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Adsorption of Molecular Hydrogen on Coordinatively Unsaturated Ni(II) Sites in a Nanoporous Hybrid Material

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Abstract: A porous hybrid inorganic/organic material, $NaNi_3(OH)(SIP)_2$ [SIP = 5-sulfoisophthalate] [**1**], is shown to strongly bind molecular hydrogen at coordinatively unsaturated metal sites. A combination of H_2 sorption isotherms, temperature programmed desorption, and inelastic neutron scattering spectroscopy show the existence of a considerable number of such strong binding sites in [**1**] along with other sites where hydrogen is more weakly physisorbed. The overall capacity for hydrogen of this material as well as the much stronger binding of hydrogen than in typical porous material represent an important step toward a possible utilization of porous media for hydrogen storage.

Introduction

The identification of materials with a very high capacity for reversible hydrogen storage represents one of the most critical challenges to an implementation of the hydrogen economy.[1] Despite the significant economic importance of achieving this goal, no fully satisfactory storage method for hydrogen has yet been demonstrated.[2] The principal strategies that have been explored to date involve either physisorption, where hydrogen is weakly adsorbed on a surface of a material with high specific surface area, or chemical binding, where hydrogen is bound by dissociative binding by strong chemical bonds within the storage material.

Carbons and most hybrid metal/organic compounds (materials where the framework is composed of both inorganic and organic building units) are two of the more prominent examples of materials that store hydrogen simply by physisorption.[3,4] Because the interaction of H_2 with carbon is by rather weak van der Waals forces, significant uptake only occurs at relatively low temperatures. Large storage densities at ambient conditions are in principle relatively easy to achieve with dissociative chemical binding of H in materials such as metal hydrides,[5] so-called complex hydrides,[6] and other chemical systems such as aminoborane.[7] However, the formation and breaking of chemical bonds that is necessary for the release and recharging of hydrogen in these materials typically leads to poor thermodynamics, kinetics, or lack of reversibility.

Recently, we and others have recognized that a realistic hydrogen storage solution may lie in the middle ground between the two extremes described above, namely with the use of a material capable of binding molecular hydrogen by much stronger chemical rather than nonbonded interactions but where the interaction is insufficient to break the dihydrogen chemical bond. Coordination of hydrogen in *molecular* form to a metal center has become well-established in organometallic chemistry since its discovery by Kubas and co-workers in 1984.[8] We provided the first evidence for *molecular chemisorption* of dihydrogen in a porous solid for dihydrogen sorbed into iron sites in Fe-ZSM-5.[9] Our subsequent study of the porous nickel phosphate VSB-5 provided the first evidence for dihydrogen sorption on a framework metal site.[10] Porous solids containing relatively narrow channels[11] and accessible, coordinatively unsaturated transition metal sites may therefore offer a promising route toward realizing a reversible hydrogen storage material with high capacity under near ambient conditions. Our work on VSB-5 has, for example, demonstrated that the presence of unsaturated metal binding sites significantly improves its

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(1) Schlapbach, L.; Züttel, A. *Nature* **2001**, *414*, 353.

(2) Service, R. F. *Science* **2004**, *305*, 958.

(3) A recent summary can be found in Züttel, A. *Naturwissenschaften* **2004**, *91*, 157.

(4) Rowsell, J. L. C.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4670.

(5) Hout, J.; Pelletier, J. F.; Liang, G.; Sutton, M.; Schultz, R. *J. Alloys Compd.* **2002**, *727*, 330.

(6) Schüth, F.; Bogdanović, B.; Felderhoff, M. *Chem. Commun.* **2004**, 2249.

(7) Gutowska, A.; Li, L.; Shin, Y.; Wang, C. M.; Li, X. S.; Linehan, J. C.; Smith, R. S.; Kay, B. D.; Schmid, B.; Sahw, W.; Gutowski, M.; Autrey, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 3578.

(8) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451.

