

The role of vacancies in the hydrogen storage properties of Prussian blue analogues

Steven S. Kaye, Jeffrey R. Long*

Department of Chemistry, University of California, Berkeley, CA 94720-1460, United States

Available online 13 November 2006

Abstract

The porosity and hydrogen storage properties of the dehydrated Prussian blue type solids $\text{Ga}[\text{Co}(\text{CN})_6]$, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, $\text{M}_2[\text{Fe}(\text{CN})_6]$ ($\text{M} = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}$), and $\text{Co}_3[\text{Co}(\text{CN})_5]_2$ are reported and compared to those of $\text{M}_3[\text{Co}(\text{CN})_6]_2$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$). Nitrogen sorption measurements suggest partial framework collapse for $\text{M}_2[\text{Fe}(\text{CN})_6]$ ($\text{M} = \text{Co}, \text{Ni}$) and $\text{Co}_3[\text{Co}(\text{CN})_5]_2$, and complete collapse for $\text{Mn}_2[\text{Fe}(\text{CN})_6]$. Hydrogen sorption isotherms measured at 77 K reveal a correlation between uptake capacity and the concentration of framework vacancies, with Langmuir–Freundlich fits predicting saturation values of 1.4 wt.% for $\text{Ga}[\text{Co}(\text{CN})_6]$, 1.6 wt.% for $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, 2.1 wt.% for $\text{Cu}_3[\text{Co}(\text{CN})_6]_2$, and 2.3 wt.% for $\text{Cu}_2[\text{Fe}(\text{CN})_6]$. Enthalpies of H_2 adsorption were calculated from isotherms measured at 77 and 87 K. Importantly, the values obtained for compounds with framework vacancies are not significantly greater than for the fully-occupied framework of $\text{Ga}[\text{Co}(\text{CN})_6]$ (6.3–6.9 kJ/mol). This suggests that the exposed metal coordination sites in these materials do not dominate the hydrogen binding interaction.

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Keywords: Hydrogen storage; Gas adsorption; Microporous solids; Prussian blue; Cyanide

1. Introduction

Due to its clean combustion and high heating value, hydrogen is currently being considered as a replacement for fossil fuels in mobile applications. In order to achieve this goal, however, an effective means of storage must be developed [1]. Although major efforts have been directed toward storing hydrogen in nanostructured carbon, metal hydrides, and chemical hydrides, all such materials have significant limitations, necessitating further research [2–4]. A few years ago, Yaghi and coworkers [5] demonstrated the potential for hydrogen storage in microporous coordination solids, showing that compounds consisting of tetrahedral $[\text{Zn}_4\text{O}]^{6+}$ units bridged by linear aryldicarboxylates adsorb up to 1.6 wt.% H_2 at 77 K and 760 Torr. This work was followed by numerous reports of hydrogen storage in other microporous frameworks, most of which also contain organic dicarboxylates as the bridging unit [6].

Recently, we [7] and others [8] reported hydrogen storage in cyanide-bridged coordination solids, specifically, Prussian blue

analogues of the type $\text{M}_3[\text{Co}(\text{CN})_6]_2$. The most promising material, $\text{Cu}_3[\text{Co}(\text{CN})_6]_2$, stored 1.8 wt.% H_2 and 0.025 kg H_2/L at 77 K and 890 Torr [7]. In these reports, it was hypothesized that H_2 binding to open coordination sites on the nitrogen-bound M^{2+} cations in the framework may contribute to the H_2 uptake. As a probe of the role of coordinatively-unsaturated metal centers in the H_2 uptake within such materials, we now report H_2 sorption studies of dehydrated Prussian blue analogues with varying concentrations of framework vacancies.

