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Zeolite-*like* Metal−Organic Frameworks (ZMOFs) as Hydrogen Storage Platform: Lithium and Magnesium Ion-Exchange and H_2-(*rho*-ZMOF) Interaction Studies

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Abstract: Zeolite-*like* metal−organic frameworks (ZMOFs) are anionic, have readily exchangeable extra-framework cations, and can be constructed with a variety of organic linkers. ZMOFs therefore can be regarded as an excellent platform for systematic studies of the effect(s) of various structural factors on H_2 binding/interaction with porous metal−organic materials. We find that the enhanced binding of molecular hydrogen in ion-exchanged ZMOFs with an anionic framework is largely governed by the presence of the electrostatic field in the cavity, which is reflected by isosteric heats of adsorption in these compounds which are greater by as much as 50% relative to those in neutral MOFs. Direct contact of the sorbed hydrogen with the exchangeable cations is shown not to be possible in the explored systems thus far, as they retain their form as aqua complexes.

Introduction

Hydrogen is widely recognized as a clean alternative fuel to address several serious, long-term energy related issues.[1] Nevertheless, several hurdles must be overcome for hydrogen to become of practical use as a fuel, especially those related to onboard H_2 storage. Two strategic pathways have been pursued to address the hydrogen storage challenges. On one hand, systems based on chemisorption offer very high gravimetric capacities but require relatively high temperatures for hydrogen desorption and suffer seriously from nonreversibility. Materials that utilize physisorption, on the other hand, offer reversibility but have a gravimetric uptake which to date is far less than that possible with chemisorption. Major current research efforts therefore are aimed at making physisorption based hydrogen storage practical.

Most of the recent work in the field of H_2 sorption has been dominated by the use of high surface area materials, such as carbons,[2] porous metal−organic frameworks (MOFs),[3] and other hybrid materials,[4] as well as a variety of light metal hydrides or other chemical hydrides.[5] Metal hydrides and chemical hydrides adsorb hydrogen by a chemisorption process (i.e., strong interaction; >50 kJ/mol) that is accompanied by dissociation of the dihydrogen molecules. However, facile reversibility, as well as unfavorable operating conditions, are problems in most of these cases, to the point where expensive and possibly impractical off-board regeneration of the storage medium has to be considered.[6]

Physisorption-based materials have a significant advantage over chemisorption-based storage media, because the adsorption/desorption kinetics are extremely facile (readily reversible) and preclude the need for chemical reactions or high temperatures to release the stored hydrogen gas.[7] Nevertheless, one shortcoming of these physisorption-based materials (including the vast majority of MOFs) stems from the fact that physisorption is, in fact, rather weak (i.e., ~5 kJ/mol);[8] that is, the fundamental interactions between hydrogen and most of the constituents

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10.1021/ja807229a CCC: $40.75

(carbon, etc.) are not sufficiently strong enough to store adequate amounts of molecular hydrogen. It therefore seems unlikely that, in their present form, these materials will meet the capacity, working pressure, and temperature targets set by the U.S. Department of Energy.[1]

Thus, there is clearly an urgent need to develop new classes of materials that have the potential to provide superior performance for hydrogen storage. The most attractive approach would seem to be materials that employ reversible molecular sorption of hydrogen with an interaction energy much greater than mere physisorption, but less than that of dissociative chemisorption. It has, in fact, been estimated that an ambient temperature, sorption-based storage system would require a host material with a binding energy for H_2 in the range 15−25 kJ/mol.[9]

Several key parameters have to be tuned to improve the binding energies of hydrogen by factors of 3−5 over that provided by simple physisorption and increase sorption at room temperature by about an order of magnitude. These include, most notably (1) availability of significant numbers of accessible open-metal binding sites; (2) tunability of organic links to contain more highly polarizable constituents without altering the overall framework structure; (3) the introduction of a strong electrostatic field in the cavity by having a charged framework, along with extra-framework cations (as in zeolites); and, finally, (4) a narrow range of pore sizes (∼1 nm), which would allow each H_2 molecule to interact with more atoms (i.e., surrounded) than on a simple surface.[10] All of these requirements must be accomplished while maintaining high surface area without an appreciable increase in framework density (necessary for high loading to maintain higher volumetric and gravimetric uptakes), which points toward lightweight constituents and substitutions.

To develop a practical porous material with the optimal combination of structural features for the required improvement in hydrogen binding energies, a platform is needed on which these aspects can be separately investigated. A newly introduced class of porous materials, zeolite-*like* metal−organic frameworks (ZMOFs), is anionic whereby tunable extra-framework H_2 sorption sites (i.e., cations) can readily be introduced. Neutral MOFs do not have this property as most of the large open space is not useful for H_2 sorption.[3b,4,11] ZMOFs, on the other hand, can be synthesized from a variety of organic linkers [e.g., 4,5-imidazoledicarboxylic acid (H_3ImDC) or 4,6-pyrimidinedicarboxylic acid][12] and can therefore be regarded as an excellent platform available for systematic studies of the effect(s) of various structural factors on H_2 binding/interaction with porous metal−organic materials.

