

Infrared Spectroscopic Examination of the Interaction of Urea with the Naturally Occurring Zeolite Clinoptilolite

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Infrared spectroscopy has shown for the first time that the naturally occurring zeolite clinoptilolite can absorb urea, $(\text{NH}_2)_2\text{C}=\text{O}$, under ambient conditions from either aqueous or ethanolic solutions. The two strongest NH stretching bands at 3441 and 3344 cm^{-1} in pure, solid urea shift to higher frequency (about 3504 and 3401 cm^{-1}) after absorption. Two of the four urea bands in the 1800–1300 cm^{-1} range (at 1683 and 1467 cm^{-1}) undergo marked downward shifts to about 1670 and 1445 cm^{-1} . The other two bands show little change in frequency. The strong band at 1602 cm^{-1} , however, diminishes in intensity to little more than an ill-defined shoulder on the 1626- cm^{-1} peak. When clinoptilolite is heated to 450°C and then treated with molten urea (ca. 140°C) for several minutes, and finally washed twice with ethanol to remove excess unreacted urea, further changes become apparent in the spectrum of the urea-treated clinoptilolite. The two NH stretching bands broaden without significant change in frequency. Two new bands appear in the midfrequency range at 1777 (weak) and 1719 (medium strong) cm^{-1} . Of the four original midfrequency peaks, the one at 1602 cm^{-1} is now absent. Two others (1627 and 1440 cm^{-1}) exhibit little change, while the fourth has broadened and shifted down to 1663 cm^{-1} , where it appears as a shoulder on the band at 1627 cm^{-1} . Both treatments clearly induce interaction between urea and the zeolite which seems to result in significant modifications in the nature of the hydrogen bonding of the substrate. © 1991 Academic Press, Inc.

INTRODUCTION

A major source of water pollution in the United States is due to farm runoff, both from animal waste and from chemical fertilizers (1). In order to investigate this problem at the molecular level, we have used infrared spectroscopy to examine how small organic molecules, such as urea, a common constituent of many nitrogen-rich fertilizers, might interact with specific soil minerals. In the present study we have examined the interaction of urea with clinoptilolite.

Clinoptilolite $[(\text{Na},\text{K})\text{Si}_7\text{Al}_2\text{O}_{16} \cdot 6\text{H}_2\text{O}]$ is an abundant, naturally occurring zeolite. It is a member of the heulandite group of zeolite minerals and is one of the most stable zeolites found in soil. These minerals consist of SiO_4 and AlO_4 tetrahedra whose corners link to form a three-dimensional network of four- and five-membered loops and double loops of silicate and aluminate tetrahedra ar-

ranged in parallel layers instead of chains (2). In turn, the loops of SiO_4 and AlO_4 tetrahedra establish an interconnected lattice of channels and cavities 440 to 720 pm in diameter. Some of the cavities are occupied by cations (e.g., Na^+ and K^+) and others are large enough to accommodate water or other small molecules. Channels comprise 34% of the total volume of clinoptilolite (3).

In some locations up to 80% of deep sea sediments consist of clinoptilolite and another zeolite, phillipsite. Also, clinoptilolite and the zeolite mordenite are often the major constituents of volcanic tuffs and volcano-clastic sediments, sometimes comprising up to 90% of such materials (2). The occurrence of clinoptilolite and other zeolites in the soil environment is restricted to soils with high pH or where acid weathering is limited. Although they are quite common in a geological setting, the process of soil formation, especially acidity, often results in their dissolution and removal (4).

In this paper we report the first infrared spectroscopic evidence for the absorption of urea by the naturally occurring zeolite, clinoptilolite.

MATERIALS AND METHODS

Materials

Chemicals and minerals. Pine Ridge clinoptilolite (Craven Creek), 60 mesh (5). Buckhorn, NM, clinoptilolite, <200 mesh, Minerals Research² (Clarkson, NY). D_2O , 99.8% D, and urea, ACS certified (Fisher Scientific, Fairlawn, NJ). Ethanol, anhydrous, denatured, special grade (EM Science, Cherry Hill, NJ).

