Hydrogen Storage Properties of Metal Nitroprussides M[Fe(CN)₅NO], (M = Co, Ni)

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The volumetric hydrogen adsorption isotherms of two isostructural dehydrated cubic metal nitroprussides M[Fe(CN)₅NO] (M = Co^{2+}, Ni^{2+}) have been measured up to a pressure of 760 Torr at 77 and 87 K. These materials are among the most efficient H_2 sorbents based on porous coordination polymers reported to date. The H_2 uptake in both materials is ∼1.6 wt % at 77 K and 760 torr. These H_2 capacities match those reported recently in the structurally related $M_3[Co(CN)_6]_2$ compounds and are approximately 25% higher than those reported for Zn_4O(1,4-benzenedicarboxylate)₃ under the same conditions of temperature and pressure. The isosteric heats of H_2 adsorption calculated from the 77 and 87 K isotherms for both materials were found to vary from ∼7.5 kJ/mol at 0.40 wt % coverage to ∼5.5 kJ/mol at 1.2 wt % coverage. The N_2 BET surface areas were determined to be 634 m²/g and 523 m²/g for M = Ni and M = Co, respectively.

Introduction

We find that the hydrogen storage capacity of Co[Fe(CN)₅NO] and Ni[Fe(CN)₅NO] metal nitroprussides are approximately 1.6 wt % at 77 K and 760 Torr. These storage capacities match those from a previous report[1] on structurally similar $M_3[Co(CN)_6]_2$ Prussian blue analogues and are ∼25% higher than reports[1-3] for Zn_4O(BDC)₃ (BDC 1,4-benzenedicarboxylate) (aka MOF-5 or IRMOF-1) under the same conditions. Thus the hydrogen storage capacities of these metal nitroprussides at 1 atm and 77 K are among the highest reported to date for crystalline microporous materials.[4,5] Additionally, the dehydrated metal nitroprusside materials maintain their structural integrity after air exposure.

New hydrogen storage materials are in critical demand for on-board hydrogen storage in fuel-cell-powered vehicles. Recent reports of moderate hydrogen storage in porous coordination polymers have demonstrated the potential of this class of materials.[1-16] However, the highest levels of storage obtained to date in these materials remain short of the 2010 DOE targets of 6 wt % and 0.045 g/cm³.

A separate but well-known class of porous coordination polymers is the transition metal cyanides. These materials are built of transition metals bridged through the linear cyanide ion. When the building unit is an octahedral hexacyano complex, reaction with another transition metal yields the cubic Prussian blues. Very recently, Kaye et al. reported the hydrogen storage properties of an analogous series of metal hexacyanocobaltates.[1] A significant and rapid uptake of hydrogen at liquid nitrogen temperature exceeding that of the more open MOF-5 was reported. The highest weight percent hydrogen in the series was achieved with $Cu_3[Co(CN)_6]_2$, with 1.8 wt % measured at 890 Torr. However, a separate report on the hydrogen storage properties of a similar series of metal hexacyanocobaltates by Chapman et al. gave significantly lower H_2 capacities with $Cu_3[Co(CN)_6]_2$ absorbing only 0.37 wt % H2 at 1 atm at 77 K.[15]

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We have concurrently been working on metal nitroprussides, which are a related class of metal cyanides. These porous networks are built from [Fe(CN)₅NO]²⁻ building units bridged though the M²⁺ ions via the CN⁻ ligands. When the bridging metal ion is Co²⁺ or Ni²⁺, the crystal symmetry is cubic and the compounds crystallize with 5 H_2O and 4 H_2O of hydration, respectively.[17,18] The inability of the NO ligand to bridge results in a 3/4 occupancy of the M²⁺ ions. These M²⁺ vacancies produce small cavities encapsulated by the nitrosyl ligands which protrude into the cubic cavity. To maintain charge balance in the structure, the M²⁺ vacancies are compensated by an equivalent number of [Fe(CN)₅NO]²⁻ vacancies. The omission of the [Fe(CN)₅NO]²⁻ unit creates a larger cubic pore where waters of hydration complete the M²⁺ coordination spheres and the remaining space is filled with hydrogen bonded water. The coordinated and hydrogen bonded waters can be removed with heating, resulting in the stable open frameworks illustrated in Figure 1. The porosity of these anhydrous materials has been determined by H_2O adsorption studies to be 0.367 cm³/g and 0.322 cm³/g for the Co and Ni analogues, respectively.[19] The large cavities present in the dehydrated metal nitroprussides contain coordinatively unsaturated metal centers, which may provide H_2 binding sites.[1,5,15,20] We were thus drawn to these metal nitroprussides as potential H_2 sorbents. The hydrogen storage properties of these compounds, until now, have yet to be reported. As we anticipated, the metal nitroprussides have significant H_2 storage capabilities.