The inclusion of electrostatic effects is important for improved hydrogen storage, as can be inferred from the increased H_2 binding energies in zeolites[13] with anionic framework and extra-framework cations, i.e., more than twice that observed in and on carbons.[14] Traditional zeolites are, however, not useful for this purpose because of their high density and difficulties with altering the framework to introduce functionalities.[15] In the case of ZMOFs, the oxygen linker (−Si−O−Si−) of regular zeolites is replaced by a larger organic molecule linker, which can also be functionalized in various ways.[12] Indeed, tunability of ZMOFs has already been introduced in our previous work, where successful cation-exchange on MOFs was reported using the original (indium-imidazoledicarboxylate)-based *rho*-ZMOF, $|(HPP^{2+})_{24}|[In_{48}(HImDC)_{96}]$ (HPP-*rho*-ZMOF), as the parent framework, where Na^+ ions replace the extra-framework organic cations, doubly protonated 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-a]pyrimidine (HPP), to give $|(Na^+)_{48}|[In_{48}(HImDC)_{96}]$ (Na-*rho*-ZMOF).[12e]

Here we present detailed and systematic thermodynamic, structural, and spectroscopic studies on the effect of the electrostatic field, as well as cation-exchange, on the binding of hydrogen in porous (In-HImDC)-based *rho*-ZMOF. In addition, we contrast our results with those of neutral MOFs and anionic zeolite frameworks, since our *rho*-ZMOF is, a MOF with an underlying zeolite-*like* topology, has an anionic framework, and exhibits facile ion-exchange capability in much the same way as zeolites. Our ion-exchange studies, in fact, indicate that the organic cations in the cavities can be fully exchanged at room temperature within 15 to 24 h (depending on the inorganic cation used), as shown by elemental microanalysis and atomic absorption studies.[12e] The fully exchanged compounds were found to retain their morphology and crystallinity (Figure S1), respectively, by optical microscopy and powder X-ray diffraction (PXRD) studies. Here, we report the effect of several extra-framework cations (dimethylammonium: DMA^+, Li^+, Mg^{2+}) on the H_2 sorption energetics and uptake.

The choice of lithium as a cation for this study was driven by its known high affinity for H_2,[16] as well as its interesting behavior in conventional inorganic zeolites,[17] where zeolite LiX is used in air separation. In addition, lithium cations are light and have a small ionic radius compared to most inorganic cations, which results in a reduced framework density and still

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maintains large enough voids for H_2 storage. The other cation of interest is magnesium, also because of its high affinity for H_2,[16] in addition to the fact that only half the number of divalent cations are needed to balance the framework charge. Magnesium is relatively similar in size to the monovalent lithium and therefore an excellent complementary cation for charge/space comparison studies of electrostatic effects on sorption energetics and uptake of H_2.

Experimental Details

Synthesis. To obtain the (In-ImDC)-based *rho*-ZMOF on a larger scale than previously reported,[12e] the original reaction conditions were slightly modified. 4,5-Imidazoledicarboxylic acid (H_3ImDC, 0.029 g, 0.174 mmol), $In(NO_3)_3 \cdot 2H_2O$ (0.030 g, 0.087 mmol), and *N,N′*-dimethylformamide (DMF, 4 mL) were added, respectively, to a 40-mL Parr acid digestion vessel, which was sealed and heated to 120 °C at a rate of 1 °C/min for 3 days and then cooled to room temperature at a rate of 1 °C/min. The colorless polyhedral crystals were collected and air-dried, yielding 0.043 g of DMA-*rho*-ZMOF {$|(DMA^+)_{48}|[In_{48}(HImDC)_{96}]$, Supporting InformationTable S1} [82% based on $In(NO_3)_3 \cdot 2H_2O$] where DMA represents the dimethylammonium extra-framework cations (generated in situ from degradation of DMF).

Ion-Exchange. Crystals of DMA-*rho*-ZMOF were washed several times with the mother liquor, then with a mixture of ethanol (EtOH) and water (0.75:0.25). The crystals were then soaked in a solution containing $NaNO_3$ [1 M in EtOH/water (0.75:0.25)] and washed as described in our original ZMOF communication[12e] (to replace all 48 DMA cations with Na^+). Then, the Na^+-exchanged compound was soaked in a solution containing $LiNO_3$ [1 M in EtOH/water (0.75:0.25)]. The crystals were then washed several times with an EtOH/water (0.75:0.25) solution to remove excess salt, and incorporation of Li^+ ions was followed by atomic absorption (AA) experiments. After 18 h, all 48 Na^+ ions were completely exchanged with the Li^+ ions, as proven by the absence of any residual Na^+, to give Li-*rho*-ZMOF. In the case of the Mg^{2+}-exchanged compound, crystals of DMA-*rho*-ZMOF were washed several times with the mother liquor and then with EtOH/water (0.75:0.25). The crystals were then soaked in a solution containing $Mg(NO_3)_2$ [0.75 M in EtOH/water (0.75:0.25)] and washed to remove excess salt. The incorporation of Mg^{2+} ions was followed by atomic absorption experiments, and after 15 h, all 48 DMA cations were completely exchanged [AA: Mg/In ratio (calculated) = 0.5; Mg/In ratio (found) = 0.49] to give Mg-*rho*-ZMOF.

