

## Hydrogen Adsorption in Nanoporous Nickel(II) Phosphates

Paul M. Forster,<sup>†</sup> Juergen Eckert,<sup>†,‡</sup> Jong-San Chang,<sup>§</sup> Sang-Eon Park,<sup>\*,§</sup>  
G rard F rey,<sup>||</sup> and Anthony K. Cheetham<sup>\*,†</sup>

*Contribution from the Materials Research Laboratory, University of California, Santa Barbara, California 93106, LANSCE, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, Korea Research Institute of Chemical Technology, P.O. Box 107, Yusung, Taejon 305-600, Korea, and Institut Lavoisier, UMR CNRS 173, Universit  de Versailles Saint Quentin, 45 avenue des Etats-Unis, 78035 Versailles Cedex, France*

Received August 29, 2002; E-mail: rk@pado.krikt.re.kr; cheetham@mrl.ucsb.edu

**Abstract:** Hydrogen sorption in the nanoporous nickel phosphates VSB-1 and VSB-5 has been studied with a combination of BET, temperature programmed desorption (TPD), and inelastic neutron scattering (INS) measurements. H<sub>2</sub> BET isotherms for VSB-1 are similar to those seen in nanoporous zeolites, while VSB-5 adsorbs substantially more hydrogen due to a steep initial uptake at low partial pressures. TPD data show that hydrogen interacts strongly with VSB-5, with desorption peaks at 109 and 149 K in a nitrogen flow, whereas the absence of similar peaks for VSB-1 suggests a weaker interaction. INS spectra of the rotational tunnel transition of the adsorbed H<sub>2</sub> also reveal a strong interaction with the VSB-5 host. These data strongly suggest the existence of coordinatively unsaturated Ni<sup>2+</sup> sites accessible to H<sub>2</sub> molecules in the pores of VSB-5.

### Introduction

Research involving open-framework transition metal phosphates has steadily increased following the discovery of AlPOs, primarily on the basis of the possibility of preparing porous materials with novel properties not seen in traditional aluminosilicate zeolites. Particularly promising are transition metal phosphates, where novel catalytic, spectroscopic, magnetic, and electronic properties are possible. While a host of such structures have been characterized,<sup>1</sup> the nickel phosphates VSB-1<sup>2</sup> and VSB-5<sup>3</sup> are rare in exhibiting genuine zeolitic properties such as high BET surface areas, ion exchange, and shape-selective catalysis. As illustrated in Figure 1, both structures are based on 3D networks of octahedrally coordinated nickel atoms containing large, unidimensional channels. An important difference between the materials lies in the nature of the channels themselves. HPO<sub>4</sub> groups and extraframework cations (NH<sub>4</sub><sup>+</sup> or K<sup>+</sup>) line the channels in VSB-1, while the surface of VSB-5 consists of HPO<sub>4</sub>, PO<sub>4</sub>, and water molecules bound directly to octahedrally coordinated Ni<sup>2+</sup>. Catalytic results on selective hydrogenation of olefin,<sup>3</sup> as well as characterization of a modified form of VSB-5 produced by high-temperature H<sub>2</sub> reduction, strongly suggest that the water molecule bound to a Ni<sup>2+</sup> in the cavity is at least partially removed during calcination.

Molecular hydrogen has been shown<sup>4–7</sup> to be a unique and versatile probe of adsorption sites in porous materials. Its small size permits it to access most of the channels and cavities in a material; it is weakly interacting and hence does not appreciably perturb the host upon adsorption and can be observed with a high degree of sensitivity by spectroscopic methods. The latter is particularly true for INS spectroscopy of the hindered rotational transition of the adsorbed H<sub>2</sub> molecule because of the very large neutron scattering cross-section of H when compared to those of the host atoms and the fact that this transition occurs at low frequencies relative to that of the host framework vibrational modes. An alternative method<sup>4,8</sup> uses DRIFT to observe changes in the H–H stretching mode upon adsorption, but these changes are rather small when compared to the very large effect of the guest–host interactions on the molecular reorientation of the adsorbate. Here, we present a study of hydrogen in VSB-1 and VSB-5 using a combination of H<sub>2</sub> adsorption isotherms, INS spectroscopy, and TPD.