Prussian blue analogues exhibit structures based upon the cubic $\text{M}[\text{M}'(\text{CN})_6]$ framework depicted in Fig. 1, wherein octahedral $[\text{M}'(\text{CN})_6]^{n-}$ complexes are linked via octahedrally-coordinated, nitrogen-bound M^{n+} ions. In Prussian blue itself, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 14\text{H}_2\text{O}$, charge balance with the Fe^{3+} ions leads to vacancies at 25% of the $[\text{Fe}(\text{CN})_6]^{4-}$ sites in the framework [9]. Consequently, water ligands complete the octahedral coordination spheres for some of the Fe^{3+} ions. Heating the compound can remove both bound and solvate water molecules, leaving the iron-cyanide framework intact and exposing coordinatively-unsaturated Fe^{3+} sites [10]. Similarly, the combination of M^{2+} cations with $[\text{M}'(\text{CN})_6]^{3-}$ complexes affords $\text{M}_3[\text{M}'(\text{CN})_6]_2$ Prussian blue analogues, containing 33% vacancies at the hexacyanometalate sites

* Corresponding author. Tel.: +1 510 642 0860; fax: +1 510 642 8369.

E-mail address: jrlong@berkeley.edu (J.R. Long).

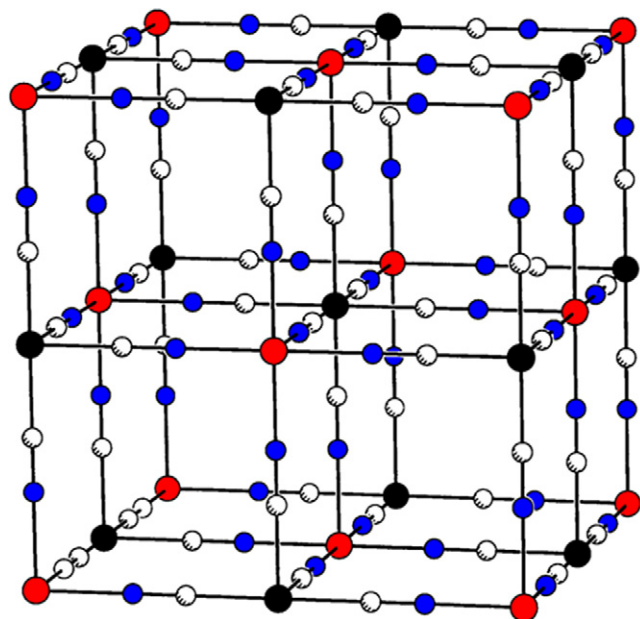


Fig. 1. Unit cell for the structure of a Prussian blue analogue, $M[M'(CN)_6]$. Red, black, white, and blue spheres represent M, M', C, and N atoms, respectively. Water solvate molecules are omitted for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

and a higher concentration of exposed metal sites upon dehydration. The compound $Co_3[Co(CN)_5]_2$ has a related structure, but with one out of every six cyanide bridges also missing from the framework, which leads to exposed carbon-bound Co^{2+} sites [11]. Although a definitive structural study has not been reported, $M_2[M'(CN)_6]$ Prussian blue analogues, formed by combining M^{2+} cations and $[M'(CN)_6]^{4-}$ complexes, may even contain 50% vacancies at the hexacyanometalate sites.

2. Experimental

Unless otherwise mentioned, all reactants were used as purchased, without further purification. The compounds $Fe_4[Fe(CN)_6]_3 \cdot 14H_2O$ [12], $Co_3[Co(CN)_5]_2 \cdot 12H_2O$ [11], and $Cu_3[Co(CN)_6]_2 \cdot 15H_2O$ [7] were prepared according to published procedures.

2.1. Synthesis of $Ga[Co(CN)_6] \cdot 4H_2O$

A solution of $K_3[Co(CN)_6]$ (300 mg, 1.10 mmol) in 10 mL of deionized water was added dropwise to a stirred solution of $Ga(NO_3)_3$ (462 mg, 1.10 mmol) in 10 mL of deionized water. The resulting precipitate was stirred at room temperature under the mother liquor for 24 h, collected by filtration, and washed with 3×50 mL of deionized water. The solid was then dried in air to give $Ga[Co(CN)_6] \cdot 4H_2O$ in quantitative yield. The powder X-ray diffraction pattern matched that of a typical Prussian blue type solid. Anal. Calcd. for $Ga[Co(CN)_6] \cdot 4H_2O$: C, 20.20; H, 2.26; N, 23.55. Found: C, 20.45; H, 2.09; N, 23.85.