Hydrogen Sorption. Samples of DMA-*rho*-ZMOF, Mg-*rho*-ZMOF, and Li-*rho*-ZMOF were activated by soaking the crystals in CH_3CN for 12 h. Approximately 45 mg of each activated sample was placed in a glass sample cell and evacuated at room temperature for 12 h and then at 115 °C for 6 h. All sorption experiments were performed on a Quantachrome Autosorb-1.

Inelastic Neutron Scattering (INS). Fresh samples were placed in a minimal amount of CH_3CN, sealed (to prevent evaporation of the solvent), and shipped to the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory (ANL). The samples were air-dried on-site at the IPNS facility and subsequently evacuated at room temperature followed by evacuation at 115 °C in a vacuum tube furnace according to the sorption protocol. Each guest-free (blank) sample was transferred (under He atmosphere) to a separate aluminum sample container, sealed under He, and connected to an external gas dosing system on the spectrometer. INS spectra for each sample were collected on the Quasi Elastic Neutron Spectrometer (QENS) at IPNS mostly in neutron energy loss. After obtaining a spectrum of "blank" sample (no H_2), H_2 was adsorbed *in situ* at various loadings with the sample at approximately 78 K and equilibrated before cooling to the data collection temperature of approximately 15 K.

Peaks in the INS spectra were assigned on the basis of the same phenomenological model previously used by us,[10a] namely that of a hindered rotor with 2 angular degrees of freedom in a simple double-minimum potential.[18] In the absence of a barrier to rotation, the lowest transition is that between para- and ortho-H_2, and it occurs at 14.7 meV (or 119 cm^{-1} = 2B). The interaction of the sorbed hydrogen molecule with the host material gives rise to a barrier to rotation, which, in turn, partially lifts the degeneracy of the $J = 1$ level. The lowest transition frequency for the hindered rotor (between the $J = 0$ and the $J = 1$, $mJ = \pm 1$ states, which we subsequently refer to as the "0−1" transition) decreases approximately exponentially with increasing barrier height (rotational tunnel splitting), and it is thereby extraordinarily sensitive to small differences in barrier height.

Single-Crystal X-ray Diffraction. Data of Mg-*rho*-ZMOF were collected at the Small Molecule Crystallography beamline (11.3.1) at the Advanced Light Source (Berkeley, CA). A data collection strategy was specifically designed to provide high quality data for weak, high scattering vector reflections. One scan for strongly diffracting, low scattering vector reflections was collected using 1 s. The 2θ angle was changed to collect only higher scattering vectors, and 7 s scans were used to collect a full hemisphere of data. Peaks out to 0.75 $Å^{-1}$ were used for the final refinement.

Results and Discussion

Reaction of H_3ImDC and $In(NO_3)_3 \cdot 2H_2O$ in DMF yields a homogeneous microcrystalline material (referred to as DMA-*rho*-ZMOF). The DMA-*rho*-ZMOF crystals are insoluble in water and common organic solvents. The identity and purity of the compound were confirmed by similarities between the experimental X-ray powder diffraction (XRPD) spectra of HPP-*rho*-ZMOF (original synthesis protocol[12e]) and DMA-*rho*-ZMOF (new protocol); see Figure S1. Single-crystal X-ray diffraction studies confirmed the framework structure and corresponding unit cell parameters; however, the extra-framework organic cations and their locations could not be determined on account of the large volume of the cavities and large number of guest molecules.

The DMA-*rho*-ZMOF unit cell contains 48 indium metal ions and 96 ligands to give an overall framework formula of $[In_{48}(HImDC)_{96}]^{48-}$ as in the original HPP-*rho*-ZMOF. Here, the negatively charged framework is neutralized by 48 protonated dimethylamine molecules (dimethylammonium cations, DMA). For large-scale synthesis of *rho*-ZMOF, it was necessary to modify the reaction conditions to exclude HPP cations. The DMA molecules are generated *in situ* by the decomposition of DMF solvent molecules. DMA-*rho*-ZMOF was used for the ion-exchange of DMA with sodium, lithium, or magnesium cations.