### Experimental Section

VSB-1 and -5 were synthesized as described previously.<sup>2,3</sup> Reduced VSB-5 was prepared by heating a sample to 623 K under 5% H<sub>2</sub> in He for 16 h. Deuterated samples were prepared using phosphorus pentoxide, deuterium oxide, and anhydrous nickel chloride in otherwise similar

<sup>†</sup> University of California.

<sup>‡</sup> Los Alamos National Laboratory.

<sup>§</sup> Korea Research Institute of Chemical Technology.

<sup>||</sup> Institut Lavoisier.

- (1) Cheetham, A. K.; F rey, G.; Loiseau, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268.
- (2) Guillou, N.; Gao, Q. M.; Noguez, M.; Morris, R. E.; Hervieu, M.; F rey, G.; Cheetham A. K. *C. R. Acad. Sci. Paris* **1999**, *2*, 387.
- (3) Guillou, N.; Gao, Q. M.; Forster, P. M.; Chang, J. S.; Park, S. E.; F rey, G.; Cheetham, A. K. *Angew. Chem., Int. Ed.* **2001**, *40*, 2831.

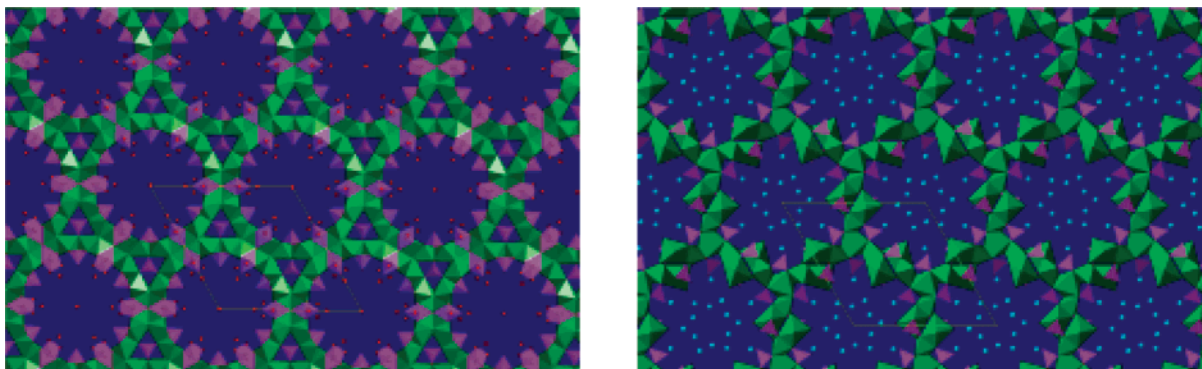
(4) Zecchina, A.; Otero-Arean, C. *Chem. Soc. Rev.* **1996**, *25*, 187.

(5) MacKinnon, J. A.; Eckert, J.; Coker, D. F.; Bug, A. L. *R. J. Chem. Phys.* **2001**, *114*, 10137.

(6) Eckert, J.; Nicol, J. M.; Howard, J.; Trouw, F. R. *J. Phys. Chem.* **1996**, *100*, 10646.

(7) Anderson, C.-R.; Coker, D. F.; Eckert, J.; Bug, A. L. *R. J. Chem. Phys.* **1999**, *111*, 7599.

(8) Kazansky, V. B.; Borokov, V. Yu.; Karge, H. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1843.