2.2. Synthesis of $M_2[Fe(CN)_6] \cdot nH_2O$ ($M = Mn, Co, Ni, Cu$)

The preparations employed involved slight modifications to a literature procedure [13]. A solution of $Na_4[Fe(CN)_6]$ (300 mg, 0.620 mmol) in 10 mL of deionized water was added dropwise to a stirred solution of $M(NO_3)_2$ ($M = Co, Ni, Cu$) or $MnCl_2$ (1.86 mmol) in 10 mL of deionized water. The resulting precipitate was stirred at room temperature under the mother liquor for 24 h, collected by filtration, and washed with 3×50 mL of deionized water. The solid was then dried in air to give $M_2[Fe(CN)_6] \cdot nH_2O$ ($M = Mn, Co, Ni, Cu$) in quantitative yield. The powder X-ray diffraction patterns matched that of a typical Prussian blue type solid. Anal. Calcd. for $Mn_2[Fe(CN)_6] \cdot 5H_2O$: C, 17.49; H, 2.45; N, 20.40. Found: C, 17.32; H, 2.73; N, 20.05. Anal. Calcd. for $Co_2[Fe(CN)_6] \cdot 5H_2O$: C, 17.16; H, 2.40; N, 20.01. Found: C, 17.70; H, 2.07; N, 19.95. Anal. Calcd. for $Ni_2[Fe(CN)_6] \cdot 7H_2O$: C, 15.82; H, 3.10; N, 18.45. Found: C, 15.84; H, 2.62; N, 18.10. Anal. Calcd. for $Cu_2[Fe(CN)_6] \cdot 7H_2O$: C, 15.49; H, 3.03; N, 18.06. Found: C, 15.65; H, 2.72; N, 18.15.

2.3. Gas sorption measurements

Sample tubes of a known weight were loaded with 100–200 mg of sample and sealed using a transeal. Samples were degassed for 24–60 h on a Micromeritics ASAP 2020 analyzer at the following temperatures: $Cu_3[Co(CN)_6]_2 = 95^\circ C$, $Fe_4[Fe(CN)_6]_3 = 40^\circ C$, $Ga[Co(CN)_6] = 95^\circ C$, $Mn_2[Fe(CN)_6] = 80^\circ C$, $Co_2[Fe(CN)_6] = 100^\circ C$, $Ni_2[Fe(CN)_6] = 80^\circ C$, $Cu_2[Fe(CN)_6] = 40^\circ C$, and $Co_3[Co(CN)_5]_2 = 50^\circ C$. Degassing was continued until the outgas rate was no more than 1 mTorr/min. The degassed sample and sample tube were weighed and then transferred back to the analyzer (with the transeal preventing exposure of the sample to air). The outgas rate was again confirmed to be no more than 1 mTorr/min. Measurements were performed either at 77 K in a liquid nitrogen bath or at 87 K in a liquid argon bath.

Enthalpies of adsorption were calculated using a variant of the Clausius-Clapeyron equation [14]:

$$\ln\left(\frac{P_1}{P_2}\right) = \Delta H_{\text{ads}} \frac{T_2 - T_1}{R \times T_1 \times T_2} \quad (1)$$

where P_n is the pressure for isotherm n , T_n the temperature for isotherm n , and R is the molar gas constant. This equation can be used to calculate the enthalpy of adsorption as function of the quantity of H_2 adsorbed. Pressure as a function of the quantity of gas adsorbed was calculated by fitting each isotherm using the Langmuir–Freundlich equation [15]:

$$\frac{Q}{Q_m} = \frac{B \times P^{(1/t)}}{1 + B \times P^{(1/t)}} \quad (2)$$

where Q is the number of moles of gas adsorbed, Q_m the number of moles of gas adsorbed at saturation, P the pressure, and B and t are the fitting constants. In order to obtain the most accurate interpolation between measured data points, only the regions of the isotherm that had been measured at both 77 and 87 K were

fitted, as only these regions would be used to calculate the enthalpy of adsorption. This is in contrast to the previously reported method, in which the entire isotherm was fitted [7]. Eq. (2) was then substituted into Eq. (1) to give enthalpy of adsorption as function of the quantity of H₂ adsorbed.