Single-crystal X-ray diffraction studies were also performed on Mg-*rho*-ZMOF on the microcrystal diffraction beamline 11.3.1 at the Advanced Light Source to determine the locations of the extra-framework cations. The Mg(II) cation was located as the strongest peak in the Fourier map in the solution of the framework structure by direct methods and least-squares refinement. Three crystallographically unique oxygen atoms were subsequently located which formed an octahedron around the Mg(II) cation. These oxygen atoms refined to chemically reasonable positions without any constraints other than the symmetry imposed by the space group. Hydrogen atoms on the aqua ligands could not be reliably extracted from the Fourier map and were not included in the final model.

Inspection of the displacement parameters suggests either the presence of considerable disorder or partial occupancy of the

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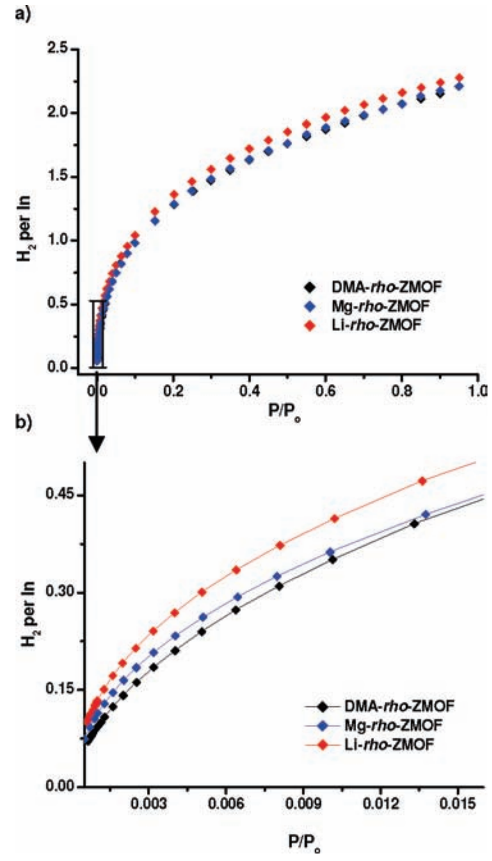

Figure 1. (a) H_2 adsorption isotherms for DMA-, Mg-, and Li-*rho*-ZMOF at 78 K. (b) An enlarged view of the low pressure range in (a).

Table 1. Sorption Data for DMA-*rho*-ZMOF, Mg-*rho*-ZMOF, and Li-*rho*-ZMOF

material	H_2 wt%[a]	H_2 per In[a]	heat of adsorption (kJ/mol)
DMA-*rho*-ZMOF	0.95	2.21	8.0
Mg-*rho*-ZMOF	0.91	2.21	9.0
Li-*rho*-ZMOF	0.91	2.28	9.1

[a] At 0.95 atm and 78 K.

cation site. Positional disorder is consistent with the long 2.9665 Å O...O hydrogen bonding distance between the aqua ligand and the free carboxylate oxygen atom. It is likely that the cation prefers a site with one shorter hydrogen bond, but disorder and symmetry constraints lead to a model containing an averaged superposition for multiple possible geometries, with correspondingly large anisotropic displacement parameters. Positional disorder is further favored by the lack of any peaks consistent with a Mg(II) cation elsewhere in the structure.

Hydrogen Adsorption. H_2 adsorption isotherms were recorded after complete evacuation at 115 °C of the fully exchanged [with CH_3CN] materials (Figure 1a). Hydrogen loadings are reported in terms of H_2/In to directly compare the three materials on a structural basis, as well as directly correlate the isotherms to the loading dependence of the INS spectra. For example, a loading of 1 H_2/In corresponds to 0.40, 0.41, and 0.43 wt % for Li-, Mg- and DMA-*rho*-ZMOF, respectively. Gravimetric capacities and other sorption related properties for the three materials are given in Table 1.

The Li^+-exchanged material, Li-*rho*-ZMOF, can store slightly more H_2 molecules per indium at 1 atm than both Mg-*rho*-ZMOF and the parent DMA-*rho*-ZMOF framework, namely 2.28, 2.21, 2.21 molecules, respectively. We note that recent studies on lithium ion-exchange in other MOFs have shown that the effect on the overall hydrogen storage capacity was not significant,[19a] and enhanced H_2 uptake via framework reduction and doping with Li^0/Li^+ has been largely attributed to displacement of interpenetrated frameworks.[19b,c] It is also worth mentioning that, in a more recent paper, a higher H_2 gravimetric capacity was recorded for a Li^+-exchange *pts*-like MOF compared to the parent framework, but was attributed to an increase of the accessible pore volume on the Li^+-exchanged compound.[19d]

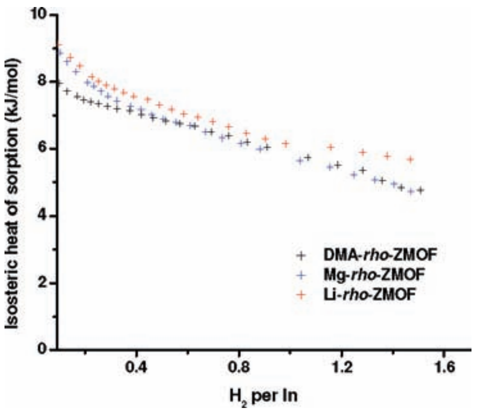

Figure 2. Isosteric heats of adsorption for Li-, Mg-, and DMA-*rho*-ZMOF calculated from the corresponding isotherms at 78 and 87 K.