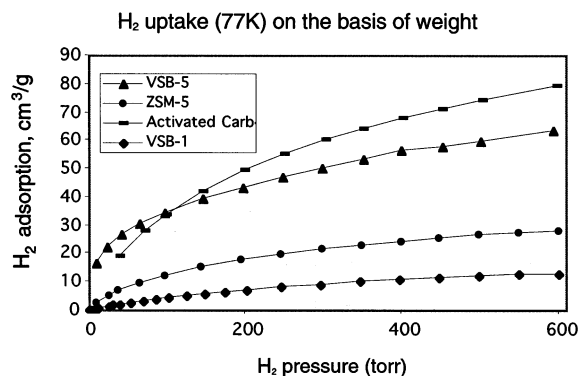
**Figure 1.** Representations of VSB-1 (a) and -5 (b) viewed down the  $c$  axis, with octahedral nickel represented in green and tetrahedral phosphorus represented in purple. Disorder is omitted for clarity.

reactions. In all cases, samples were calcined under vacuum overnight using a tube furnace and handled under vacuum or inert atmosphere to prevent rehydration. H-ZSM-5 zeolite (BET surface area  $428 \text{ m}^2/\text{g}$ ,  $\text{Si}/\text{Al} = 15$ ) was obtained from the PQ Corp. Activated carbon (BET surface area  $1050 \text{ m}^2/\text{g}$ ), manufactured by Darco, was obtained from Aldrich. Hydrogen adsorption experiments at 77 K were performed in a static vacuum volumetric apparatus (Micromeritics ASAP 2000C) with stainless steel tubing and all-metal greaseless valves. Before  $\text{H}_2$  adsorption, the sample was initially dehydrated at 623 K for 2 h under vacuum. The adsorption pressure was chosen in the range from 10 to 700 Torr. INS spectra were collected using the QENS instrument at the Intense Pulsed Neutron Source of Argonne National Laboratory on dehydrated samples sealed in Al cans, which were loaded in situ at 100 K with the desired number of  $\text{H}_2$  molecules per Ni site from an external gas-handling system. QENS is an inverse-geometry INS spectrometer in which the energy of the scattered neutrons reaching the detector is fixed by diffraction from graphite analyzer crystals and the incident neutron energies determined by the time-of-flight of the neutrons. Most of the INS spectrum from QENS is thereby collected by energy loss of the incident neutrons.

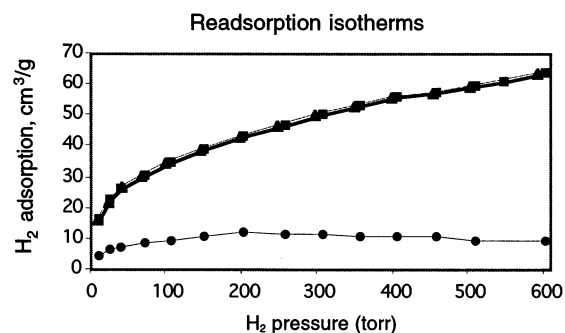
TPD experiments were carried out in a fixed-bed tubular reaction system equipped with a specially designed heater for control between 77 and 373 K and a thermal conductivity detector. Typically, 100 mg of the sample was loaded into the glass reactor. It was first dehydrated in a  $\text{N}_2$  stream (50 mL/min) at 623 K for 1 h. The temperature of the reactor was then adjusted to the adsorption temperature (83 K) under flowing nitrogen. A 20%  $\text{H}_2$ /80%  $\text{N}_2$  mixture was introduced into the reactor for 10 min. After the hydrogen adsorption, 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 85 to 303 K.

## Results and Discussion

Figure 2 compares the relative  $\text{H}_2$  adsorption capacities of VSB-1 and VSB-5 at 77 K with those of an aluminosilicate zeolite hydrogen sorbent (ZSM-5) and an activated carbon. ZSM-5 was selected as a control compound because it displayed the highest  $\text{H}_2$  uptake for zeolites in a recent survey.<sup>9</sup> Adsorption measurements for these porous materials reveal two important differences between VSB-5 and other materials. First, VSB-5 exhibits a capacity for  $\text{H}_2$  sorption (on a per-weight basis) that is approximately 5 times higher than that of VSB-1, twice that of ZSM-5, and similar to that of the activated carbon. Moreover, the slope of the adsorption curve is dramatically different at low pressures for VSB-5 than for the other materials studied, suggesting a different sorption mechanism in VSB-5. VSB-1, ZSM-5, and the porous carbon show the typical physisorption