(9) Mojet, B. L.; Eckert, J.; van Santeen, R. A.; Albinati, A.; Lechner, R. E. *J. Am. Chem. Soc.* **2001**, *123*, 8147.

(10) Forster, P. M.; Eckert, J.; Chang, J. S.; Park, S. E.; Férey, G.; Cheetham, A. K. *J. Am. Chem. Soc.* **2003**, *125*, 1309.

(11) Jhung, S. H.; Kim, H. K.; Yoon, J. W.; Chang, J. S. *J. Phys. Chem. B* **2006**, *110*, 9371.

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hydrogen sorption characteristics, in terms of both quantity and effective sorption temperature compared with that of similar materials without unsaturated metals sites.

More recently, several groups have looked at coordinatively unsaturated metal sites in metal/cyano frameworks[12] and several porous hybrid materials (HKUST-1 and MOF-505) that contain accessible Cu(II) sites.[13] However, the metal sites in these materials appear to associate very weakly compared to the interactions seen in Kubas-type molecular dihydrogen complexes. In the case of the metal cyano frameworks, recent atomic pair distribution function[14] (PDF) and crystallographic studies[15] show that hydrogen molecules sit preferentially in a nanopore within the compound, only occupying unsaturated metal sites at higher loadings. In the case of HKUST-1, gas sorption and IR measurements indicate that the hydrogen binding is not appreciably different from that seen in hybrid materials without accessible metal sites.[16] For MOF-505, Chen et al. found very high hydrogen uptake but no evidence that the high observed capacity was related to the accessible Cu(II) sites rather than MOF-505's very high surface area. Very recently, the hybrid PCN-9 demonstrated a high enthalpy of adsorption for H_2 (10.1 kJ/mol) as well as other gases.[17] Since the framework contains unsaturated Co(II) sites, it is very likely that further crystallographic or spectroscopic investigations into this remarkable hybrid material will demonstrate that the accessible metal sites are responsible for its promising gas sorption properties. Additional investigations have undoubtedly been hindered by the scarcity of materials with demonstrable unsaturated transition metal sites.[18]

Here, we report the use of hydrogen sorption isotherms, temperature programmed desorption (TPD), and inelastic neutron scattering (INS) spectroscopy of the rotations of the bound hydrogen molecule to demonstrate the existence and characteristics of several coordinatively unsaturated metal sites in our new porous hybrid metal/organic material,[19] $NaNi_3(OH)(SIP)_2$ [SIP = 5-sulfoisophthalate] [**1**].

Experimental Details

Samples of [**1**] were prepared using a scaled-up version of the published preparation.[19] Because the synthesis also yields an impurity phase, clusters containing large crystals of [**1**] had to be manually separated from a powder of the second unidentified phase. Our reference used for comparison in sorption experiments was the zeolite H-ZSM-5 (Si/Al = 40, $S_{BET} = 425$ m^2/g), obtained from Zeolyst.

H_2 adsorption−desorption experiments at low temperature were performed in a static vacuum volumetric apparatus (Micromeritics Tristar 3000) or a glass vacuum system equipped with a diffusion pump. Prior to the sorption experiments, [**1**] was slowly activated by heating (1 K/min) from room temperature to the designated temperature (between 573 and 623 K), where it was held for 0.5 h under vacuum ($<10^{-5}$ Torr). The heat of H_2 adsorption (ΔH_{ads}) was calculated with the Clausius−Clapeyron equation using the H_2 adsorption isotherms at 77 and 87 K.[20]

TPD experiments were carried out in a fixed-bed tubular reaction system equipped with a specially designed heater for control between 77 and 373 K and a thermal conductivity detector.[11] After the hydrogen adsorption at 80 K, the sample was flushed with nitrogen at the same temperature. Once the baseline of the integrator was stable, the TPD run was started with flowing nitrogen as a carrier gas at a heating rate of 5 K/min from 80 to 250 K.

