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An FT-Raman Study of Sorbate-Induced Structural Changes in Zeolite ZSM-5

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Many zeolites undergo temperature-induced phase transitions. These phase changes can also be induced by sorbed organic molecules. Much of the interest in the structures of these materials derives from a desire to understand their molecular sieving characteristics which are crucial to their use as catalysts and sorbents. During last 15 years, ^{29}Si MAS NMR spectroscopy and XRD have been extensively used to investigate sorbate-induced phase transitions.[1] Recently, Raman spectroscopy has been used in exploring the crystallization processes of zeolites and characterization of zeolite structures.[2] In the present work, we demonstrate, for the first time, that FT-Raman spectroscopy is also a very sensitive technique for probing the sorbate-induced phase transitions of zeolites and that Raman spectra can provide unique information complementary to that obtained using other methods. Zeolites usually exhibit very weak Raman signals due to their intrinsically small Raman scattering cross sections. However, this can be particularly advantageous in the investigations of sorbate−framework interactions because the weak background of the zeolites allows Raman scattering arising from the sorbed species to be detected. Recent advances in FT-Raman instrumentation enable the measurement of Raman spectra with much improved S/N ratios since the FT capability enables faster signal averaging. The value of the complementary IR data is diminished by the fact that the IR signals (below 1200 cm^{-1}) of the guest molecules are often masked by the very strong adsorption bands of the zeolite framework, which restricts the IR study to the limited spectral region between 4000 and 1200 cm^{-1}. We have chosen to study the adsorption of *p*-xylene on zeolite H-ZSM-5 as there are considerable literature data available against which to measure the viability and reliability of this approach. Previous NMR and XRD studies have suggested that the structure of calcined ZSM-5 with a high Si/Al ratio is monoclinic ($P2/n$) at ambient conditions.[3] The structure of ZSM-5 with a loading of *p*-xylene (2 molecules/unit cell, low-loaded form) is orthorhombic ($Pnma$),[1b] while the high-loaded form (8 molecules/u.c.) is also orthorhombic but has a different space group ($P2_12_12_1$).[4] In the present study, particular attention was paid to the sorbate-induced phase transition between the two orthorhombic forms.

FT-Raman spectra of *p*-xylene adsorbed on ZSM-5 were measured as a function of the loading from 1.5 to 8 molecules/u.c.[5] Assignments of the vibrational modes of *p*-xylene were based on those previously reported.[6] To assist in interpreting the data, the spectrum of pure *p*-xylene liquid was also obtained. Within the loading range of 1.5−4 molecules/u.c., the spectra of *p*-xylene were independent of the coverage, *i.e.* the spectra did not change upon increasing the loading. This suggests that in the low-coverage situation (up to 4 molecules/u.c.), the additional *p*-xylene molecules access identical adsorption sites inside the framework, presumably the intersections of the straight and sinusoidal channels, and that there is little interaction between *p*-xylene molecules. The data also indicate that the structure of ZSM-5 remains unchanged throughout the loading range mentioned above. These results are in good agreement with those of previous studies.[7] The spectrum of pure *p*-xylene is similar to those from low loadings of 1.5−4 molecules/u.c. in the range of 3000−100 cm^{-1}. The only major changes occurred at frequencies above 3000 cm^{-1}, in the ring C−H stretching region. The ring C−H stretching modes centered at 3054, 3028, and 3012 cm^{-1} in the spectrum of pure *p*-xylene shifted by 11, 20, and 6 wavenumbers to 3065, 3048, and 3018 cm^{-1}, respectively. It is worth noting that the kinetic diameter of *p*-xylene (0.585 nm) is quite close to the cross-sectional dimensions of the channels.[3,4] The “tight fit” of *p*-xylene within the framework may result in the perturbation of the ring C−H stretching vibrations. Thus, the observed large shifts to higher energies may be attributed to the restriction of the C−H stretching motions from the surrounding framework. Interestingly, the frequencies of the C−H stretching modes for the methyl groups (the bands at 2920 and 2863 cm^{-1}) remain essentially unchanged upon absorption. This implies that the long axis of *p*-xylene is oriented along the channel axis and, consequently, the methyl C−H stretching vibrations are much less restricted by the framework.