Sample treatments. Five different samples of urea-treated clinoptilolite were prepared for examination:

(1 and 2) Unheated clinoptilolite was treated twice (once overnight) with 0.5 M urea in water or in ethanol.

(3 and 4) Clinoptilolite was first heated to 450°C for 1 h and then treated twice (once overnight) with 0.5 M urea in water or in ethanol.

(5) Clinoptilolite, heated to 450°C, was treated with molten urea (ca. 140°C) for several minutes and then washed twice (once overnight) with ethanol to remove excess, unreacted urea.

Preparation of deuterated clinoptilolite. About 1 g clinoptilolite was suspended in 5 ml D_2O under dry N_2 at ambient temperature and pressure in a closed, glass vial. After the sample had been warmed for 1–2 h by immersing the vial in a water bath, the mixture was frozen with liquid nitrogen and then freeze dried under vacuum. Thereafter, the sample of dry, powdered, deuterated clinoptilolite was always stored and handled under dry N_2 .

Infrared Spectra

For each sample, including the two starting materials, spectra were obtained as both Nujol and Halocarbon mulls. The mulls were prepared from about 1–2 mg of sample. (The KBr pellet method was eschewed to preclude the possibility that the

high pressure required to prepare the pellet might induce additional interaction between the urea and the zeolite or cause ion exchange between the alkali halide matrix and the mineral.) Infrared (IR) spectra of thin films of the mulls between KBr plates were collected at ambient temperature, 2 cm^{-1} resolution, 0.44 s/scan on a Nicolet 740 Fourier transform infrared (FTIR) spectrometer system (equipped with a water-cooled Globar source, a Ge-coated KBr beamsplitter, and a broad-range MCT detector). Each spectrum consisted of 4096 scans, collected as eight sets of 512 coadded double-sided interferograms; each set was multiplied by the Happ-Genzel apodization function, Fourier transformed, and then coadded to give the final spectrum.

A spectrum of a thin film of neat Nujol or Halocarbon, obtained under conditions identical to those of the sample mulls, has been subtracted from each of the spectra presented in the figures. Broken lines around $3050\text{--}2750$, $1440\text{--}1420$, and $1385\text{--}1365\text{ cm}^{-1}$ indicate regions of the spectrum where minor subtraction artifacts were blanked.

RESULTS

Infrared Spectra of Isolated Clinoptilolite and Pure Urea

Figure 1A is the infrared spectrum of finely ground clinoptilolite; it is similar to that reported by van der Marel and Beutelspacher (6). SiO and AlO stretching vibrations of the aluminosilicate framework give extremely strong and very broad absorptions in the region from about 900 to 1300 cm^{-1} ; skeletal deformation modes produce a series of weaker peaks below 900 cm^{-1} . The weak band around 1420 cm^{-1} may be an overtone or a combination band. The other bands near 1632 cm^{-1} and around 3624 , 3410 (sh), and 3220 cm^{-1} are characteristic of H_2O mol-

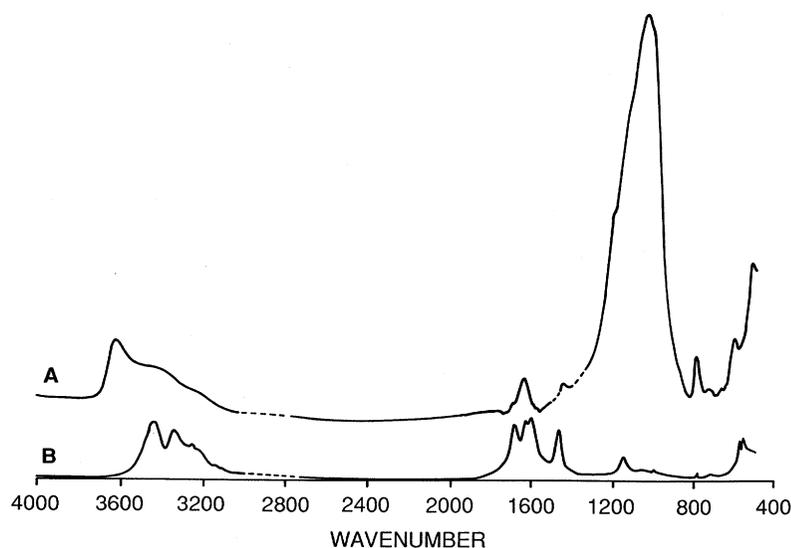


FIG. 1. Infrared spectra of Nujol mulls of (A) finely ground, unreacted clinoptilolite; (B) pure, solid urea. (Nujol bands have been subtracted.)