Inelastic neutron scattering spectra were collected on the QENS[21] spectrometer at the Intense Pulsed Neutron Source at Argonne National Laboratory. Our sample of [**1**] was dehydrated overnight in a tube furnace set to 573 K. A quantity of 5.5 g of this material was subsequently sealed inside an aluminum sample container in a solvent-free N_2 glovebox. The container was then mounted in a closed-cycle He refrigerator, connected to an external gas loading manifold, and placed into the QENS instrument. After the sample was degassed for 1 h, the sample was cooled to 15 K and a "blank" spectrum of the material was collected for approximately 12 h. A measured amount of hydrogen was then loaded in situ from the external gas handling system into the sample by warming to a temperature between 40 and 100 K, allowing hydrogen to adsorb into the sample, and subsequent lowering of the temperature to 15 K. Each of a total of five loadings delivered 5.9×10^{-3} mol of H_2 gas to the sample.

Results and Discussion

The as-synthesized structure of [**1**] (Figure 1) can be described as $Na_2Ni_6O_{34}$ clusters bridged by 5-sulfoisophthalate to form a 3D network. An extended description of the structure has been published previously.[19] Although this hydrated form does not appear to contain large enough channels to support permanent porosity, dehydration at temperatures between 573 and 623 K results in a highly porous material with BET surface areas above 700 m^2/g. Evidently, structural changes that occur when water molecules coordinated to Ni(II) octahedra are removed lead to the formation of a pore system rather than the more typical situation of a collapse of the structure.[22] Significant rearrangements to the local structure do occur, as evidenced by changes to position and intensities of all peaks in the powder XRD pattern during the course of dehydration.[19] Unfortunately, the resulting structure of the dehydrated material is rather complex and all powder patterns measured on it show severe peak broadening. It has therefore not yet been possible to determine the structure of the porous phase. Attempts to index the unit cell (described previously)[19] suggest a triclinic unit cell expanded by 7.5% compared to the hydrated structure. Previous thermogravimetric studies[19] under flowing nitrogen show full removal of all coordinated water molecules at about 603 K. [**1**] can withstand dehydrations up to at least 623 K, where the sample is held at the final temperature for several hours. BET surface area measurements following slow dehydration under vacuum at 573 and 623 K show comparable surface areas, suggesting that vacuum is able to remove at least a significant portion of the coordinated water molecules by 573 K.

Several observations strongly support the existence of accessible, coordinatively unsaturated Ni(II) sites within the pore

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(12) (a) Chapman, K. W.; Southon, P. D.; Weeks, C. L.; Kepert, C. J. *Chem. Commun.* **2005**, 3322. (b) Kaye, S. S.; Long, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 6506. (c) Chapman, K. W.; Chupas, P. J.; Kepert, C. J. *J. Am. Chem. Soc.* **2005**, *127*, 11232.

(13) Chen, B.; Ockwig, N. W.; Millward, A. R.; Contreras, D. S.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4745.

(14) Chapman, K. W.; Chupas, P. J.; Maxey, E. R.; Richardson, J. W. *Chem. Commun.* **2006**, 4014.

(15) Hartman, M. R.; Peterson, V. K.; Liu, Y.; Kaye, S. S.; Long, J. R. *Chem. Mater.* **2006**, *18*, 3221.

(16) Prestipino, C.; Regli, L.; Vitillo, J. G.; Bonino, F.; Damin, A.; Lamberti, C.; Zecchina, A.; Solari, P. L.; Kongshaug, K. O.; Bordiga, S. *Chem. Mater.* **2006**, *18*, 1337.

(17) Ma, S.; Zhao, H. C. *J. Am. Chem. Soc.* **2006**, *128*, 11734.

(18) Maggard, P. A.; Yan, B. B.; Luo, J. H. *Angew. Chem., Int. Ed.* **2005**, *44*, 2553.

(19) Kim, D. S.; Forster, P. M.; Le Toquin, R.; Cheetham, A. K. *Chem. Commun.* **2004**, 2148.

