Evidence for Chemisorbed Molecular Hydrogen in Fe-ZSM5 from Inelastic Neutron Scattering

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Fe-containing zeolites have recently attracted attention because of their promising catalytic activity in oxidation of benzene to phenol,[1] selective oxidation of methane,[2] NO_x reduction,[3,4] and N_2O decomposition.[5,6] The activity is thought to result from the special redox character of the iron species present in the zeolite.[7,8] Several studies illustrated that both preparation method and zeolite support greatly determine the catalytic properties.[7,9−11] Various characterization methods, including IR, H_2, and CO TPR, EPR, Mössbauer, and XAFS spectroscopy revealed that the catalysts contain different Fe-species varying from isolated Fe-ions to dinuclear iron clusters and larger iron oxide particles both inside the zeolite channels and on the exterior surface.[9,12−15]

Despite a large number of experimental studies it is still not completely understood why and how diverse iron species are obtained in the same zeolite. Moreover, the nature of the active Fe-species during catalytic reaction has not yet been conclusively identified either. It is therefore highly desirable that the number of techniques used to characterize metal species in zeolites be expanded.

This communication reports on the adsorption of H_2 onto the extraframework iron species in Fe−ZSM5 obtained by sublimation of $FeCl_3$.[15] We have found that adsorption of H_2 at 110 K on this type of Fe−ZSM5 results in strongly bound H_2 species, most likely chemisorbed molecular hydrogen. Moreover, the INS data show clear evidence for at least two distinguishable adsorption sites related to the iron cluster. Our results open new possibilities for catalyst characterization in general and the structure of the iron species in this catalytically interesting and important system more precisely.

Our attempt to further characterize the iron species in this important catalyst utilizes inelastic neutron scattering (INS) spectroscopy of the rotational transitions of the hydrogen molecule. This type of study has been shown to constitute a sensitive probe of the number and types of H_2 adsorption sites.[16−18] For example, H_2 adsorption on Na^+ and Ca^{2+} in zeolite A revealed different adsorption sites related to the preferred locations of the cations in the zeolite.[16,17] It is the rotational tunnel splitting of the librational ground state of a H_2 molecule[19] which is observed by INS spectroscopy (this transition is akin to the ortho−para H_2 for the free molecule, and it is forbidden in optical spectroscopy[15]). This splitting is an extremely sensitive measure of the rotational barrier height,. For example, the rotational tunnel splitting is 3.8 meV for H_2 physisorbed in CoNaA zeolite at temperatures below 100 K. On the contrary, molecular hydrogen ligands in metal complexes form a three-center, two-electron chemical bond with the metal which can result in a much lower tunnel splitting[16] for the dihydrogen ligand (0.025 to 2.5 meV). In addition, it was recently shown that structural information on $M-H_2$ interactions in molecular hydrogen complexes could be remarkably well extracted from INS data.[21]A related approach that uses hydrogen as a probe molecule for adsorption in zeolites is to observe changes in the internal mode ν(HH) of the molecule upon adsorption.[22] However, these changes are much more subtle than those in the external rotational transitions of the molecule. It should be noted that the “ortho−para splitting” observed in some of these experiments is the difference between the $Q(0)$ and $Q(1)$ vibrational bands, and therefore a different quantity from the purely rotational tunnel splitting in our experiment.

The Fe−ZSM5 catalyst was prepared following the method proposed by Chen and Sachtler, and in detail described by Battiston et al.[15] The elemental composition of the sample is characterized by Si/Al = 17 and Fe/Al = 1. The calcined and dried sample was transferred to an aluminum sample container connected to a gas-dosing system. INS spectra were collected at 5 K on the cold neutron time-of-flight spectrometer NEAT of the Hahn-Meitner Institut using an incident neutron wavelength of 5.1 Å on the sample with and without hydrogen. H_2 was adsorbed in the amount of one molecule per Fe with the catalysts at 110 K, and equilibrated before cooling to 5 K, The results for the spectra of the sample with adsorbed hydrogen are shown in Figure 1. Two pairs of peaks are evident, at approximately $\pm$ 4.2(1) cm^{-1} and, a much weaker pair at about 8.3(2) cm^{-1}. The barriers to rotation corresponding to these transitions would be 3.3 and 2.6 kcal/mol, respectively, if we take the rotational constant to be that of the free molecule, and the molecules have two rotational degrees of freedom. In addition, a broad, unstructured background centered at zero energy is also evident. Each pair (corresponding to “up”: and “down” rotational tunneling transitions within the librational ground state) can be associated with H_2 molecules at a well-defined adsorption or binding site. We take these sites to be at the Fe since the zeolite framework itself gives rise to much weaker adsorption of H_2. In fact, these values for the rotational tunnel splittings are appreciably smaller