At pressures below 0.02 atm (Figure 1b), we find that the Li-*rho*-ZMOF and Mg-*rho*-ZMOF isotherms appear to have a steeper rise than the isotherm of the parent compound. This is in accord with the isosteric heats of adsorption (Figure 2) derived from the isotherms (H_2 sorption isotherms were also recorded at 87 K for calculation of the isosteric heats of adsorption), where Li-*rho*-ZMOF and Mg-*rho*-ZMOF exhibit higher values (9.1 and 9.0 kJ/mol, respectively) at low loading than the parent compound (8.0 kJ/mol). It is important to note that the slightly higher value for Li-*rho*-ZMOF is in contrast to results observed in previous Li^+-exchanged MOFs, which show no evidence for strong H_2−Li^+ interaction(s).[19] In addition, the values for all three compounds are considerably higher than those observed in most neutral MOFs (no open metal sites, typically 5−6 kJ/mol)[8,20] and comparable to some neutral MOFs with open metal sites.[21] These high values associated with the *rho*-ZMOFs must primarily be the result of having a charged framework along with the compensating cations. A similar comparison may be made between H_2 adsorbed in zeolites and on various (neutral) carbons, where the isosteric heat of adsorption is up to 50% higher in the former depending on the extra-framework cation.[14]

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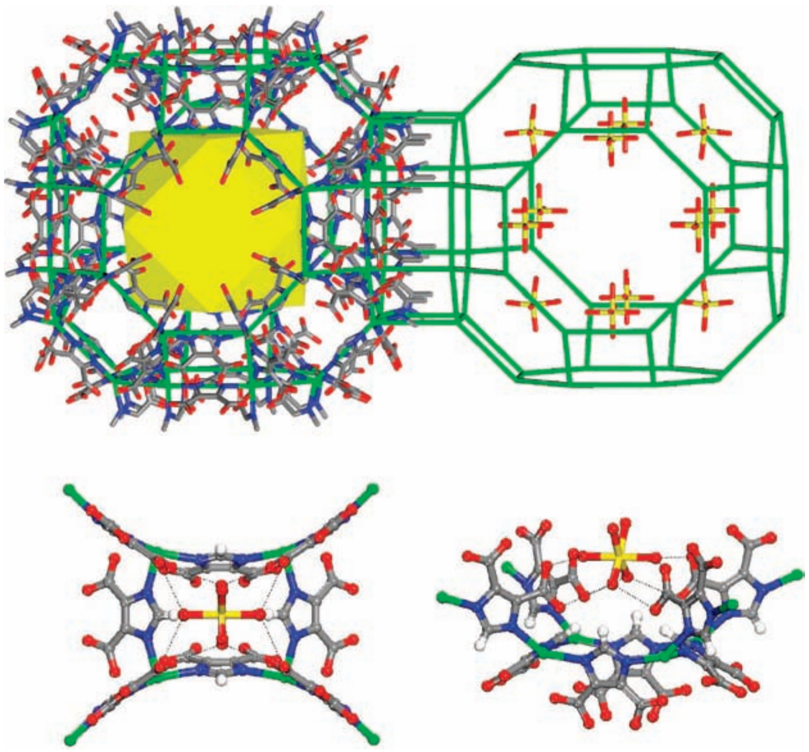

Figure 3. Top: A fragment of the single-crystal structure of Mg-*rho*-ZMOF showing the α-cages (green) and the cubohemioctahedral arrangement (shown as a yellow polyhedron) of the 12 $[Mg(H_2O)_6]^{2+}$ per cage. All H atoms have been omitted for clarity. Bottom: Hexaaqua magnesium complex is situated near each of the 12 four-membered rings of each α-cage, interacting with the framework through hydrogen bonds (shown as black dotted lines; oxygen to oxygen distance is ~2.9 Å) with four of the aqua ligands. Intra-cubohemioctahedron Mg...Mg and Mg...center of cubohemioctahedron distances are equidistant, 9.451 Å; Mg...In (from the closest four-membered ring) is 6.532 Å.

The similarity of the adsorption isotherms of the three materials strongly suggests that the extra-framework metal cations may not be directly accessible for binding the adsorbed hydrogen molecules, since much larger differences between the ion exchanged *rho*-ZMOF (Li^+ or Mg^{2+}) and the parent compound would be expected. To obtain direct structural information on the location of the extra-framework metal cations, and consequently their accessibility, we obtained additional single-crystal X-ray diffraction data on Mg-*rho*-ZMOF. The studies reveal the expected anionic (In-HImDC)-based *rho-like* framework with charge-balancing, extra-framework Mg^{2+} cations.