(20) Thomas, J. M; Thomas, W. J. *Introduction to the Principles of Heterogeneous Catalysis*; Academic Press: New York, 1967; p 102.

(21) Bradley, K. F.; Chen, S. H.; Brun, T. O.; Kleb, R.; Loomis, W. A.; Newsam, J. M. *Nucl. Instrum. Methods* **1988**, *A270*, 78.

(22) Rosseinsky, M. J. *Microporous Mesoporous Mater.* **2004**, *73*, 15.

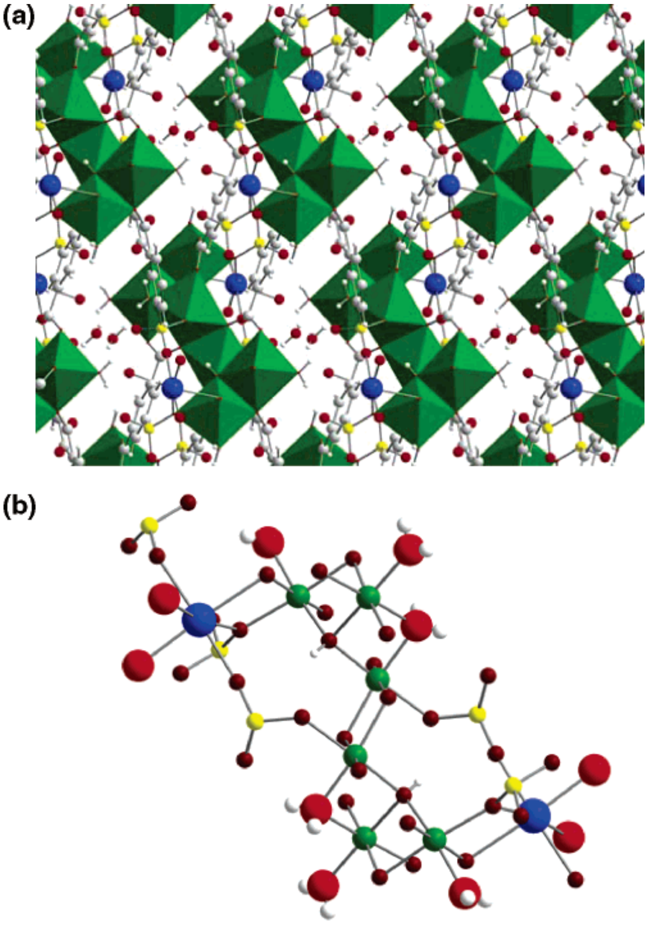

Figure 1. (a) Crystal structure for hydrated [**1**] viewed in the *ab* plane. NiO_6 octahedra are illustrated as green polygons. Sodium, sulfur, carbon, oxygen, and hydrogen atoms are shown as blue, yellow, gray, red, and white spheres, respectively. (b) View of a single cluster from [**1**] with nickel, sodium, sulfur, carbon, oxygen, and hydrogen atoms colored green, blue, yellow, gray, maroon, and white, respectively. Water molecules lost during dehydration are colored red and highlighted by an enlarged size. The organic portions of the structure have been omitted for clarity.

system for this compound following full dehydration. First, there are four sites where water coordinates to NiO_6 octahedra per three crystallographically unique Ni(II) atoms. It is unlikely that structural rearrangements would be able to block all of these sites. Moreover, the dehydrated form rehydrates very quickly on exposure to air, accompanied by a visible change from yellow-brown back to its original green color in less than 1 min. Since the powder diffraction pattern and TGA trace of the rehydrated form are identical to the as-synthesized form,[23] water must be able to reach the Ni(II) sites quickly, implying that they must be easily accessible to the channel. Finally, adsorption of solvent molecules (methanol, ethanol, and acetonitrile) invariably led to two-step TGA curves, which suggests that a fraction of these molecules was able to coordinate to metal sites.