ecules lodged in the channels and cavities of the zeolite. When this zeolite is suspended in D₂O at room temperature, frozen at liquid nitrogen temperatures, and once again taken to dryness under a vacuum, these four bands disappear. In their place are a new series of bands with similar intensities at 2680, 2505, and 2400 cm⁻¹ attributable to the heavy water. (The expected low frequency band of D₂O is obscured by the strong absorptions of the mineral in the vicinity of 1200 cm⁻¹.)

Figure 1B gives the spectrum of solid urea (a planar molecule which belongs to the C_{2v} symmetry group); this spectrum corresponds to a recently published FTIR spectrum of this molecule (7). Older data from dispersive instruments appear to have been measured at lower resolution (8, 9). Four moderately strong bands are seen in the N-H stretching region at 3441, 3344, 3256, and ca. 3220 (sh) cm⁻¹. Four more bands of comparable intensity are observed at 1683, 1628, 1602, and 1467 cm⁻¹. Normal coordinate calculations by J. L. Duncan (10) suggest that the first and third of these latter four bands result from the in-phase deformation (A₁ symmetry) of the pair of NH₂ groups and the C=O stretching vibration (A₁), respectively. The oscillations of these three moieties are strongly coupled, however, and do not represent pure group vibrations. The bands at 1602 and 1467 cm⁻¹ also arise from normal modes involving mixed vibrations. To a first approximation, the former may be represented by the out-of-phase NH₂ deformation (B₁), and the latter, by the antisymmetric NCN stretch (B₁). Additional urea bands are found at lower frequencies. These fall in regions where the skeletal vibrations of the zeolite give very intense absorptions. Thus, in the samples of urea-treated zeolite, these low frequency urea absorptions are obscured by the strong zeolite bands and cannot easily be used for the purposes of this study.

Infrared Spectra of Urea-Treated Clinoptilolite

Figure 2 compares the high frequency region of two urea-treated clinoptilolite samples with the two parent materials: (A) is the spectrum of unreacted solid urea; (B) the spectrum of unreacted clinoptilolite; (C) the spectrum of clinoptilolite treated with 0.5 M aqueous urea (sample 1) (the spectra of samples 2-4 are very similar to C); and (D) the spectrum of clinoptilolite heated to 450°C and then treated with molten urea (sample 5).

Treatment of the zeolite with aqueous urea (sample 1, Fig. 2C) results in marked shifts of the two principal NH stretching bands of urea from 3441 and 3344 cm⁻¹ in the pure compound to 3504 and 3401 cm⁻¹ in the complex. The 3625-cm⁻¹ band observed for the OH stretching vibration of H₂O entrained in the unreacted mineral is virtually unchanged after treatment with urea. This suggests that some water may remain after treatment. Except for some changes in relative intensity, the spectrum of the zeolite treated with molten urea and then washed with ethanol (sample 5, Fig. 2D) is quite similar in this region to the previous spectrum (Fig. 2C).