However, each magnesium cation was found to be in the form of a hexaaqua complex, $[Mg(H_2O)_6]^{2+}$, in Mg-*rho*-ZMOF, $|\{[Mg(H_2O)_6]^{2+}\}_{24}|[In_{48}(HImDC)_{96}]$. Each hexaaqua complex is bound to the framework by the formation of HOH...OOCR hydrogen bonds (O...O distance of ~2.9 Å, well within the expected range for such interactions) between four of the six aqua ligands (avg. O...Mg distance of 1.9 Å) and carboxylate oxygen atoms of the framework (Figure 3). The two remaining aqua ligands with longer O...Mg distances of 2.2 Å (i.e., weaker interactions), in principle, could be removed to create open-metal binding sites on the extra-framework cation.[22] However, even at the highest temperature used for activation of this material (115 °C), we do not observe removal of any aqua ligands (heating beyond this temperature results in progressive degradation of the framework, see Figure S2). This can be expected, since water molecules coordinated to extra-framework cations in ion-exchanged zeolites normally require temperatures well above 300 °C for removal.[22] We may consequently assume that the Li^+ cation in Li-*rho*-ZMOF also is fully coordinated with aqua ligands, most likely in a tetrahedral geometry (tetraaqua lithium complex),[23] so that the adsorbed H_2 molecules can not, in either case (Mg^{2+} or Li^+), interact directly with the extra-framework cations, but most likely with the H atoms on the coordinated water molecules. The similarity of the adsorption properties of the three materials can thereby readily be accounted for. This, in turn, leads to the conclusion that the enhanced isosteric heats of adsorption for these materials may largely be attributed to the presence of the electrostatic field in the cavity from the charged framework and counterions, and not from a direct interaction with the cations. The fact that the isosteric heats of adsorption for H_2 are highest in the ion-exchanged *rho*-ZMOFs for most of the range of loadings is likely a reflection of a higher electrostatic field in the cavities because of the large charge/size ratio of the Mg^{2+} and Li^+ cations. This hypothesis is supported by the fact that the Li-*rho*-ZMOF isosteric heats of adsorption value is higher than Mg-*rho*-ZMOF, as there is a higher concentration of Li^+ cations per unit cell (i.e., larger distribution of the electrostatic field).

Inelastic Neutron Scattering. Some molecular-level details on binding sites for hydrogen in the reported compounds can be obtained from the INS spectra of the hindered rotations of adsorbed H_2. The INS spectra (Figure 4) of hydrogen adsorbed at various loadings in Li-, Mg-, and DMA-*rho*-ZMOF exhibit a great deal of similarity, as one might expect given their respective thermodynamic adsorption properties of hydrogen described above. All spectra show some reasonably well-defined, but broad, peaks that can be tentatively assigned using the model

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(22) Davis, M. E. *Nature* **2002**, *417*, 813–821.

(23) CSD-Li: Of the 42 aqua lithium species in the CSD (January 2008), 28 are tetrahedral tetraaqua lithium.