When the loading was increased from 4 to 5 molecules/u.c., the spectrum of adsorbed *p*-xylene started showing distinct changes, which were complete at a coverage of 6 molecules/u.c., indicating that the host framework begins to undergo phase transition at a loading of 5 molecules/u.c. and that the transformation is complete once the loading reaches 6 molecules/u.c. Further increasing the loading up to the maximum coverage (8 molecules/u.c.) does not result in any noticeable changes in the spectra, implying that the high-loaded phase is stable up to the maximum loading. The phase transition behavior of the ZSM-5 framework is readily followed by the changes in the line width of the vibrational modes of *p*-xylene absorbed in ZSM-5. For example, Figure 1A illustrates a sudden increase in the width of ν_8 at a loading of 5 molecules/u.c. Upon transition from the low- to high-loaded form, many of the Raman modes showed quite large shifts to higher energies. Figure 1B shows an abrupt change in the wavenumber of the C−CH$_3$ in-plane bending mode, where the phase transition occurring at a loading of 5 molecules/u.c. is evident. The ring C−H vibrations also exhibited large shifts to higher energies: they moved from 3065, 3048 (shoulder), and 3018 cm^{-1} in the spectrum of the low-loaded phase to 3074, 3059, and 3024 cm^{-1}, respectively, in the high-loaded phase. The transition from the low-loaded to high-loaded phase was accompanied by the splitting of several fundamentals into doublets in the Raman spectra. Figure 2 illustrates that two bands at 828 and 809 cm^{-1} corresponding to the ring breathing and ring C−H out-of-plane bending modes, respectively, appearing in the spectra of the low-loaded phase were split into doublets. Similarly, the band at 1570 cm^{-1}, due to an asymmetric C−C stretching mode, was also split into two components in the high-loaded phase (not shown). Single-crystal data have suggested that in the high-loaded structure, there are two different kinds of *p*-xylene molecules.[4] The splittings observed in the high-loaded form confirm the XRD

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(1) (a) Gies, H. In *Advanced Zeolite Science and Applications*; Jansen, J. C., Stocker, M., Karge, H. G., Weitkamp, J., Eds.; Elsevier: Amsterdam, 1994; pp 295−327 and references therein. (b) Fyfe, C. A.; Mueller, K. T.; Kokotailo, G. T. In *NMR Techniques in Catalysis*; Bell, A. T., Pines, A., Eds.; Marcel Dekker Inc.: New York, 1994; pp 11−67 and references therein.

(2) (a) Dutta, P. K. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1995**, *21*, 215−237 and references therein. (b) Bremard, C; Bougeard, D. *Adv. Mater*. **1995**, *7*, 10−25 and references therein.

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(4) van Koningsveld, H.; Tuinstra; F.; van Bekkum, H.; Jansen, J. C. *Acta Crystallogr.* **1989**, *B45*, 423−431.

(5) ZSM-5 samples were obtained from Chemie Uetikon AG (Si/Al = 336). All Raman spectra were recorded at room temperature on a Bruker RFS-100 FT-Raman spectrometer equipped with a Nd:YAG laser. The resolution was 2 cm^{-1}.

(6) Varsanyi, G. *Vibrational Spectra of Benzene Derivatives*; Academic Press: New York, 1969.

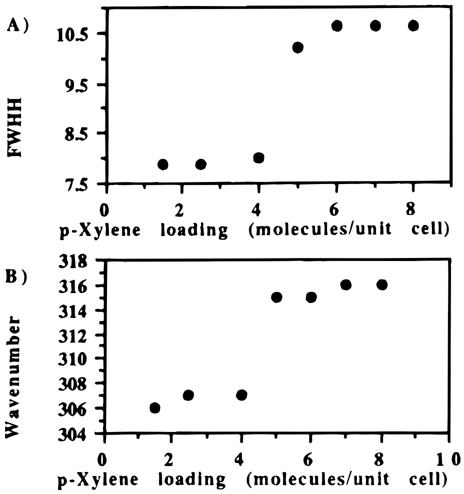

Figure 1. (A) Plot of the full width at half-height (FWHH) in cm^{-1} of the Raman band ν_8 (1620 cm^{-1}), an aromatic C$-$C stretching mode, of *p*-xylene adsorbed in H-ZSM-5 as a function of the loading. (B) Plot of the frequency in cm^{-1} of the C$-$CH$_3$ bending mode of *p*-xylene adsorbed in H-ZSM-5 as a function of the loading.