**Figure 2.** Hydrogen uptake for several microporous sorbents.

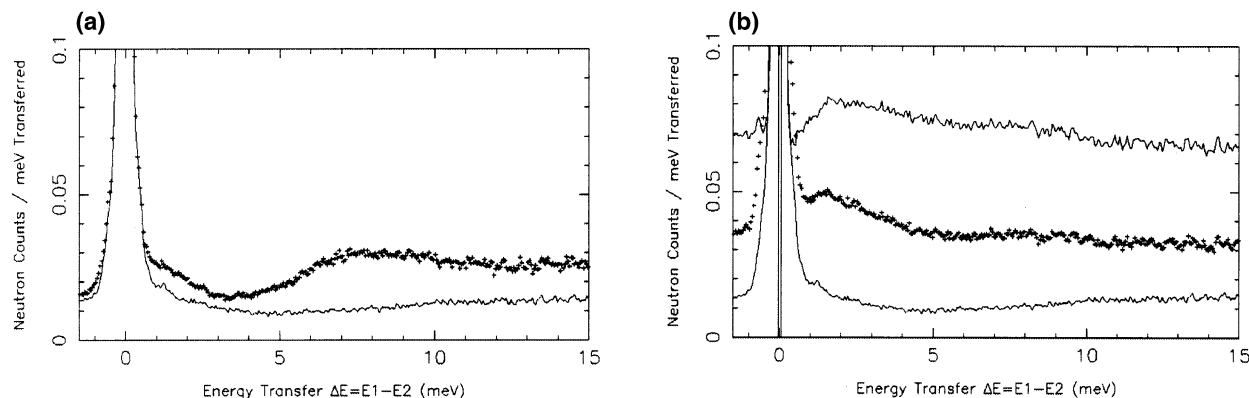


**Figure 3.**  $\text{H}_2$  adsorption isotherms for VSB-5 at 77 K: initial adsorption ( $\blacktriangle$ ) and re-adsorption after desorption at room temperature ( $\blacksquare$ ) and after desorption at 77 K ( $\bullet$ ).

behavior of a nanoporous material, while VSB-5 appears to strongly interact with  $\text{H}_2$  at low loadings and then continues to adsorb additional  $\text{H}_2$  through weaker physisorption as the pressure is increased. This is not a pore size effect because the channels in VSB-5 are comparable in size to those of VSB-1 and larger than in ZSM-5 and the porous carbon studied. An adsorption isotherm for VSB-5 (Figure 3) collected after evacuating a loaded sample at 77 K shows a dramatic decrease in capacity, suggesting that a portion of the hydrogen remains in the channel after evacuation under these conditions. None of the other materials studied exhibits such hysteresis. The capacity can be completely restored by warming the sample to room temperature.

Because the unusual  $\text{H}_2$  adsorption curves for VSB-5 suggest a different mechanism from the simple physisorption seen in zeolites, we collected INS spectra of the rotational tunneling transition of the adsorbed  $\text{H}_2$  for several samples using the

(9) Weitkamp, J.; Fritz, M.; Ernst, S. *Int. J. Hydrogen Energy* **1995**, *20*, 967.



**Figure 4.** INS spectra obtained on the QENS spectrometer of IPNS at  $T = 10$  K: (a) dehydrated VSB-1 (bottom) and with 3  $\text{H}_2$  per formula unit (top) adsorbed; and (b) dehydrated VSB-5 (bottom), and with one  $\text{H}_2$  molecule (middle) and 3  $\text{H}_2$  (top) adsorbed per formula unit. Spectra are offset in part b.