Experimental Section

Synthesis of M[Fe(CN)₅NO] Compounds. The M[Fe(CN)₅NO]·xH₂O compounds (M = Co²⁺, $x = 5$; and M = Ni²⁺, $x = 4$) were synthesized by the reported method.[18] Specifically, 1 mmol of the appropriate metal nitrate was dissolved in 100 mL of H_2O and added dropwise to a stirred solution of 1 mmol sodium nitroprusside in 100 mL H_2O. The mixture was stirred for an additional 60 min after addition of the metal nitrate solution was complete. The microcrystalline precipitate that formed (pinkish-orange for the cobalt compound, and grayish-

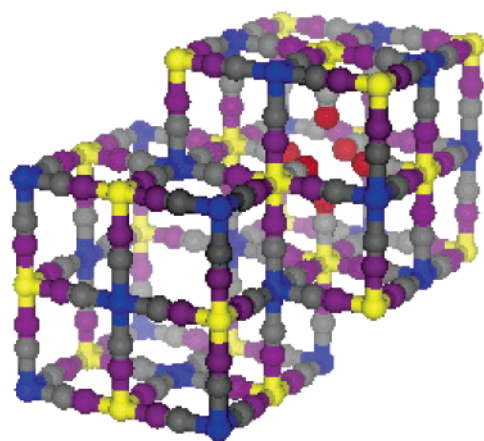**Figure 1.** Structure of M[Fe(CN)$_5$NO] compounds showing the two pore environments formed by the absence of M^{2+} ions (upper right cube) and [Fe(CN)$_5$NO] ions (lower left cube). Key: Fe (yellow), C (violet), N (gray), O (red), M (blue). Cell parameters taken from Mullica et al.[17]

Figure 2. Powder XRD patterns verifying the structural stability of the M[Fe(CN)$_5$NO] materials through the H$_2$ adsorption measurements. (A) Co[Fe(CN)$_5$NO] after isotherm measurements, (B) Co[Fe(CN)$_5$NO] as synthesized, (C) Ni[Fe(CN)$_5$NO] after isotherm measurements, (D) Ni[Fe(CN)$_5$NO] as synthesized.

green for the nickel compound) was filtered off and washed copiously with water and allowed to air dry for several days before TGA and XRD measurements were performed. The yields for both materials were nearly quantitative. To determine the level of Na$^+$ impurity, metals analysis was performed by ICP on ~0.10 g samples previously dehydrated at 95 °C under vacuum for 24 h. To dissolve the samples, each was digested in 8 mL aqua regia + 1 mL H$_2$O$_2$ by a microwave digester. The results were averaged over two runs. For Co[Fe(CN)$_5$NO], (theoretical wt %) Fe 20.32; Co 21.44; Na 0.00 (actual wt %) Fe 19.96; Co 20.69; Na 0.13. For Ni[Fe(CN)$_5$NO], (theoretical wt %) Fe 20.33; Ni 21.37; Na 0.00 (actual wt %) Fe 19.69; Ni 20.69; Na 0.17.

Synthesis of Cu$_3$[Co(CN)$_6$]$_2$·xH$_2$O. The Cu$_3$[Co(CN)$_6$]$_2$· xH$_2$O material was prepared from K$_3$[Co(CN)$_6$] and Cu(NO$_3$)$_2$· 6H$_2$O according to the method of Kaye,[1] and verified by X-ray powder diffraction.

