Communication

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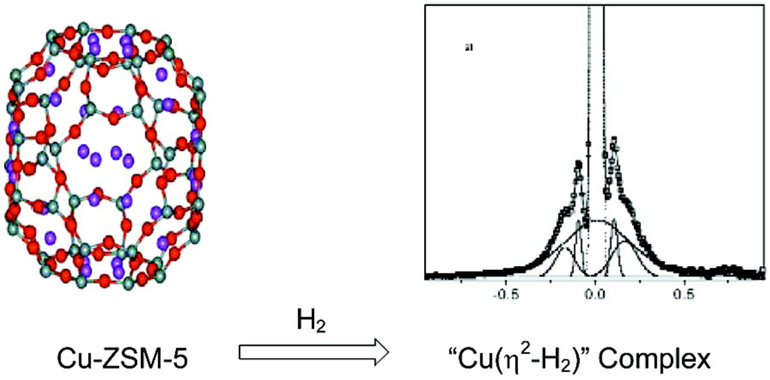

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Observation of Exceptionally Strong Binding of Molecular Hydrogen in a Porous Material: Formation of an η^2-H_2 Complex in a Cu-Exchanged ZSM-5 Zeolite

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Perhaps the most serious outstanding problem in the potential utilization of porous materials, as a medium for hydrogen storage in mobile applications, is the fact that the binding energies for physisorbed hydrogen are too low to reduce the equilibrium pressure of adsorbed hydrogen, at ambient temperature, much below that of a cylinder of compressed hydrogen with the same capacity. While the surface areas of some porous materials have reached the values necessary to meet the storage capacities envisaged by the U.S. Department of Energy, they do so at low-temperature rather than ambient temperature because of the weak binding of adsorbed molecular hydrogen. It has, therefore, been recognized that it is extremely urgent to design materials where hydrogen is bound by molecular chemisorption, as in metal−dihydrogen complexes, and thus have a binding energy of 5−10 kcal/mol compared with 1−2 kcal/mol for physisorption.[1]

While zeolites themselves are not likely candidates for hydrogen storage materials, because of the high density of the aluminosilicate framework, they do offer a unique opportunity to systematically study the effect on hydrogen binding of a variety of charge-compensating extraframework cations as well as that of metal clusters that have been incorporated in some zeolites such as ZSM-5. Some of us have, in fact, previously reported the first example[2] of nondissociative, molecular chemisorption of hydrogen in a porous material, namely Fe−ZSM-5, on the basis of inelastic neutron scattering spectra (INS) that closely resembled those of well-established molecular dihydrogen complexes of Fe.[3] The existence of such molecular dihydrogen complexes, in coordination compounds, was first shown by Kubas who prepared the tungsten dihydrogen complex $W(\eta^2\text{-}H_2)(CO)_3(PCy_3)_2$[4] in 1984. A large number of both neutral and cationic complexes of many transition metals have since been characterized and are described in an extensive review by Kubas.[5] We note, however, that molecular dihydrogen complexes with first row transition metals are rare, with the notable exception of Fe, while those with Cu or Ni have never been isolated.

Metal-dihydrogen interactions have been studied by a number of techniques including IR spectroscopy, solution and solid-state NMR, and neutron and X-ray diffraction as well as INS. The latter technique is the only method to observe the rotational tunneling spectrum of the librational ground state of the molecular hydrogen ligand, the fingerprint of coordinated dihydrogen,[5−9] which unequivocally proves the presence of the M-(η^2-H_2) moiety. These ground-state rotational transitions of dihydrogen are the most sensitive probe of the nature of the interaction between the metal atom and the H_2 ligand and its degree of activation, as they cover an observable range of well over 2 orders of magnitude from 119 cm^{-1} for unhindered rotation (the "ortho−para" H_2 transition), and >/∼ 30 cm^{-1} for weakly bound dihydrogen, to well below 1 cm^{-1} for coordinated dihydrogen.

These types of INS studies have recently been used to identify the presence of molecular chemisorption in two Ni-based porous materials: the Ni phosphate VSB-5[10] and the hybrid compound Ni-SIPA[11] where the removal of coordinated water creates an unsaturated metal binding site available for coordinating H_2.

Recent IR studies[12−15] on hydrogen adsorbed in Cu−ZSM-5 have revealed rather low absorption frequencies at about 3070 and 3125 cm^{-1} assigned to the intramolecular stretching mode of hydrogen molecules interacting with a Cu(I)-ion, coordinated to the oxygens of an AlO_4^- tetrahedron. DFT calculations[12,15] on related model systems indicate a strong interaction between the hydrogen molecule and the Cu^+ ion and the formation of an η^2-complex with a H−H separation of 0.82 Å, which gives a calculated red shift of the H−H stretching mode very close to the experimentally observed values.

To obtain further details on the nature of the binding of hydrogen to the zeolite host and the Cu ions in particular, we have carried out high-resolution INS studies on hydrogen adsorbed in Cu−ZSM-5 both as a function of hydrogen content and temperature. INS spectra were collected at 4K on the direct geometry cold neutron chopper spectrometer IN5 (see Supporting Information) at the Institut Laue-Langevin, with the use of an incident wavelength of 7 Å.