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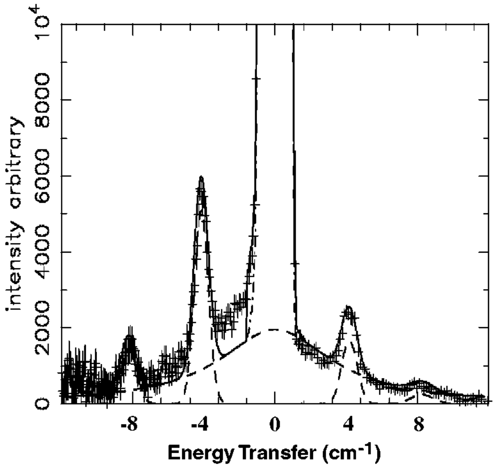

Figure 1. Inelastic neutron scattering spectrum collected on the NEAT spectrometer at HMI at 5 K for Fe−ZSM5 with one molecule H_2 adsorbed per Fe. Dashed line indicates the best fit to the data.

than those previously observed in zeolites A[12,13] or X[23] and are, in fact of comparable magnitude than those in some Fe dihydrogen complexes, namely 6.4 cm^{-1} in[24] $FeH_2(H_2)(PEtPh_2)_3$ and 2.1 cm^{-1} in[25] $[FeH(H_2)PPh_2CH_2CH2PPh_2)_2]BF_4$. In both of these cases the identity of hydrogen as a chemically bound molecular ligand is clearly established by a variety of experimental and theoretical techniques, including neutron diffraction. On the basis of these comparisons we conclude that the hydrogen adsorbed at low temperature in Fe−ZSM5 binds chemically to Fe at the active site, which is consistent with the observation that at higher temperatures H_2 is known to reduce the Fe in this catalyst.

As far as the origin of the two sets of transitions are concerned, we can only speculate because of the absence of a detailed picture of the structure of the active sites. Information from recent XAFS studies[10] do support the existence of binuclear Fe clusters, but further details cannot reliably be inferred from these data. A possible origin for the difference in these two adsorption sites could be that one Fe site is more accessible to H_2 than the other because of differences in the proximities of the O's coordinated to the Fe. Both the Fe-to-H_2 distance and direct interaction[14] of H_2 with O's near the binding site will affect the barrier to rotation, and thus could give rise to the observed difference of 0.7 kcal/mol in the two barrier height values. Differences in the oxidation state of the Fe could, of course, also account for this observation.

A considerable number of hydrogen molecules appear to be adsorbed at a distribution of sites with slightly varying coordination environments as is suggested by the broad band centered at zero energy below the tunneling peaks. This may well be the result of the relatively high loading of Fe used in this sample, which may be deposited in a variety of different places in the ZSM-5 host. Each of these sites may then give rise to a slightly different barrier to rotation for the adsorbed H_2 and thus result in the observed distribution of transition frequencies. This type of distribution of rotational transitions has previously been observed, for example, for methane adsorbed in MCM-41[26] where no well defined binding sites (marked by sharp rotational transitions) could be observed because the relatively weak interaction of methane with the accessible adsorption sites, namely framework O atoms and −OH groups, does not favor a specific location. Moreover, some previous EXAFS and Mössbauer studies of Fe−ZSM-5 have also indicated that a small amount of Fe_2O_3 particles could form under some experimental conditions. H_2 molecules adsorbed on such particles would be likely to also contribute to the broad band in the INS spectrum. The computer modeling studies developed by some of us[14,27] could readily be used to model this distribution of barrier heights and associated transitions on the basis of actual adsorption sites found in the simulation. However, a knowledge of the crystal structure including that of the Fe sites is essential for this purpose. Nonetheless, with the enormous sensitivity of the rotational tunneling splitting to the guest/host interaction potential a combined study of the molecular rotations of adsorbed H_2 by INS with computer simulation[14,27] would make it possible to derive a great deal of information on the nature of the adsorption sites in general, and the active sites in particular.

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