Figure 3 displays spectra of the same four samples between 1900 and 1300 cm⁻¹. Here the two urea-treated zeolites have spectra which differ not only with respect to each other, but also are quite distinct from the spectra of the parent species. In the clinoptilolite treated with aqueous urea (Fig. 3C, sample 1) the

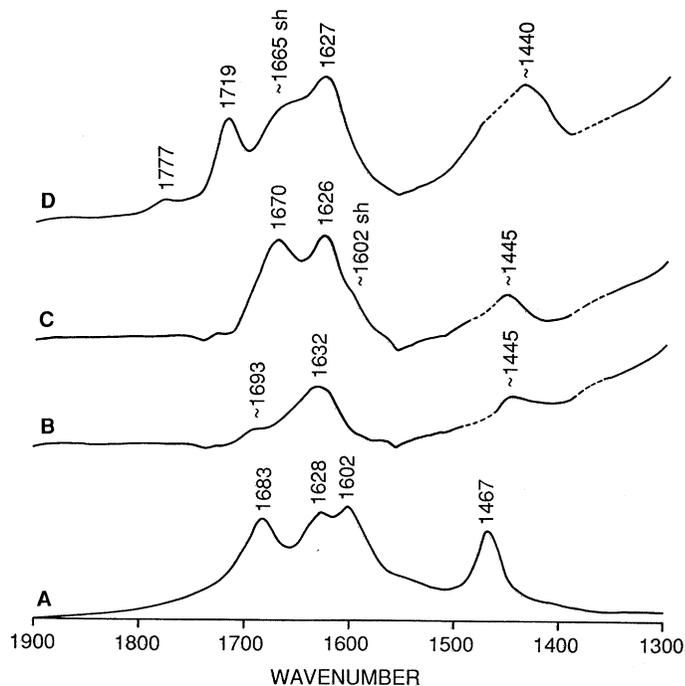


FIG. 2. High frequency infrared spectra of Nujol mulls of (A) solid urea; (B) unreacted clinoptilolite; (C) clinoptilolite treated twice with 0.5 *M* aqueous urea (sample 1); and (D) clinoptilolite, heated to 450°C, treated with molten urea, and then washed twice with ethanol (sample 5). (Nujol bands have been subtracted.)

band at highest frequency in the pure urea has decreased 13 cm^{-1} to 1670 cm^{-1} . The next two bands (1626 and 1602 cm^{-1}) show little change in frequency, but the intensity of the latter has dropped sharply. The fourth band is now about 1445 cm^{-1} and is somewhat decreased in peak height.

For the zeolite exposed to molten urea (Fig. 3D, sample 5), there are two new bands at 1777 (weak) and 1719 (medium) cm^{-1} , not found in any of the other spectra. The next two bands are at 1665 cm^{-1} (medium, shoulder) and 1627 cm^{-1} . The final feature is a broad peak centered about 1440 cm^{-1} .

In the lower frequency regions (not shown), the spectra are dominated by the Al-O and Si-O skeletal vibrations and little change is observed between the spectrum of the zeolite and those of the urea-treated mineral.

DISCUSSION

The presence of bands characteristic of the OH stretching (ν) and bending (δ) of water (near 3624 and 1632 cm^{-1}) in the infrared spectrum of native clinoptilolite suggests that the zeolite, prior to treatment with urea, has a certain amount of water entrapped. Presumably, the two hydrogens of such water molecules may hydrogen bond to the oxygen of the aluminosilicate network, or to a second water molecule, in either of two distinct ways: in one case, the interaction with the two