QENS instrument at the Intense Pulsed Neutron Source at Argonne National Laboratory. Rotational tunneling spectroscopy by inelastic neutron scattering is a powerful method for the direct study of the interaction between the adsorbed  $\text{H}_2$  and sorbents, including porous materials such as zeolites<sup>5–7</sup> and carbon nanotubes.<sup>10,11</sup> The rotational tunneling transition for the hindered rotor is the equivalent of the ortho–para transition<sup>12</sup> observed at 14.8 meV for free  $\text{H}_2$ . A barrier to rotation for the adsorbed molecule arises from its interaction with the chemical environment and results in a strong decrease of this transition frequency. This rotational tunnel splitting varies approximately exponentially with barrier height, thereby giving the method its great sensitivity.<sup>13,14</sup> Moreover, the large inelastic scattering cross-section of  $^1\text{H}$  ensures that these spectra are nearly free of interference by other elements.

Deuterated forms of VSB-1 and VSB-5 were used to improve the signal, lower the background, and minimize the chances that framework hydrogen phosphate or hydroxide modes would interfere with the measurement. Long background scans, collected on all samples tested, revealed no detectable interferences. INS spectra collected on  $\text{H}_2$  in VSB-1 (Figure 4a) show a very broad intensity distribution between 5 and 12 meV, which we attribute to hydrogen molecules that are physisorbed on a distribution of sites on the basis of our extensive studies<sup>5–7</sup> with zeolite hosts and related work with weakly binding hosts such as Vycor glass.<sup>15</sup> Spectra were collected on VSB-5 at several levels of loading. At the lowest loading (approximately 1  $\text{H}_2$  per unit cell), a moderately sharp peak appears at 1.5 meV (Figure 4b). This energy is appreciably lower than typical rotational tunneling energies observed for physisorbed  $\text{H}_2$  adsorbed at cations in zeolites (including, for example,  $\text{Co}^{2+}$  in  $\text{CoNaA}$ <sup>16</sup>) and suggests a stronger overall interaction. In fact, the rotational tunneling transitions for dihydrogen ligands in transition metal complexes, where  $\text{H}_2$  is chemically bound to the metal center, are usually observed at considerably lower frequencies than those for physisorbed  $\text{H}_2$ . However, no stable nickel dihydrogen complex has, to our knowledge, been reported

to date. This represents the first report of rotational tunneling for hydrogen bound at a  $\text{Ni}^{2+}$  site, and the relatively low value of the observed rotational transition (i.e., high barrier to rotation) may suggest weak chemisorption at this site. A similar finding was recently reported<sup>17</sup> for  $\text{H}_2$  adsorbed in the overexchanged FeZSM-5 catalyst, where the observed rotational tunneling transitions closely matched those of dihydrogen ligands in well-characterized Fe complexes.

For higher loadings (3 and 6  $\text{H}_2$ /unit cell), the peak centered at 1.5 meV remains, but broadens considerably. The broadening likely arises from the presence of several similar binding sites around the  $\text{Ni}^{2+}$  cation that could be occupied by  $\text{H}_2$  in a manner recently illustrated<sup>5</sup> by a computer simulation of  $\text{H}_2$  in zeolite NaA. Some of this broadening may also be the result of incomplete removal of coordinated  $\text{H}_2\text{O}$  upon dehydration. A neutron powder diffraction study of dehydrated VSB-5 is currently underway to investigate the geometry of  $\text{Ni}^{2+}$  sites in the dehydrated material.