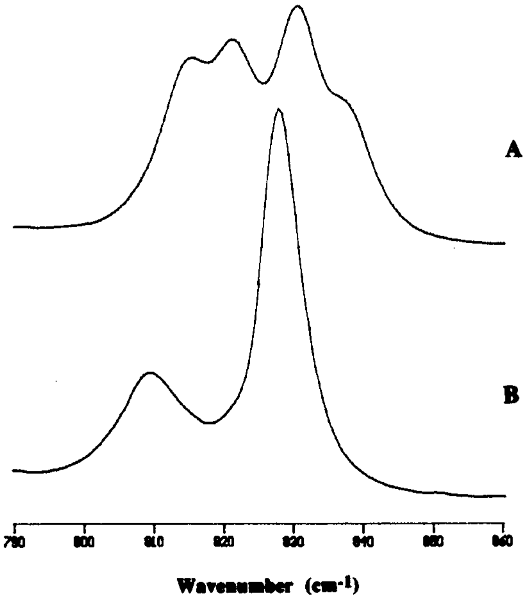

Figure 2. FT-Raman Spectra of *p*-xylene adsorbed in H-ZSM-5 in the region of 790$-$860 cm^{-1} at a loading of (A) eight and (B) four molecules per unit cell.

results and also indicate that there are strong interactions between the two types of *p*-xylene molecule.

The present work was mainly focused on the detection of a transition between the two orthorhombic phases. No attempt was made to examine the transition from the monoclinic phase to the low-loaded orthorhombic phase by monitoring the spectra of *p*-xylene because the monoclinic phase is only stable in a very small loading range (0$-$1.5 molecules/u.c.).[7] However, the three phases of ZSM-5 can be identified from the zeolitic framework vibrations. Figure 3 shows the spectra of ZSM-5 in the T$-$O$-$T bending region where the most intense Raman bands of the zeolite framework are located. The spectra are characteristic of each phase: in the spectrum of the calcined sample (unloaded) corresponding to the monoclinic phase, the strongest framework band was observed at 380 cm^{-1} with a prominent shoulder at 368 cm^{-1}. This band has been previously assigned to the symmetrical T$-$O$-$T bending mode, ν_s(T$-$O$-$T).[8] In the low-loaded phase, the band and the shoulder shifted to 385 and 364 cm^{-1}, respectively, and a new peak appeared as a weak shoulder at 354 cm^{-1}. Upon transformation to the high-loaded phase, all three bands observed in the spectrum of the low-loaded phase suddenly became a single profile centered at 371 cm^{-1}. It has been proposed that the frequency of the ν_s(T$-$O$-$T) mode has an inverse dependence on the magnitude of the T$-$O$-$T angle.[9] If this argument is accepted, it may be tentatively suggested that the average T$-$O$-$T angle in the monoclinic phase is slightly smaller than that in the high-loaded form.

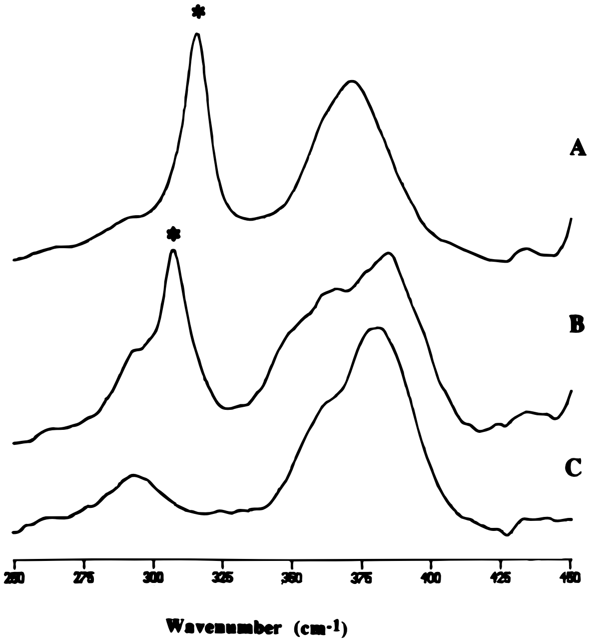

Figure 3. FT-Raman spectra of ZSM-5 framework vibrations in the region of 250$-$450 cm^{-1} at a loading of (A) eight (B) four, and (C) zero molecules per unit cell. The band labeled * is due to *p*-xylene.

In conclusion, this work demonstrates that FT-Raman spectroscopy is a powerful tool for the investigation of sorbate-induced phase transitions in zeolites. The spectral parameters of the guest molecule such as band frequency, splitting, and line width, are very sensitive to structural changes in the host framework. For the *p*-xylene/ZSM-5 system, our results are in agreement with those of NMR and XRD. We feel that there is great potential for using the FT-Raman technique to investigate unknown or poorly described sorbate$-$framework systems. Experiments of this type are currently in progress using the general approach described in the present communication.

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