Instrumentation. Gas adsorption measurements were performed using a Quantachrome Autosorb 1C volumetric isotherm apparatus on samples (~230 mg) degassed under dynamic vacuum for 48−64 h at 95 °C. At this point, outgassing rates were less than 0.5 mTorr/sec and the typical mass loss was ~15−20%. After the initial degassing, no further mass losses were seen with any subsequent degassing steps. After each run, samples were briefly degassed under dynamic vacuum at 95 °C for 3 h. A solid quartz filler rod was used to reduce the void volume in the sample cell. Powder X-ray diffraction measurements were performed on a PANalytical X'Pert Pro MPD powder diffractometer having a theta-theta configuration, a Cu X-ray source operated at 45 kV and 40 mA, and an X'Celerator detector with a monochromator. Patterns were recorded over a 2Θ range of 5−50° using a step size of 0.008 degrees 2Θ and a scan step time of 100 seconds. Thermogravimetric analyses were performed on ~5 mg samples using a Perkin-Elmer TGA7 Thermogravimetric Analyzer under a N$_2$ purge of 20 mL/min. The samples were held at 30 °C for 10 min before raising the temperature to 1000 °C at a rate of 5 °C/min. (See Supporting Information)

Isotherm Fits and Calculation of H$_2$ Isosteric Heats of Adsorption. Isotherms were fit to the Langmuir−Freundlich (L−F) equation. The L−F equation allowed for H$_2$ storage values at saturation coverage to be estimated. It also allowed
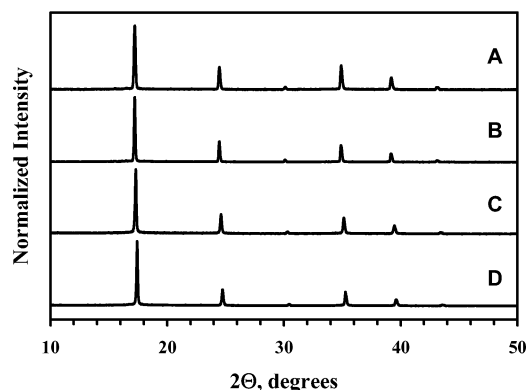
for a smooth interpolation between experimental data points for isosteric heat calculations. The coverage as a function of pressure in the L−F equation is given by

$$\frac{Q}{Q_m} = \frac{B*P^{(1/t)}}{(1 + B*P^{(1/t)})}$$

where Q = amount of gas adsorbed, Q_m = amount of gas adsorbed at saturation coverage, P = pressure, and B and t are constants.

The L−F equation easily rearranges to yield the pressure as a function of Q/Q_m at a constant temperature. From this equation and the fits obtained from the experimental data, plots of $\ln(P)$ as a function of Q could be generated from the experimental data at 77 and 87 K. Isosteric heats (at a given coverage) were then calculated using the differential equation $q_{st} = -R[\partial \ln(P)/ \partial(1/T)]n$. Isosteric heats calculated in this manner from our data on the Cu$_3$[Co(CN)$_6$]$_2$ agree exceptionally well with the method and data published by Kaye and Long,[1] therefore verifying the accuracy of our measurements.

Results and Discussion

For any porous material to find function as a molecular host, it is critical that the material maintain its porosity after the removal of any guests incorporated into the structure during synthesis. The X-ray diffraction measurements shown in Figure 2 verify that the M[Fe(CN)$_5$NO] compounds are structurally stable after evacuation and reexposure to the atmosphere. Powder diffraction measurements on the as-synthesized materials match the patterns calculated from their crystallographic parameters. Powder diffraction measurements taken on the same samples at the conclusion of the isotherm measurements and after reexposure to the atmosphere show nearly identical results. Estimated particle sizes derived from the Scherrer equation[21] were ~650 Å for the Co[Fe(CN)$_5$NO] sample prior to the gas adsorption measurements and ~500 Å after the gas adsorption measurements. For the Ni[Fe(CN)$_5$NO] material, similar particle sizes of ~600 Å were determined both prior to and after the isotherm runs.

The N$_2$ BET surface areas of the Ni and Co samples were 634 m^2/g and 523 m^2/g, respectively, and are similar to those determined by Ar BET for the M$_3$[Co(CN)$_6$]$_2$ compounds.[1] The estimated pore volumes for the two materials were determined to be 0.27 cm^3/g for Co[Fe(CN)$_5$NO] and 0.33 cm^3/g for Ni[Fe(CN)$_5$NO] from their respective 77 K N$_2$ adsorption

H₂ Absorption on M[Fe(CN)₅NO]