Hydrogen sorption isotherms for [**1**] are shown in Figure 2 and compared with those for H-ZSM-5. The gravimetric capacity for H_2 uptake at 77 K is approximately 105 mL/g (~0.94 wt %) and greater than that for H-ZSM-5. The adsorption curve exhibits a very steep rise that is associated with unusually strong interactions of H_2 with some binding sites, a conclusion that is supported by the pronounced hysteresis evident in the desorption and readsorption isotherms (see Supporting Information S-4). This indicates that the interaction between hydrogen and certain adsorption sites is sufficiently strong that they cannot be removed at 77 K by vacuum. (The hysteresis present at higher partial pressures may be the result of structural reorganizations that could accompany gas sorption.) In contrast to our findings, the isotherms for transition metal/cyano frameworks, which also contain accessible, coordinatively unsaturated metal sites, do not show such hysteresis.[12a] Application of a variant of the Clausius–Clapeyron equation leads to an estimate of the enthalpy of adsorption of 9.4–10.4 kJ/mol (see Supporting Information S-2), a value notably higher than those that have been reported for any metal/cyano framework or MOF-5 by Kaye and Long.[12b] Because the isotherms used to determine this value include contributions from both strong and weak sorption sites, this value of the enthalpy likely underestimates the interaction between the dihydrogen and the Ni(II) sites.

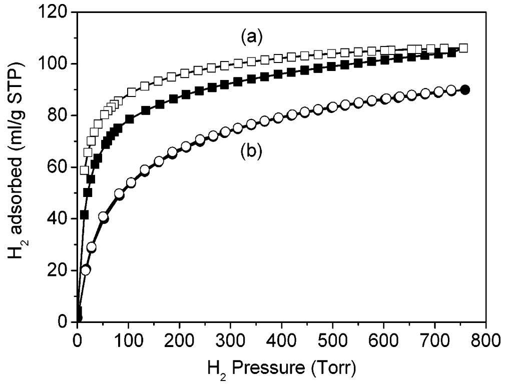

Figure 2. Hydrogen adsorption–desorption isotherms for (a) [**1**] at 77 K, showing pronounced hysteresis on desorption and for comparison (b) ZSM-5 zeolite at 77 K. Symbols: closed symbol (adsorption) and open symbol (desorption).

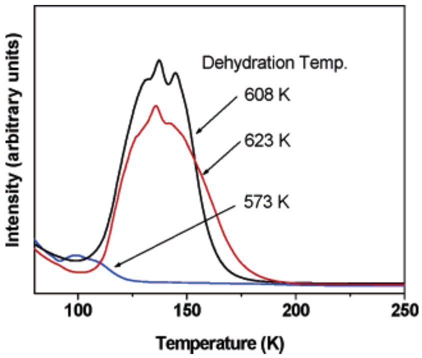

Figure 3. Low-temperature H_2-TPD profiles of [**1**] depending on dehydration temperatures. Ramping rate: 5 K/min.

TPD curves (Figure 3) showing that desorption of hydrogen occurs at temperatures between 140 and 160 K further support the presence of unsaturated metal binding sites for hydrogen in [**1**]. TPD peaks at comparable temperatures were previously observed in another material containing accessible Ni(II) sites, VSB-5.[10] The peak in the TPD curve exhibits pronounced structure, which persists when the measurement was repeated at various ramping rates (figures shown in Supporting Information S-6). This observation suggests that multiple, strong metal binding sites are responsible for the observed hydrogen retention.

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(23) Peak broadening does occur following the initial de/rehydration. This is most likely the result of a decrease in crystallite size during dehydration rather than a change in local structure since the inelastic neutron spectroscopy indicates a very regular local structure.

