close enough; they may even be exchanging between sites, especially on the NMR timescale [9].

Dehydration forces the Cd^{2+} ions to coordinate more strongly with the framework oxygens. This effect is clearly seen in X-ray results for a partially dehydrated sample of zeolite A, where under mild conditions, such as evacuation at room temperature, Cd^{2+} cations become approximately three-coordinate [8]. The loss of water leads to a closer approach of Cd cations to the framework oxygens, affording donation of electron density from the oxygen π orbitals of the framework into the 5s orbital of cadmium. The result is the appearance of an absorption band in the visible range. The formation of the zeolite–cadmium complex increases the paramagnetic contribution to the chemical shift, leading to deshielding of cadmium nuclei in this environment, consistent with the shift data shown in figure 2. In these samples LMCT may happen in both Cd environments; those sites, however, that are associated with shorter Cd–O bonds are responsible for the pale yellow color and the deshielded NMR peak. We find no evidence from our NMR spectra of the presence of any metallic Cd species [28]. Given that approximately 40% of the Cd ions are associated with the deshielded site, it is tempting to associate these ions with those that were originally in the trigonal bipyramidal coordination (~13% of the Cd ions) [8].

A similar effect is seen for Cd-ZK-5. The present model suggests that dehydration in this material produces a ligand-to-metal charge-transfer state at even lower energy, resulting in the apparent brick-red color. A lower-energy transition *vis-à-vis* the Cd-A material is expected to increase the paramagnetic contribution to the Cd shift, since the paramagnetic contribution to the chemical shift is proportional to the average inverse of the energy difference between the ground electronic state and the first excited state [29]. These qualitative arguments are consistent with the very large shift (~500 ppm) observed for the deshielded peak in the Cd-ZK-5 material.

5. Conclusions

^{113}Cd NMR spectroscopy senses both the local electronic state at the cadmium site through the chemical shift and the structural features through dipolar couplings; absorption spectra of the materials probe the electronic structure as well. The combined use of these methods yields a picture of the local geometry and electronic structure that is consistent with structural changes that occur upon dehydration. The Cd NMR spectra of hydrated samples show few differences with the zeolite structure; the observed differences are relatively small and not particularly diagnostic of the local environment. Upon dehydration, NMR and UV–visible absorption spectroscopies detect changes in the electronic structure of a fraction of the cadmium ions in Cd-A zeolite and Cd-ZK-5 zeolite. The Cd-Al dipolar-recoupling

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[*] An estimate of the change in cadmium–aluminum may be made by assuming that the dipole recoupling experiment produces total decoupling during the first period and that the cadmium and aluminum dipolar interactions are pairwise coupled. Under these assumptions, the areas of the two peaks in figure 1 may be used in the relevant SEDOR equations to estimate that a 14% decrease in atomic separation occurs upon dehydration. It is worth noting, however, that the recoupling experiment is not perfect; thus the 14% is a lower bound on the change in distance between the cadmium and aluminum atoms.

[†] The resonance of bulk cadmium is ~4300 ppm [27].

experiment, as well as the literature X-ray data on Cd-A zeolite, indicates that these cadmium ions are closer and more strongly associated with the framework than in the hydrated state. The spectroscopic data indicate that for these sites a low-lying electronic excited state is stabilized by dehydration.

Acknowledgments

J.A.R. and A.T.B. acknowledge support from the National Science Foundation CTS 9713143. C.D. acknowledges support of the Donors of the Petroleum Research Fund of the American Chemical Society through Grant 33633-AC5. G.E.P. acknowledges the generosity of the Colorado State University NMR facility. We acknowledge P. Hollins for the preparation of these materials.

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