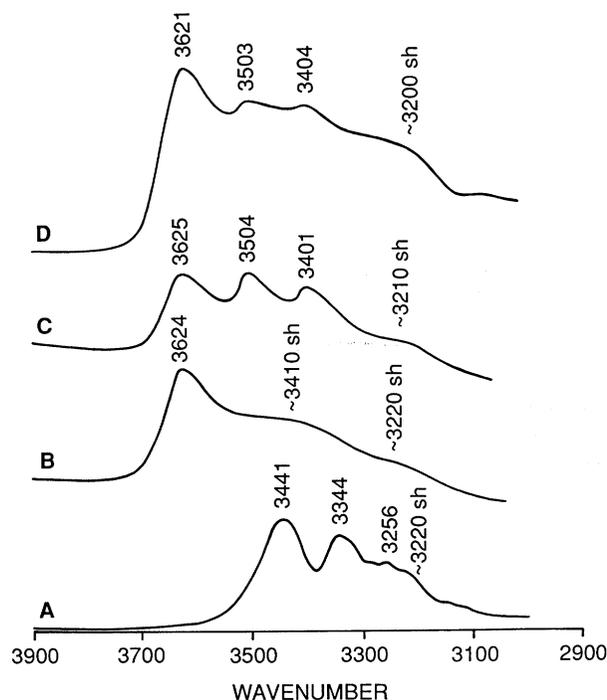


FIG. 3. Midrange infrared spectra of Nujol mulls of (A) solid urea; (B) unreacted clinoptilolite; (C) clinoptilolite treated twice with 0.5 M aqueous urea (sample 1); and (D) clinoptilolite, heated to 450°C, treated with molten urea, and then washed twice with ethanol (sample 5). (Nujol bands have been subtracted.)

hydrogens of water is symmetric; in the other, the hydrogen bonds are of different lengths, and probably of unequal strengths as well.

In pure liquid water itself, Scherer *et al.* (11) have provided spectroscopic evidence that almost all of the molecules also exhibit one or the other of these two types of hydrogen bonding. At ambient conditions, symmetrically bound molecules with two strong hydrogen bonds (type I) exhibit a pair of OH frequencies, corresponding to out-of-phase (antisymmetric, ν_d^a [B_1]) and in-phase (symmetric, ν_d^s [A_1]) OH stretching modes, at approximately 3440 (strong) and 3240 cm^{-1} (weak), respectively. For the asymmetrically hydrogen-bonded species (type II), the stretching frequency of the longer OH moiety with the weaker hydrogen bond (ν_w OH) is about 3625 cm^{-1} (weak), while that of the shorter and more strongly hydrogen-bonded OH (ν_b) is near 3410 cm^{-1} (strong). (In general, the OH stretching frequency is inversely correlated to the strength of the hydrogen bond (12, 13) between the proton of the OH group and the donor atom.) At room temperature and pressure, the two forms of water exist in roughly comparable amounts, so that the observed infrared spectrum of liquid water has maximal absorbance near 3440 cm^{-1} (ν_d^a plus ν_b) with a noticeable shoulder around 3220 cm^{-1} (ν_d^s). (The first overtone (2δ) of the HOH deformation (δ) mode also contributes to the absorption near 3220 cm^{-1} .) Increasing temperature apparently favors the asymmetric spe-

cies (type II) and shifts the observed maximum in the water spectrum to higher frequencies, while lower temperatures promote the symmetric type (I) and lowers the frequency of the observed band maximum.

Two of the observed OH stretching infrared bands in the room temperature spectrum of water lodged in the zeolite appear at values remarkably similar to those calculated for the asymmetrically hydrogen-bonded molecules in liquid water (11): 3624 and 3410 cm^{-1} . Similar effects are found for water dissolved in aprotic hydrogen-bonding solvents such as ketones (14) or dimethyl sulfoxide (11), where the asymmetric complex predominates. The third distinct band in the hydrated clinoptilolite occurs at 3220 cm^{-1} and is probably associated with the overtone of the deformation (2δ) at 1632 cm^{-1} plus the symmetric OH stretching vibration of some symmetrically bound water in the zeolite. The relative intensities of these three bands suggest that the majority of the water held within the channels and cavities of the zeolite is asymmetrically hydrogen-bonded.

Deuteration studies of two different clinoptilolites (Pine Ridge and Buckhorn) provide further evidence for both the mode of hydrogen bonding of the molecules caged in the zeolite and the relative ease with which they may have access to solvent molecules in which the mineral is suspended. We have observed that, at ambient pressure, the water held by clinoptilolite exchanges reasonably readily and rapidly with D_2O upon warming for a few hours. For the Buckhorn sample, almost complete exchange occurred: As observed in Fig. 4, the OH stretching bands of bound water (near 3624 , 3410 , and 3220 cm^{-1}) shift down to about 2680 , 2505 , and 2400 cm^{-1} upon deuteration; the 1632 cm^{-1} HOH deformation mode