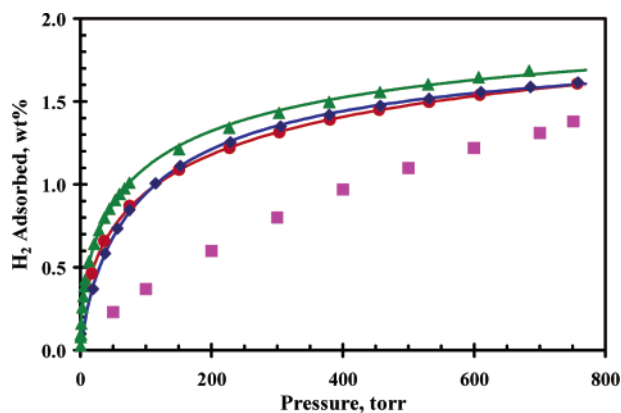*J. Phys. Chem. B, Vol. 110, No. 16, 2006* **8327**

Figure 3. Hydrogen adsorption isotherms versus pressure measured for (▲) Ni[Fe(CN)₅NO], (●) Co[Fe(CN)₅NO], and (◆) Cu₃[Co(CN)₆]₂ at 77 K. Data for (■) Zn₄O(BDC)₃ taken from Rowsell[2] are shown for comparison. The solid lines are Langmuir–Freundlich fits to the data.
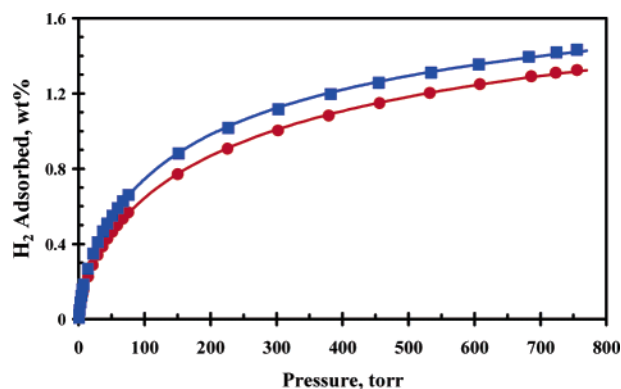

Figure 4. H₂ adsorption isotherms for (■) Ni[Fe(CN)₅NO] and (●) Co[Fe(CN)₅NO] measured volumetrically at 87 K. Solid lines are fits to the data using the Langmuir–Freundlich equation.
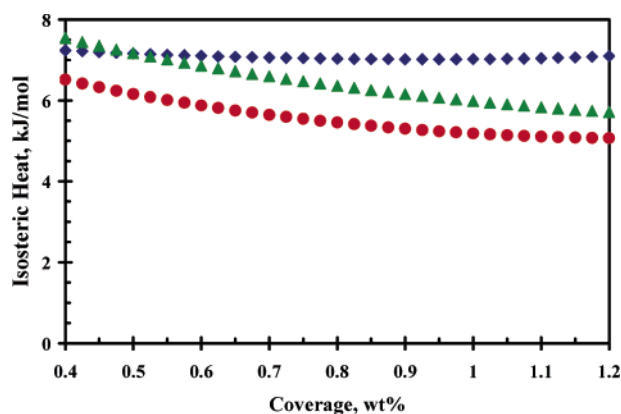

Figure 5. Calculated isosteric heats of H₂ adsorption versus coverage for (▲) Ni[Fe(CN)₅NO], (●) Co[Fe(CN)₅NO], and (◆) Cu₃[Co(CN)₆]₂ at 77 K.

isotherms at $p/p_0 = 0.90$. The calculated dehydrated densities of the materials are also similar to the M₃[Co(CN)₆]₂ compounds, with the Co and Ni compounds having densities of 1.26 g/cm³ and 1.24 g/cm³, respectively. These similarities in surface areas and densities are reflected in the H₂ adsorption properties shown in Figure 1. The Ni and Co nitroprussides show nearly identical H₂ uptakes of 1.68 wt % and 1.61 wt %, respectively, at 77 K and 720 Torr. We have also independently prepared a sample of Cu₃[Co(CN)₆]₂ and measured its H₂ adsorption isotherm. Our results for the H₂ adsorption on Cu₃[Co(CN)₆]₂ are included in Figure 1 and agree with those reported by Kaye et al.[1] The H₂ uptakes measured in these metal cyanide systems are approximately 25% higher than those observed in the more open MOF-5 material at 1 atm H₂.[1–3] The hydrogen uptakes equate to ~6 H₂ per M[Fe(CN)₅NO] unit cell, which yields a H₂ storage density of ~0.020 g/cm³. For comparison, the more open MOF-5 material with a desolvated density of 0.59 g/cm³ and a hydrogen uptake of ~1.4 wt % at 77 K and 1 atm has a H₂ storage density on the order of 0.008 g/cm³. Fits to the isotherms using the Langmuir–Freundlich equation give saturation values of 2.3 wt % for Co[Fe(CN)₅NO], 2.2 wt % for Ni[Fe(CN)₅NO], and 1.9 wt % for Cu₃[Co(CN)₆]₂. Our saturation value determined for Cu₃[Co(CN)₆]₂ is in close agreement with the 2.1 wt % value reported by Kaye et al.[1]