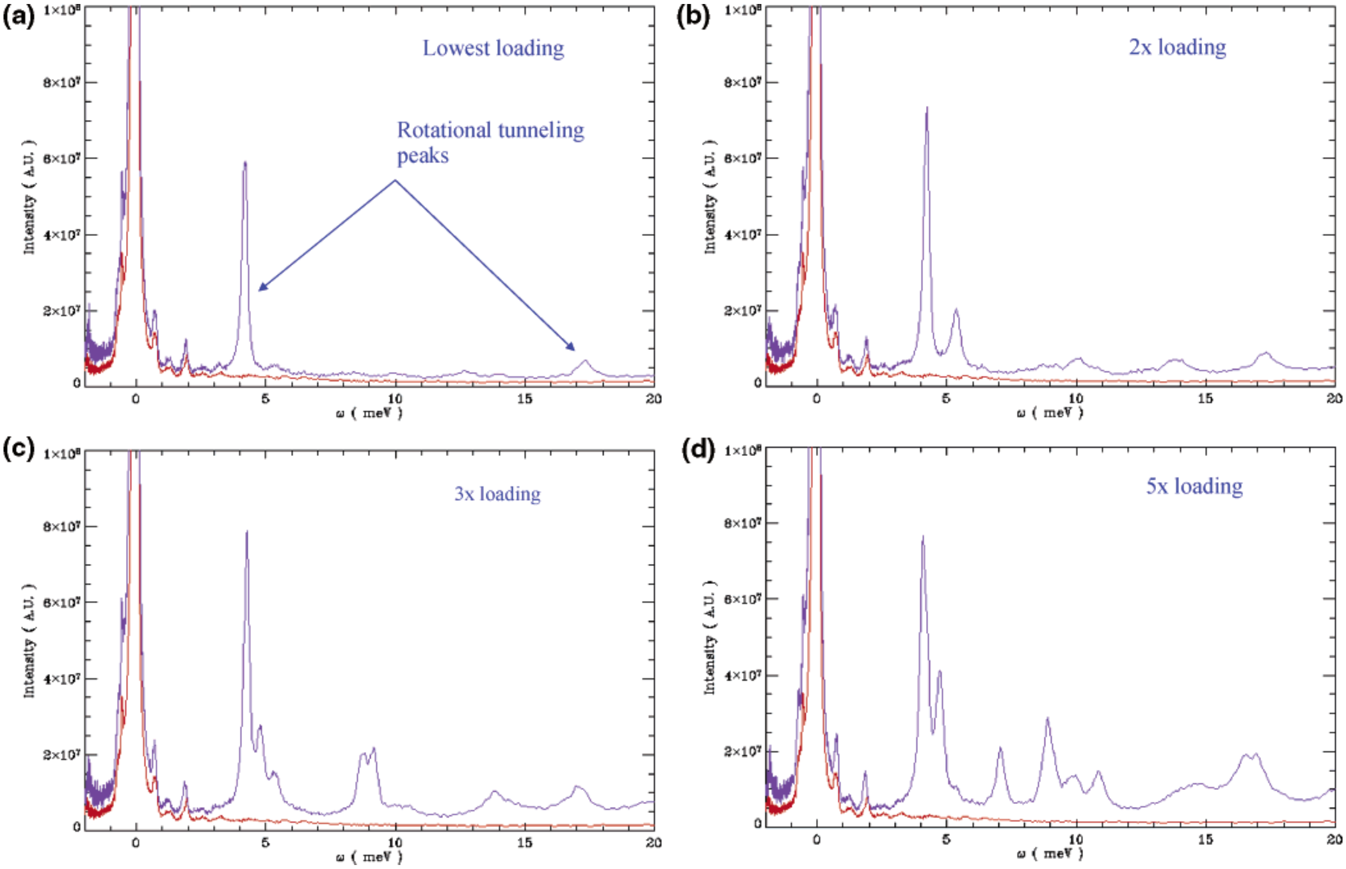

Figure 4. Inelastic neutron spectra for different loading levels. Various loadings are shown in purple, with an unloaded measurement in red for comparison. The intensity is expressed in arbitrary units (A.U.).