2.4. Other physical measurements

Carbon, hydrogen and nitrogen analyses were obtained from the Microanalytical Laboratory of the University of California, Berkeley. Powder X-ray diffraction data were collected using Cu K α (λ = 1.5406 Å) radiation on a Siemens D5000 diffractometer. Thermogravimetric analyses were carried out at a ramp rate of 0.5 °C/min under a dinitrogen atmosphere, using a TA Instruments TGA 2950.

3. Results and discussion

3.1. Effects of framework vacancies on H₂ adsorption

The gas sorption properties of three Prussian blue analogues were measured in order to compare the effects of varying the concentration of vacancies at the hexacyanometalate sites: Ga[Co(CN)₆] (0%), Fe₄[Fe(CN)₆]₃ (25%), and Cu₃[Co(CN)₆]₂ (33%). Hydrated forms of the three compounds were synthesized by the usual means of combining aqueous solutions of the corresponding metal salts and hexacyanometalate complexes. The powder X-ray diffraction patterns of the products were fully consistent with the Prussian blue structure type, and elemental analysis confirmed the composition of each compound. The compounds Ga[Co(CN)₆] and Cu₃[Co(CN)₆]₂ were completely dehydrated by heating at 95 °C for 48 h under dynamic vacuum. Due to greater thermal sensitivity, Fe₄[Fe(CN)₆]₃ was dehydrated by heating at 40 °C for 60 h under dynamic vacuum. Attempts to dehydrate the compounds more rapidly at higher temperatures resulted in decreased gas uptake, presumably due to partial collapse of the framework.

The porosity of the dehydrated samples was probed via N₂ sorption measurements performed at 77 K. All compounds showed type I sorption isotherms characteristic of microporous materials (See Figs. S12–S15 in the Supporting Information). The surface areas, calculated by applying the BET model to the data, are listed in Table 1, and range from 550 m²/g for Fe₄[Fe(CN)₆]₃ to 750 m²/g for Cu₃[Co(CN)₆]₂. The observed variation is likely due to a combination of differences in the degree of framework collapse and micropore volume, which is a function of the number of vacancies at the [M'(CN)₆]^{n−} sites.

Using the same volumetric apparatus, H₂ sorption isotherms were measured at 77 K for the three dehydrated compounds (see Fig. 2). Table 1 lists the storage capacities at the maximum attainable pressure of 890 Torr. The observation of H₂ uptake in Ga[Co(CN)₆] demonstrates that open coordination sites are *not* required for H₂ adsorption. This is in contrast to previous measurements performed on Cd[Pt(CN)₆], another Prussian blue analogue with no coordinatively-unsaturated metal centers, in which no H₂ uptake was observed [8]. By employing the Langmuir–Freundlich equation [15] to fit the isotherms,

Table 1

Gas sorption properties of dehydrated Prussian blue analogues

Compound	SA ^a (m ² /g)	wt.% H ₂ ^b	Maximum wt.% H ₂ ^c	ΔH_{ads} (kJ/mol)
Ga[Co(CN) ₆]	570	1.1	1.4	6.3–6.9
Fe ₄ [Fe(CN) ₆] ₃	550	1.2	1.6	6.3–7.6
Cu ₃ [Co(CN) ₆] ₂	750	1.8	2.1	6.6–6.8
Mn ₂ [Fe(CN) ₆]		0.0	0.0	
Co ₂ [Fe(CN) ₆]	370	0.7	0.9	
Ni ₂ [Fe(CN) ₆]	460	0.9	1.1	
Cu ₂ [Fe(CN) ₆]	730	1.6	2.3	6.0–6.6
Co ₃ [Co(CN) ₅] ₂	730	1.4	1.8	5.7–7.0

^a Surface area calculated by applying the BET model to N₂ sorption isotherms.

^b Measured at 77 K and 890 Torr.

^c Predicted through application of the Langmuir–Freundlich equation.

estimates were obtained for the maximum H₂ uptake for each compound. Note that the predicted maximum storage capacities increase with increasing concentration of [M'(CN)₆]^{n−} vacancies in the lattice, varying from 1.4 wt.% for Ga[Co(CN)₆] to 1.6 wt.% for Fe₄[Fe(CN)₆]₃ to 2.1 wt.% for Cu₃[Co(CN)₆]₂. Assuming no framework collapse, these capacities correspond to 8.0, 6.9, and 8.7 H₂ molecules per unit cell (see Fig. 1), respectively. Thus, the results are consistent with adsorption of one H₂ molecule per octant of the unit cell for the fully-occupied framework of Ga[Co(CN)₆], and are suggestive of partial collapse of Fe₄[Fe(CN)₆]₃.