The H₂ sorption at 87 K has also been measured for the two compounds. As expected, the H₂ uptake shown in Figure 4 is lower at the higher temperature with the Ni and Co compounds taking 1.33 wt % H₂ and 1.43 wt % H₂ at 760 Torr, respectively. The H₂ adsorption isotherms at 77 and 87 K for the two materials were fit using the Langmuir–Freundlich equation and the isosteric heats of adsorption estimated from the fits by application of the equation $q_{st} = -R[\partial \ln(p)/ \partial(1/T)]n$. The results of the calculations for the two M[Fe(CN)₅NO] compounds, along with our results for Cu₃[Co(CN)₆]₂, are plotted in Figure 5. Both nitroprussides show relatively high isosteric heats of ~7.5 kJ/mol for the Ni compound and ~6.5 kJ/mol for the Co compounds at 0.40 wt % coverage. The heats of adsorption drop consistently to approximately 5 kJ/mol for the Co material and 5.7 kJ/mol for the Ni material at the highest coverages obtained. The isosteric heats at low coverage are similar to the M₃[Co(CN)₆]₂ compounds[1] and higher than the 4.7–6.4 kJ/mol values observed for activated carbons[22] and MOF-5.[1–3] Unlike the M₃[Co(CN)₆]₂ compounds which showed

a nearly constant heat of adsorption versus coverage, the isosteric heats of the M[Fe(CN)₅NO] materials decrease as loadings increase.

The similar isosteric heats at low coverages between the Prussian blue analogues and the metal nitroprussides suggest the presence of similar adsorption environments within the two classes of materials. One adsorption site that is likely similar between the M[Fe(CN)₅NO] and M₃[Co(CN)₆]₂ materials is the ~7 Å diameter pore site created by the metal cyanide vacancies. These cavities are bordered by coordinatively unsaturated bridging metal ions which may provide a favorable H₂ adsorption site in both families of materials. While the actual H₂ binding site in these materials is speculative at this point, previous reports of H₂ sorption in materials with unsaturated metal sites have suggested that open metal sites may influence the hydrogen storage behavior of coordination polymers and MOFs.[5,20] The divergence in the heats of adsorption at high coverages between the two classes of materials suggests that an additional, less energetically favorable, sorption site may exist in the M[Fe(CN)₅NO] compounds. This additional site could result from the smaller ~4 Å nitrosyl-lined pore created by the M²⁺ vacancies.[19] Further evidence for this addition pore site is gained when comparing the estimated saturation values for the M[Fe(CN)₅NO] and Cu₃[Co(CN)₆]₂, which give ~9 H₂ per unit cell and ~8 H₂ per unit cell, respectively. The saturation value of 9 H₂ per unit cell appears reasonable when compared with the previously reported saturation values of 7.2 CO₂ and 8.7 N₂ per unit cell.[19]

Conclusion

The results reported herein for the $M[Fe(CN)_5NO]$ materials further the suggestion that the inclusion of unsaturated metal sites within the host lattice may strengthen the H_2 binding efficiency of porous coordination polymers and may lead to enhanced H_2 storage at lower pressures and higher temperatures.[5,16,20] However, further studies are needed to determine the H_2 adsorption sites in materials with open metal sites and to discern what effects these sites have on the hydrogen storage properties of coordination polymers and MOFs. In addition, the higher hydrogen storage densities of 0.020 kg/L at 760 Torr observed in the $M[Fe(CN)_5NO]$ materials demonstrate the potential benefits of using higher density materials as hydrogen sorbents,[9] as these H_2 storage densities are more than double those reported for the low-density MOF-5 material under the same conditions of temperature and pressure.

Supporting Information Available: TGA plots for $Co[Fe(CN)_5NO] \cdot 5H_2O$ and $Ni[Fe(CN)_5NO] \cdot 4H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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