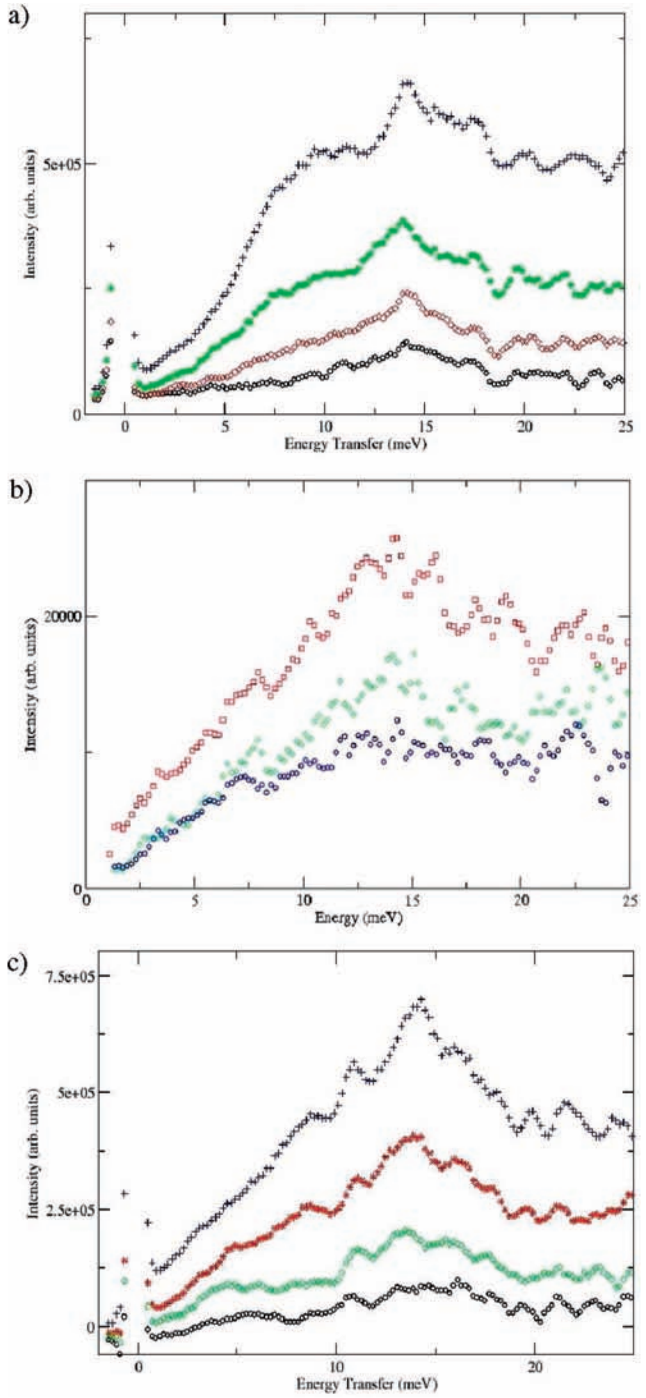

Figure 4. (a) INS spectra of Li-*rho*-ZMOF at 0.5, 1, 2, and 4 H_2 per In. (b) INS spectra of Mg-*rho*-ZMOF at 0.25, 0.5, 1 H_2 per In (minus blank). (c) INS spectra of DMA-*rho*-ZMOF at 0.5, 1, 1.5, and 3 H_2 per In.

for the hindered rotations of bound H_2 that we have previously used (Table S7). The spectra do, in addition, exhibit a great deal of very broad intensity underneath that must arise from a wide distribution of nonspecific binding sites.

At the lowest loading each of these compounds appears to have at least four reasonably well-defined binding sites for H_2 in addition to the broad, near-continuum underneath.

In the case of Li-*rho*-ZMOF, we may make some inferences based on the INS spectra and structural information gained from similar studies on Li^+-exchanged zeolites.[24] The enhanced affinity of zeolites for hydrogen relative to that of neutral hosts such as carbons has its origin in the presence of an electrostatic field in the cavity arising from the charged framework, as well as in the direct contact of the sorbed H_2 with some of the extra-framework cations. The following comparison with H_2 in the well characterized Li-exchanged zeolites will serve to attribute the enhanced H_2 binding in the *rho*-ZMOF's to one or both of these factors.

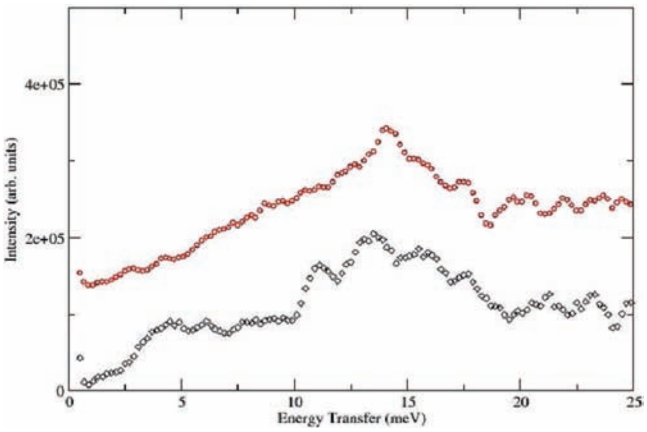

Figure 5. INS spectra of Li-*rho*-ZMOF (red) and DMA-*rho*-ZMOF (black) at a loading of 1 H_2/In.

Studies of H_2 sorbed on LiX (Li^+-exchanged zeolite FAU) and LiA (Li^+-exchanged zeolite LTA) reveal multiple binding sites due to the presence of various "types" of extra-framework Li^+ ions based on their location in the framework cavities. For H_2 sorbed at Li^+ sites in the six-membered ring windows of LiX (type II) or LiA (type I), the rotational transitions occur in a broad band around 7.5 meV, whereas for the type III cation in LiX a sharp transition is observed at 1 meV. The Li^+ cation in the six-membered ring site in these zeolites is likely to be partially blocked by the framework oxygen atoms in the surrounding ring, which reduces the accessibility of the cation to H_2 and thereby leads to more interaction(s) with the surrounding O atoms. The cation in the type III site, on the other hand, is highly under-coordinated and, hence, provides a strong binding site for H_2. The absence of a strong peak at very low energies in the Li-*rho*-ZMOF INS spectra, in turn, suggests that those cations are not directly accessible to H_2. This conclusion is, by analogy, in accord with our finding for the Mg^{2+}-exchanged compound, namely that the cation may be taken to exist in the form of an aqua complex. H_2 sorbed near the Li^+ cation can therefore only interact with the coordinated water molecules of the tetraqua complex and, hence, have rotational transitions closer to those associated with the six-membered ring site in zeolites in the range of 6 to 10 meV, which is indeed the case.