The strength of the interaction between H₂ and the framework was probed by measuring a second sorption isotherm at 87 K. Using the 77 and 87 K data, the enthalpy of adsorption as a function of the quantity of hydrogen adsorbed was calculated using a variant of the Clausius–Clapeyron equation [14]. The results are plotted in Fig. 3, and vary narrowly within the range 6.3–7.6 kJ/mol. Surprisingly, Ga[Co(CN)₆], which has no open coordination sites, has an initial enthalpy of adsorption nearly identical to that of Cu₃[Co(CN)₆]₂, which has an average of two open coordination sites per Cu²⁺ ion. As shown, in Fig. 4, the initial enthalpy of adsorption for Ga[Co(CN)₆] is also similar to that of

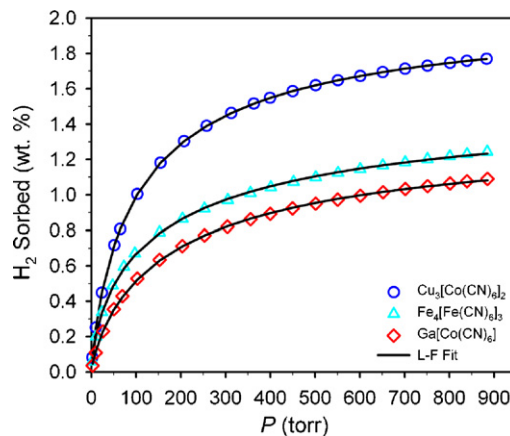


Fig. 2. Hydrogen sorption isotherms for the Prussian blue analogues Ga[Co(CN)₆], Fe₄[Fe(CN)₆]₃, and Cu₃[Co(CN)₆]₂. Solid lines represent the best fits of the Langmuir–Freundlich (L–F) equation to the data.

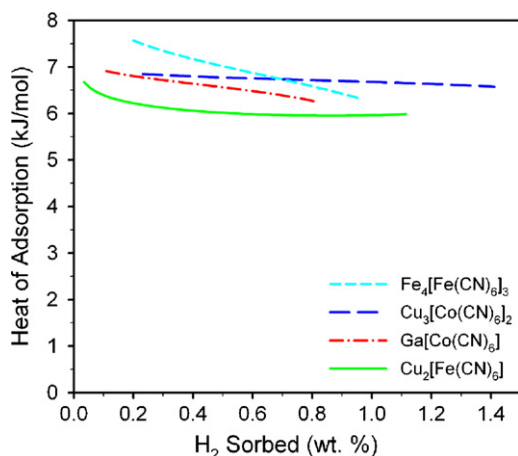


Fig. 3. Enthalpy of H_2 adsorption for $Ga[Co(CN)_6]$, $Fe_4[Fe(CN)_6]_3$, $Cu_3[Co(CN)_6]_2$, and $Cu_2[Fe(CN)_6]$.

$M_3[Co(CN)_6]_2$ ($M = Fe, Co, Zn$), and greater than that of $Mn_3[Co(CN)_6]_2$ [16]. This suggests that if any hydrogen does adsorb onto the open metal coordination sites within these materials, the strength of the interaction is not greater than that of simple physisorption onto the metal–cyanide framework. Notably, $Fe_4[Fe(CN)_6]_3$ and $Ni_3[Co(CN)_6]_2$ have initial enthalpies of adsorption ca. 0.5 kJ/mol higher than that of $Ga[Co(CN)_6]$, suggesting that weak metal–hydrogen could be enhancing binding. However, this small difference could also simply be due to variation in the strength of physisorption of hydrogen as the M^{n+} cation is varied, as can be seen for $M_3[Co(CN)_6]_2$ ($M = Mn, Fe, Co, Cu, Zn$). Or it might somehow be associated with a smaller particle size for the $Fe_4[Fe(CN)_6]_3$ and $Ni_3[Co(CN)_6]_2$ samples, which both showed significantly broadened peaks in the powder X-ray diffraction pattern.