Rotational tunneling INS spectra obtained from two samples with loadings of 0.4 and 2.0 H_2/Cu, respectively, are shown in Figure 1a and 1b along with the peak decomposition. Two pairs of transitions at ±0.80 and ±1.37 cm^{-1} are observed at low-hydrogen loading, each corresponding to a different coordinated hydrogen molecule and suggesting the presence of at least two binding sites with a corresponding intensity ratio of about 1:2. The very low values of the rotational tunneling frequencies imply that the interaction of H_2 with Cu in ZSM-5 is significantly stronger than that with Fe in ZSM-5.[2] In the latter case the tunneling frequencies were observed at approximately ±4.2 and ±8.3 cm^{-1}.

A theoretical barrier to rotation of 3.1 kcal/mol and a Cu−H_2 bond dissociation energy of 14.1 kcal/mol were estimated from our DFT calculations on model clusters similar to those investigated in previous studies.[12,16] To derive an experimental barrier to rotation for comparison purposes, we used the value of 0.82 Å for d(HH)

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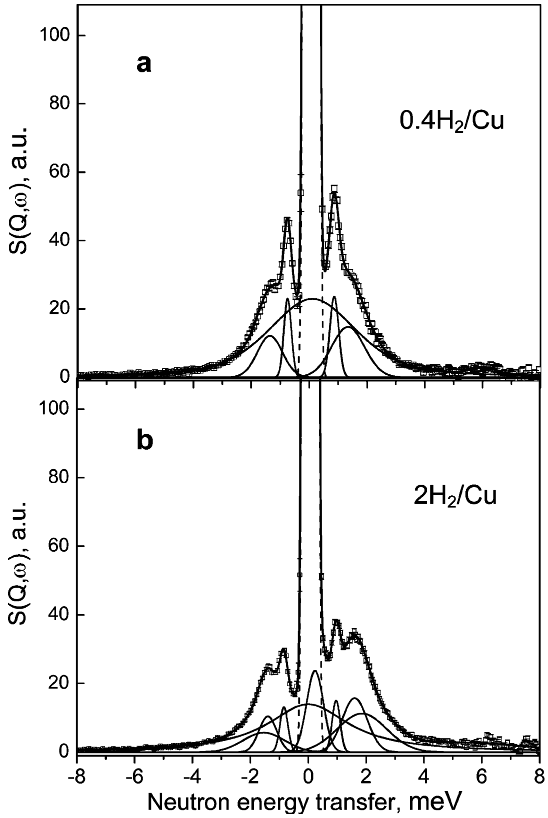

Figure 1. INS spectra of 0.4 and 2H$_2$/Cu measured at 4 K are shown in panels a and b, respectively. Neutron energy loss processes are shown on the positive side of the elastic line.

from our DFT calculation to obtain the rotational constant B. For planar rotation of H_2 in a double-minimum potential we then obtain barriers, at the two different sites, of 2.1 and 1.8 kcal/mol, respectively. These results are in reasonable agreement with the calculated value, given the various approximations used.

A broad feature underneath the sharp tunneling lines may reflect the presence of a distribution of additional binding sites, resulting from heterogeneity of the Cu binding sites (nonuniform distribution, isolated or neighboring Cu centers, etc.) in the ZSM-5 channels.

An increase of the hydrogen loading to about 2 H_2/Cu resulted in a more complicated inelastic spectrum, Figure 1b, with the two main tunneling features shifted to ± 0.88 and ± 1.49 cm^{-1} and a third pair of lines appearing at about ± 1.69 cm^{-1}. The appearance of new peaks may be due to the coordination of two H_2 molecules at the same metal center or the interactions between closely spaced dihydrogen complexes.

The fourfold increase of the H_2 concentration leads to only a 2% increase in the total scattered intensity, within the measured energy range, which suggests that the strong binding sites were largely saturated at the lower loading of H_2/Cu. Much of the additional hydrogen must, therefore, be adsorbed on sites of the zeolite framework, which bind hydrogen by relatively weak physisorption. Peaks at approximately 93 and 113 cm^{-1}, respectively, have in fact been observed in an earlier study[17] on this system. In contrast to an earlier report on H_2 adsorption in Ag exchanged zeolite-A,[8] the dihydrogen complex in Cu−ZSM-5 did not show any dissociation or conversion to a classical hydride up to 200 K (cf. Supporting Information).

The present study clearly demonstrates that a considerable amount of hydrogen adsorbed into Cu−ZSM-5 binds by molecular chemisorption as a L_nM-(η^2-H_2) complex. The spectra are consistent with the presence of two well-defined binding sites. The first type of site is more homogeneous and represents up to 13% of the total Cu-content. The second family of sites has a broader distribution of rotational barriers due to a greater heterogeneity of the site morphology and a lower barrier. These sites amount to up to 26% of the total Cu content. The very strong binding of hydrogen in Cu−ZSM-5 is in marked contrast to what has been observed for open Cu binding sites in metal organic framework[19] compounds or in partially Cu^{2+} exchanged zeolite A.[20] In the former case typical rotational frequencies are observed at about 65 cm^{-1}, while in the latter they are observed near 20 cm^{-1}. The present results suggest that molecular chemisorption of hydrogen can indeed provide the high binding energies along with the favorable kinetics that are an essential ingredient for the utilization of porous materials as hydrogen-storage media at room temperature.

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Supporting Information Available: Sample preparation, composition and treatments; INS, H_2 loading, and DFT calculations details. This material is available free of charge via the Internet at http://pubs.acs.org.

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