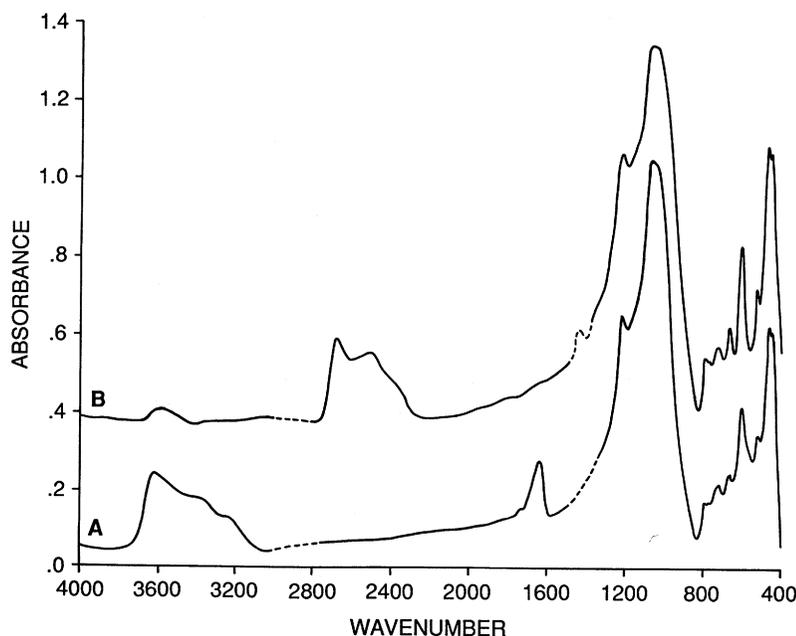


FIG. 4. Infrared spectra of Nujol mulls of finely ground Buckhorn clinoptilolite: (A) untreated; (B) after being suspended in warm D_2O and then freeze dried. (Nujol bands have been subtracted.)

simply disappears because the corresponding DOD mode (ca. 1230 cm^{-1}) is obscured by the intense absorptions of the aluminosilicate framework in the same region. These data indicate that virtually all of the water bound by this zeolite is easily accessible to the bulk liquid. The frequencies of the bound D_2O are quite similar to those calculated for the pure liquid (11), with the most intense bands being associated with asymmetrically bound D_2O . Exchange also occurs for the Pine Ridge clinoptilolite, but to a somewhat lesser extent under these relatively mild conditions.

When the zeolite clinoptilolite is treated with urea, the marked change in position and intensity of many of the principal bands of this simple organic molecule indicates distinct modifications in the nature of the hydrogen bonding to the guest and the host. The resulting material is not simply a physical mixture, but a complex system that involves a significant degree of interaction between the lattice and the bound species. For example, the observed increase in frequency of the two highest energy NH stretching bands of urea after interaction with the zeolite (Figs. 2A, 2C, and 2D) implies that the nature of the hydrogen bonding to the amino groups of the urea molecules entrapped by the clinoptilolite is altered compared with that in the pure substrate. This sort of spectral change would certainly occur if urea molecules have entered the zeolite channels where some of their hydrogen atoms would then be hydrogen-bonded to the aluminosilicate oxygens rather than to the carbonyl oxygen or the amino nitrogen of a second urea molecule. In such a situation, the local symmetry and geometry of the zeolite cavity or channel would alter the symmetry and geometric arrangement, and perhaps also the strength, of the hydrogen bonds of the urea from the state in which they exist in the pure solid. Furthermore, the spectroscopic data suggest that the urea may be held more tightly by the zeolite than is pure water or ethanol (competitive binding) because the changes described above were observed even when the mineral was subjected only to the mild treatment of suspension at ambient conditions in a 0.5 M aqueous or ethanolic solution of urea. In addition, although urea is very soluble in ethanol, washing the clinoptilolite treated with molten urea with ethanol for several hours (sample 5) did not remove the urea from the mineral.