3.2. H_2 adsorption in $M_2[Fe(CN)_6]$ ($M = Mn, Co, Ni, Cu$)

The N_2 and H_2 sorption properties of a series of Prussian blue analogues of the type $M_2[Fe(CN)_6]$ ($M = Mn, Co, Ni, Cu$)

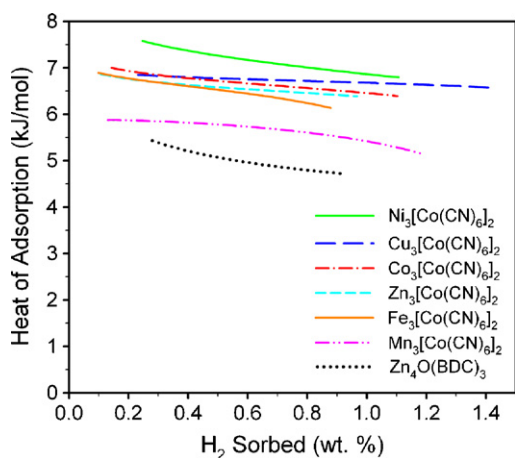


Fig. 4. Enthalpy of H_2 adsorption for $M_3[Co(CN)_6]_2$ ($M = Mn, Fe, Co, Ni, Cu, Zn$) and $Zn_4O(BDC)_3$ ($BDC = 1,4$ -benzenedicarboxylate) [7,16].

were also investigated. While there have been no definitive experiments probing the nature of the vacancy distribution within these materials, their X-ray powder diffraction patterns do indicate a Prussian blue structure type [17]. Charge balance is likely achieved either through vacancies at 50% of the $[Fe(CN)_6]^{4-}$ sites or through a combination of vacancies and $[M(H_2O)_6]^{2+}$ ions in the pores of the framework. Hydrated forms of the four compounds were synthesized using a somewhat modified version of a literature procedure [13]. The X-ray powder diffraction patterns of the products were indeed consistent with the usual Prussian blue structure type, and elemental analysis confirmed the compositions. Unfortunately, these materials were found to be considerably less thermally stable than the other Prussian blue analogues. Even under gentler dehydration conditions, the N_2 storage capacities indicated significant framework collapse for $Co_2[Fe(CN)_6]$ and $Ni_2[Fe(CN)_6]$ (see Table 1), and complete collapse for $Mn_2[Fe(CN)_6]$. The BET surface area of 730 m^2/g obtained for $Cu_2[Fe(CN)_6]$, however, suggests that its framework is largely intact.

The H_2 sorption isotherms measured for these compounds are also consistent with varying degrees of framework collapse upon dehydration. For example, increasing the dehydration time for $Ni_2[Fe(CN)_6]$ at 80 °C from 24 to 48 h resulted in a decrease in H_2 uptake at 77 K and 890 Torr from 0.9 to 0.4 wt.%. Further reduction in the dehydration time or temperature, however, resulted in an incompletely-dehydrated sample, as measured by mass change. Fig. 5 displays sorption isotherms for materials dehydrated under the best conditions identified. Uptake at 77 K and 890 Torr varied from 0.0 wt.% in $Mn_2[Fe(CN)_6]$ to 1.6 wt.% H_2 in $Cu_2[Fe(CN)_6]$. Although the value for $Cu_2[Fe(CN)_6]$ is slightly less than the 1.8 wt.% observed for $Cu_3[Co(CN)_6]_2$, its isotherm also rises less steeply, such that the Langmuir–Freundlich equation actually predicts a slightly greater maximum uptake of 2.3 wt.%. This represents the highest predicted saturation capacity for any of the measured Prussian blue analogues, and is perhaps consistent with the presence of a greater concentration of framework vacancies within the material.