Moreover, virtually no TPD peaks are seen in samples that were dehydrated at temperatures less than 573 K, despite the fact that these samples also have high measured surface areas.[24] The most likely explanation for this observation is that the material becomes porous before the water molecules coordinating to active Ni(II) sites are removed, and that the coordinatively unsaturated Ni(II) sites then become accessible in the pore system once these water molecules are removed at higher dehydration temperatures.

Considerably more molecular level detail on the interaction and binding of H_2 with [**1**] can be obtained by inelastic neutron scattering from the hindered rotor states of the bound molecule. The transition energies between these quantum mechanical rotational states for an adsorbed hydrogen molecule are very sensitive to the shape and height of the barrier to rotation, which in turn is a rather direct measure of the guest−host interactions. For low to medium barrier heights (as in the present case) the transition between the lowest two states (rotational tunneling transition) decreases approximately exponentially with an increase of the barrier to rotation from the molecule's chemical environment. Moreover, the very large inelastic scattering cross section of ^1H compared to that of any other atoms present in our system makes rotational tunneling spectroscopy by INS a highly specific method to characterize the interaction between dihydrogen and its host. This method has been previously applied to porous carbons,[25] zeolites,[26] nickel phosphates,[10] and hybrid inorganic/organic compounds[4,27] and has been described in more detail in the study of hybrid materials.[28]

Rotational tunneling spectra collected at 15 K with five different levels of hydrogen loading are shown in Figure 4. Despite the fact that the crystallinity of this material is adversely affected by the dehydration process, the local structure (and thus the rotational potential energy surface) at the actual binding sites must be rather well-defined as is indicated by the sharpness of the INS hindered rotor spectra. Assignments of the observed peaks are made with reference to a particular model for the hindered rotation and its associated energy level diagram as a function of barrier height.[29] Physisorbed hydrogen molecules invariably retain both rotational degrees of freedom of the dumbbell molecule and in the simplest case may be treated in terms of reorientations in a double-minimum potential. We have successfully used this model[29] to analyze such spectra for H_2 in a wide variety of systems including zeolites and MOFs.[4,25−29] In cases where hydrogen is chemically bound in molecular form, most notably the metal dihydrogen complexes,[30] reorientation

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[24] Samples dehydrated at 300 °C for the TPD experiments showed a surface area of 450 m^2/g, somewhat lower than the 743 m^2/g surface areas seen on other samples. Since our previous investigations of the surface area of this sample (which used a different dehydration setup) found that 300 °C was the ideal dehydration temperature for dehydrating this material, the difference is likely the result of a small offset between the measured and actual dehydration temperatures for one setup.

[25] Brown, C. M.; Yildirim, T.; Neumann, D. A.; Heben, M. J.; Gennett, T.; Dillon, A. C.; Alleman, J. L.; Fischer, J. E. *Chem. Phys. Lett.* **2000**, *329*, 311.

[26] MacKinnon, J. A.; Eckert, J.; Coker, D. F.; Bug, A. L. R. *J. Chem. Phys.* **2001**, *114*, 10137.

[27] Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127.

[28] Rowsell, J. L. C.; Eckert, J.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *217*, 14904.

[29] Nicol, J. M.; Eckert, J.; Howard, J. *J. Phys. Chem.* **1988**, *92*, 7117.

[30] Eckert, J.; Kubas, G. J. *J. Phys. Chem.* **1993**, *97*, 2378.

of the dihydrogen ligand is approximately constrained to a plane on account of the side-on (or η^2-) coordination to the metal so that the molecule has just one rotational degree of freedom. The spacing between the hindered rotor levels in this case differs markedly from that for the previous case, and we utilize this distinction in the following discussion to attempt to identify those sites where hydrogen is indeed molecularly chemisorbed.