The frequency shifts and intensity changes in the bands associated with the carbonyl group and the C–N bonds of the urea after interaction with the zeolite imply that the hydrogen bonding to the urea oxygen and nitrogens also changes under such conditions (Figs. 3C and 3D). Indeed, the new band observed at 1719 cm^{-1} in the clinoptilolite heated and then treated with molten urea (Fig. 3D, sample 5), may represent the C=O stretching vibration of urea molecules which no longer have hydrogen bonds to the carbonyl oxygen. One would expect approximately such a frequency for the free, non-hydrogen-bonded C=O stretching vibration of a carbonyl with neighboring electron-withdrawing amino groups (15). These results imply that some of the urea molecules are lodged in the zeolite channels in the absence of any water or other source of available polar hydrogen atoms. (Apparently the dimensions of some of the aluminosilicate channels or cavities are only slightly larger in size than the urea molecules themselves. In these portions of the zeolite, such a geometric constraint would prevent two

substrate molecules from coming into sufficiently close contact with each other for any hydrogen bonding to occur between the carbonyl oxygen of one and the amine hydrogens of the second. Also, no water molecules are present to interact with the substrate because the zeolite was heated to 450°C before treatment with anhydrous, molten urea.) The disappearance of the band representing the hydrogen-bonded carbonyl at 1602 cm^{-1} in the pure urea (Figs. 3A) further corroborates this assumption. The other two bands (Fig. 3D, sample 5) at 1665 and 1627 cm^{-1} then represent the pair of deformations of the NH_2 moieties hydrogen-bonded to oxygens of the aluminosilicate framework. The higher frequency band is nearly 20 cm^{-1} lower than in the pure, solid urea because the in-phase NH_2 deformation is now only weakly coupled to the C=O stretching motion (1719 cm^{-1}).

The observation of only two distinct bands at 1670 and 1626 cm^{-1} , plus a weak shoulder near 1602 cm^{-1} for the clinoptilolite treated with aqueous urea (Fig. 3C, sample 1), may represent an intermediate state. Presumably, the loss of intensity of the 1602- cm^{-1} band again indicates that the carbonyl oxygens of many of the substrate molecules are no longer hydrogen bonded to the amino hydrogens of neighboring urea molecules as they are in the pure substance. But the absence of any band near 1720 cm^{-1} suggests that in these samples few urea molecules have carbonyl groups free of all hydrogen bonding interactions. Instead, the carbonyl oxygen of many of the urea molecules may weakly interact with hydrogens on water molecules which have not been displaced from the zeolite network. In such a case the C=O stretching vibration of the urea carbonyl would appear at a frequency intermediate to that found in the pure urea (1602 cm^{-1} , Fig. 3A) and in the clinoptilolite heated and then treated with molten urea (1719 cm^{-1} , Fig. 3D). So in this instance the 1670- cm^{-1} band most likely represents a composite of the in-phase NH_2 deformation band near 1665 cm^{-1} and the C=O stretching band of the weakly hydrogen-bonded carbonyl.

CONCLUSION

Infrared spectroscopy discloses that the characteristic absorption bands of urea undergo significant changes in frequency and intensity when this substrate interacts with the naturally occurring zeolite clinoptilolite. These results indicate that clinoptilolite can absorb urea from aqueous or ethanolic solutions under ambient conditions, as well as when the mineral is first heated to 450°C for 1 h and then treated with molten urea (about 140°C). The observed changes in the spectra suggest that in both instances the urea undergoes a clear modification in hydrogen bonding as it intercalates into the zeolite channels. The current investigation cannot verify the exact nature of the geometry of the interaction at the molecular level, but future studies involving isotopically substituted ureas may offer additional insights. Nonetheless, the results reported here indicate that urea from agricultural fertilizers may undergo significant interactions with soil minerals. This finding, in turn, suggests that the type of soil to which a fertilizer is applied can strongly influence the extent to which the active components are available to plants, the ease with which these compounds may be carried through the soil by rain or irrigation water, and thus, the potential which they may have for contam-

ination of ground water. An ancillary benefit of this study is that it points to the possibility for using urea-saturated zeolites as slow-release nitrogen fertilizers. Of course, the retention and release mechanisms inherent to a particular zeolite will determine its suitability for such a purpose.

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