A side-by-side comparison of the INS spectra for a loading of one H_2 molecule per formula unit (Figure 5) of Li-*rho*-ZMOF and the parent material shows that, in the case of Li-*rho*-ZMOF, there is an additional, rather broad, intensity in the region between ~6 and 10 meV. It is in this frequency range that transitions for H_2 sorbed at Li^+ located in the six-ring window

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(24) (a) Eckert, J.; Trouw, F. R.; Mojet, B.; Forster, P.; Lobo, R. *J. Nanosci. Nanotechnol.* **2008** (in press). (b) Eckert, J; Trouw, F; Bug, A. L. R.; Lobo, R. *Proceedings of the 12th International Zeolite Conference*; Materials Research Society: Boston, 1999; Vol. 1, pp 119−125.

of LiA and LiX are observed. It is therefore apparent that the weight of the INS spectrum of H_2 in Li-*rho*- ZMOF is shifted to lower frequency (i.e., stronger H_2/host interactions) around the Li^+−water complex; this persists at higher loadings (Figure 4) as well. We only speculate at this point as to the reason for the slightly stronger interaction of H_2 in Li-*rho*-ZMOF, which may lie in the more open tetrahedral coordination geometry of Li^+ versus the octahedral geometry of Mg^{2+}, as well as the potentially higher electrostatic field in the cavity due to the presence of a greater number of such binding sites (higher concentration of Li ions). A qualitative comparison of the INS spectra of H_2 in Mg-*rho*-ZMOF with DMA-*rho*-ZMOF, on the other hand, shows these to be rather similar, except at the lowest loading (0.5 H_2/In). Here again, there seems to be somewhat greater weight in the spectrum for Mg-*rho*-ZMOF at frequencies below 10 meV, which indicates the presence of some stronger binding sites.

This observation is qualitatively in accord with our result that the isosteric heat of adsorption for H_2 in Mg-*rho*-ZMOF is greater than that in DMA-*rho*-ZMOF at low loadings, but similar at higher loadings, where the strongest peaks in the INS spectrum occur in the range above 10 meV. This may be compared with studies of H_2 adsorption on the (100) surface of MgO,[25] in which a well-defined peak at 11 meV for the surface layer of H_2 was attributed to the molecule being located over a Mg position surrounded by an intervening layer of oxygen atoms. With values below 10 meV at low loadings, sorption of H_2 in Mg-*rho*-ZMOF may therefore be concluded to be stronger than that on the surface of MgO or in DMA-*rho*-ZMOF, which may, again, be attributable to electrostatic effects.

Conclusion

The present study on the binding of molecular hydrogen in ion-exchanged ZMOFs with anionic frameworks clearly demonstrates that the presence of an electrostatic field in the cavity is largely responsible for the observed improvement in the isosteric heats of adsorption in these compounds by as much as 50% relative to those in neutral MOFs. This conclusion is based on the fact that the extra-framework cations are fully coordinated by aqua ligands and, hence, are not directly accessible to the H_2 molecules. Thus, open-metal sites do not contribute to the increased binding energies, unlike the case of some zeolites where under-coordinated extra-framework cations can provide exceptionally strong binding sites. This result may be viewed as the first of several steps toward improving binding energies to values around 20 kJ/mol. ZMOFs offer great potential for reaching this goal by tuning the accessible extra-framework cations and/or introducing open-metal sites, along with a reduction in pore size and functionalization on the organic links. All these factors will be assessed by modifications introduced into the platform provided by ZMOFs.

Future directions to be taken in this research will involve substituted and functionalized organic linkers and modifications to create considerable numbers of open-metal sites in these materials. We furthermore intend to study the potential effects of extra-framework cation ligand exchange [e.g., substitute phosphines (or more polarizable ligands) for H_2O in the hexaaqua magnesium complex] on hydrogen uptake. We expect that the combination of these approaches, along with the aid of computational studies, will permit the synthesis of a material with a high hydrogen storage capacity and with enhanced sorption energetic, and will point toward a suitable synthetic route for constructing a physisorption-based porous material with H_2 binding energies in the range of 20 kJ/mol.

Acknowledgment. We gratefully acknowledge the financial support of the DOE-BES (DE0FG02-07ER4670), NSF (Grant DMR 0548117). This work has benefited from the use of facilities at the Intense Pulsed Neutron Source, a national user facility funded as such by the Office of Science, U.S. Department of Energy. The authors also thank Simon J. Teat for experimental assistance on the ALS microcrystal diffraction beamline 11.3.1. The Advanced Light Source is supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Supporting Information Available: PXRD spectra, TGA spectra, elemental analyses, and single-crystal X-ray crystallography data. This material is available free of charge via the Internet at http://pubs.acs.org.

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