At the lowest loading used in our experiments, we observe a strong peak at 4.2 meV along with a weaker peak at 17.3 meV from hindered rotational transitions of the bound dihydrogen molecule. This value of 4.2 meV for the energy of the lowest rotational transition (or the rotational tunnel splitting) may be compared with about 1.5 meV for H_2 in VSB-5 [**2**] and 2.9 meV in NiNaA [**7**], where it must be kept in mind that a lower energy indicates a larger barrier to rotation. A larger barrier to rotation may not necessarily be equivalent to stronger binding of the sorbed hydrogen, but in a general sense this seems to be the case and these results provide nice confirmation of this general trend. Thus, INS spectra of H_2 in Ni-SIP appear to strongly suggest that binding of molecular hydrogen first occurs by molecular chemisorption at the unsaturated Ni(II) binding sites created by dehydration, as the series of transitions[31] at 4.1 (0−1) and 17.3 (1−2) and 22 meV (0−2; not shown) cannot be assigned on the basis of a model for physisorbed H_2 (i.e., double minimum with TWO rotational degrees of freedom), but can be fitted to the model used for coordinated dihydrogen (PLANAR rotation in a double-minimum potential) with a barrier height $V/B = 3.1$, where the rotational constant B for H_2 is 7.35 meV.

A second site becomes occupied when the hydrogen loading is increased to twice the initial loading (Figure 4) with a set of transitions at 5.4 meV (overlapping 0−1 and 1−2) and about 10 meV (0−2) which again fit to the model for planar rotation ($V/B = 1.7$) indicative of molecular chemisorption. Two additional binding sites for hydrogen become evident at three times the lowest loading: another strong binding site characterized by peaks at 4.8 (0−1) and 13.8 meV (1−2) and a second one by a doublet at 8.5 and 9.2 meV. This latter set of transitions, however, corresponds to (0−1) and (1−2) for a physisorbed molecule (two-dimensional reorientation) and a barrier of 3.4B. Another site for physisorbed hydrogen becomes progressively occupied at four and five times the original loading with transitions at 10.8 (0−1) and 7 meV (1−2) and a shoulder at approximately 17.2 meV (0−2) which correspond to a barrier of 2.2B. At the highest loading, we also observe a peak close to the free rotor value (14.7 meV) which would suggest some agglomeration of hydrogen molecules into bulk solid particles.[32]

Conclusion

We have presented evidence based on INS spectra of the hindered rotations of the bound hydrogen molecules, on the structural and physical properties of [**1**] and on sorption and TPD measurements, that several accessible, coordinatively unsaturated Ni(II) sites exist in [**1**] when it is dehydrated at sufficiently high temperature to remove aquo ligands from the Ni octahdedra. The high enthalpy of adsorption from these sites provides a clear example of their ability to increase the temperatures at which porous sorbents are useful. Additional sites in the structure, where we find hydrogen to be physisorbed, nonetheless bind the molecule much more strongly than do carbon supports. The development of highly porous solids with a sufficiently strong affinity toward hydrogen for room-temperature storage applications, yet where the interaction is not so strong that it leads to disassociative binding and hence irreversibility, slow kinetics, or large energy losses associated with cycling, represents a major challenge in materials science. We have hereby demonstrated that highly porous materials containing coordinatively unsaturated metal sites are a realistic and highly promising means of achieving this goal.

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Supporting Information Available: Additional sorption isotherms and TPD traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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[31] Energy levels for the hindered H_2 rotor are labeled with increasing energy as 0, 1, and 2. Transitions between these levels are represented as, for example, (0−1). Since the rotation in this case is hindered, the numbers should not be taken as rotational quantum numbers (J), which are only appropriate for free rotation.

[32] We should comment that to a certain extent our assignments must be regarded as tentative and should be verified with detailed computational studies (see ref 21). The reason for this is that in general the bound H_2 molecule may be subject to separate barriers to in-plane and out-of-plane rotation, whereas we have, for reasons of simplicity, chosen limiting cases in the analysis of our rather complex spectra.