Reduction of VSB-5 under flowing  $\text{H}_2$  results in a color change from light green to gray-black and dramatically changes the catalytic properties of the material, particularly toward hydrogenation reactions. No significant structural changes take place during the treatment, as evidenced by a lack of noticeable changes in powder XRD patterns or BET surface areas for the reduced compound. If we are correct in inferring the formation of nickel hydride on the active sites, this material represents a form of VSB-5 with similar porosity, but lacking unsaturated  $\text{Ni}^{2+}$  sites. The changes in  $\text{H}_2$  sorption are dramatic. A  $\text{H}_2$  adsorption isotherm at 77 K reveals a dramatic decrease in overall  $\text{H}_2$  uptake as compared with that of unreduced VSB-5 (Figure 5). More significantly, the slope is no longer sharp at low loading pressures, and the readsorption capacity (after desorption at 77 K) is comparable to the initial adsorption capacity. INS rotational tunneling spectra for the adsorbed  $\text{H}_2$  show a broad intensity distribution corresponding to physisorption, similar to the spectra obtained for VSB-1.

To further test our hypothesis that unusually strong binding sites exist in the VSB-5 framework, we collected TPD data (Figure 6). VSB-1, with no unsaturated  $\text{Ni}^{2+}$  sites, shows only one very small peak at 117 K. Because of the very small quantity of  $\text{H}_2$  involved, this is probably due to a surface or defect adsorption site not present in the simplified crystallographic

(10) Brown, C. N.; 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.

(11) Ren, Y.; Price D. L. *Appl. Phys. Lett.* **2001**, *79*, 3684.

(12) See, for example: Silvera, I. F. *Rev. Mod. Phys.* **1980**, *52*, 393.

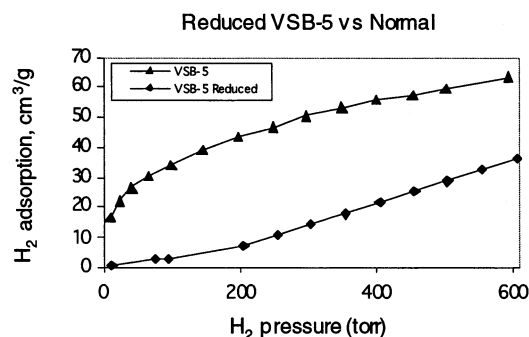
(13) Press, W. *Single Particle Rotations in Molecular Solids*; Springer Tracts in Modern Physics Vol. 92; Springer: Berlin, 1981.

(14) Eckert, J.; Kubas, G. J. *J. Phys. Chem.* **1993**, *97*, 2378.

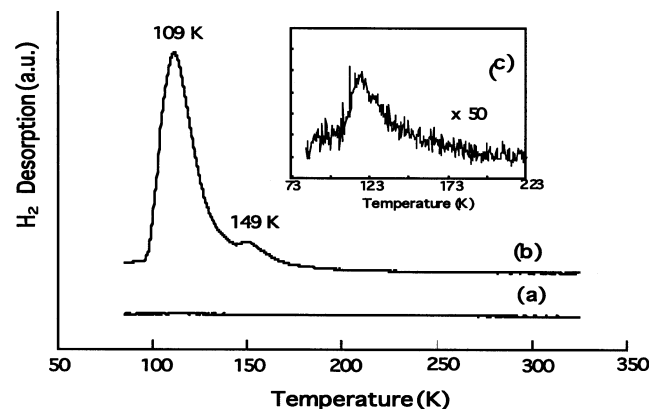
(15) Brown, D. W.; Sokol, P. E.; FitzGerald, S. A. *Phys. Rev. B* **1999**, *59*, 13258.

(16) Nicol, J. M.; Eckert, J.; Howard J. *J. Phys. Chem.* **1988**, *92*, 7117.

(17) Mojat, B. L.; Eckert, J.; van Santen, R. A.; Albinati, A.; Lechner, R. E. *J. Am. Chem. Soc.* **2001**, *123*, 8147.



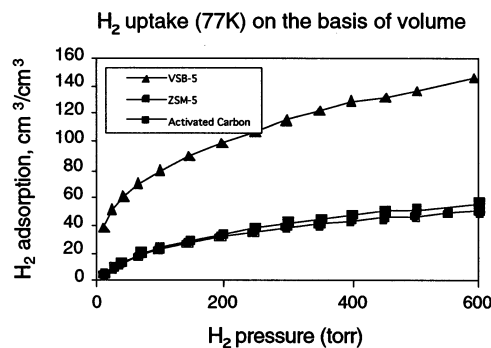
**Figure 5.** Relative H<sub>2</sub> adsorption capacities for calcined and reduced VSB-5.



**Figure 6.** TPD profiles of (a) VSB-1 and (b) VSB-5. Inset (c) shows the TPD trace of VSB-1 magnified by 50 times as compared to (a).

description. By contrast, VSB-5 releases H<sub>2</sub> in two successive stages (109 and 149 K) according to its TPD scan. Although the reason several types of adsorption sites apparently exist remains unclear, these data point toward the existence of multiple sites for H<sub>2</sub> adsorption in VSB-5.

Because of the unique hydrogen adsorption mechanism of VSB-5, we are currently investigating this and related systems for hydrogen storage potential.<sup>18</sup> Hydrogen storage by adsorption solely at the active sites would not meet the DOE goal for H<sub>2</sub> storage of 6.5 wt %. However, the overall capacity of VSB-5 for hydrogen storage compares favorably with that of many other porous materials on a weight basis. In volumetric terms, which are of particular interest for stationary applications, the capacity is significantly higher than the zeolite or activated carbon under the conditions studied (Figure 7). Single point isotherms are currently being measured to compare the performance of VSB-5 with that of other sorbents under more practical storage conditions where other storage mechanisms may be present. Sorption on unsaturated metal sites may be useful for other applications, such as hydrogen scavenging for processes at low temperatures, separations (based on Lewis basicity), or size-selective detection (based on spectroscopic changes accompanying coordination).



**Figure 7.** Hydrogen uptake for VSB-5, ZSM-5, and activated carbon based on densities. The crystallographic density was used for VSB-5 and ZSM-5, and a typical particle density (0.7 g/cm<sup>3</sup>) was used for the activated carbon sample.

## Conclusion

Sorption, neutron scattering, and temperature desorption experiments all point toward the existence of unsaturated Ni<sup>2+</sup> sites in VSB-5 that strongly interact with H<sub>2</sub>. Such sites are unique in the field of porous materials and stem from the unusual surface chemistry of VSB-5's pores, which possess coordinatively unsaturated Ni<sup>2+</sup> sites accessible in the pores. In addition, VSB-5 also shows H<sub>2</sub> physisorption properties competitive with those of zeolites and activated carbons. Porous nickel phosphates offer a new class of materials with potential in the hydrogen storage area, offering high surface areas, unsaturated metal coordination sites, and novel frameworks. For example, we have recently reported the synthesis of mesoporous nickel phosphates,<sup>19</sup> and we<sup>20</sup> and others<sup>21,22</sup> have prepared metal-organic hybrid materials containing unsaturated metal centers. The discovery of unique interactions with molecular hydrogen in these materials should motivate a search for new compounds in this family tailored for H<sub>2</sub> uptake.

**Acknowledgment.** This work was supported by the U.S. Department of Energy under Grant No. DE-FG0396ER14672. Work in Korea was supported by the Korean Ministry of Science and Technology (Institutional Research Program, KK-0202-I0). The authors thank R. Connatser for experimental assistance on QENS, M.-S. Park and D. S. Kim for assistance with the adsorption isotherms and H<sub>2</sub> TPD data, and A. R. Burbank for useful discussions. 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.

JA028341V

- (18) Schlappbach, L.; Züttel, A. *Nature* **2001**, *414*, 353.
- (19) Klotz, M.; Wiggins, S.; Stucky, G.; Cheetham, A. K., to be submitted.
- (20) Forster, P. M.; Cheetham, A. K. *Angew. Chem., Int. Ed.* **2001**, *241*, 457.
- (21) Chui, S. S. Y.; Lo, S. M. F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148.
- (22) Chen, B.; Eddaoudi, M.; Reineke, T. M.; Kampf, J. W.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2000**, *122*, 11559.