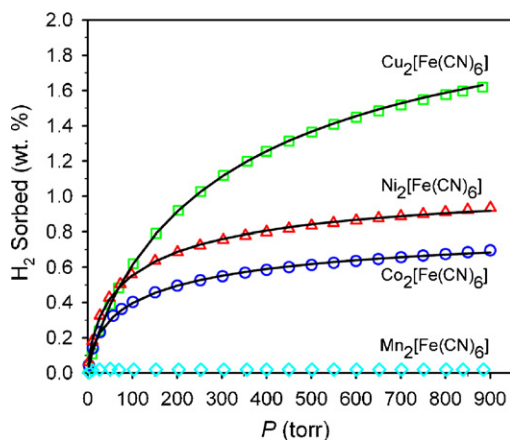


Fig. 5. Hydrogen sorption isotherms for the Prussian blue analogues $M_2[Fe(CN)_6]$ ($M = Mn, Co, Ni, Cu$). Solid lines represent the best fits of the Langmuir–Freundlich (L–F) equation to the data.

The enthalpy of H_2 adsorption was also determined for $Cu_2[Fe(CN)_6]$, and observed to vary within the range 6.0–6.6 kJ/mol (see Fig. 3). Note that its values track below those for all of the other Prussian blue analogues, with the exception of $Mn_3[Co(CN)_6]_2$ (see also Fig. 4). The ca. 0.5 kJ/mol difference with the results obtained for $Cu_3[Co(CN)_6]_2$ is again most likely indicative of the dependence of the strength of the H_2 physisorption interaction upon the nature of the framework metal centers.

3.3. H_2 adsorption in $Co_3[Co(CN)_5]_2$

The foregoing results indicate that divalent first-row transition metals coordinated by nitrogen within a Prussian blue framework have little affinity for H_2 . As an initial test of whether open coordination sites at the more electron-rich, carbon-bound metal centers might give rise to stronger interactions, we chose to study H_2 adsorption in $Co_3[Co(CN)_5]_2$ [11]. The hydrated form of this compound, $Co_3[Co(CN)_5]_2 \cdot 12H_2O$, features square pyramidal $[Co(CN)_5]^{3-}$ complexes linked by octahedrally-coordinated Co^{2+} ions in a Prussian blue type framework. With one exposed coordination site $[Co(CN)_5]^{3-}$ reacts reversibly with H_2 in solution to generate $[Co(CN)_5(H)]^{3-}$ [18]. However, this reaction is known to proceed through a mechanism that is bimolecular in $[Co(CN)_5]^{3-}$, which is probably not possible when the $[Co(CN)_5]^{3-}$ units are part of a rigid extended framework.

Dehydration of the vacancy-riddled $Co_3[Co(CN)_5]_2$ framework was accomplished by heating at 50 °C for 48 h under dynamic vacuum. Subsequent N_2 sorption measurements at 77 K revealed a type I isotherm, with application of the BET model affording a surface area of 730 m²/g. This is slightly lower than the 800 m²/g observed for $Co_3[Co(CN)_6]_2$ [7], potentially indicating some framework collapse. Hydrogen sorption experiments performed at 77 K once again produced a fully reversible isotherm (see Fig. 6). Note that the uptake of 1.4 wt.% at 890 Torr is also slightly below the 1.5 wt.% of $Co_3[Co(CN)_6]_2$ [7]. As before, H_2 binding enthalpy was determined by measuring additional data at 87 K (see Fig. 7).

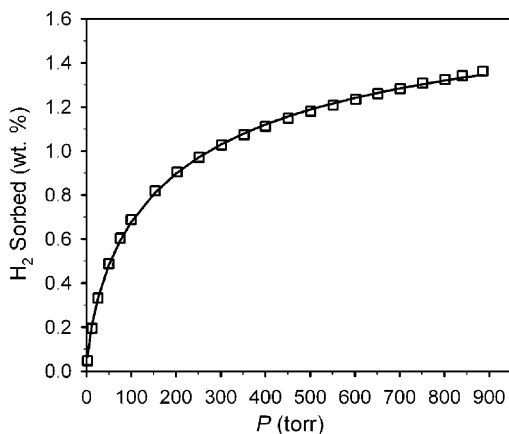


Fig. 6. Hydrogen sorption isotherm for the Prussian blue analogue $Co_3[Co(CN)_5]_2$. Solid line represents the best fits of the Langmuir–Freundlich (L–F) equation to the data.

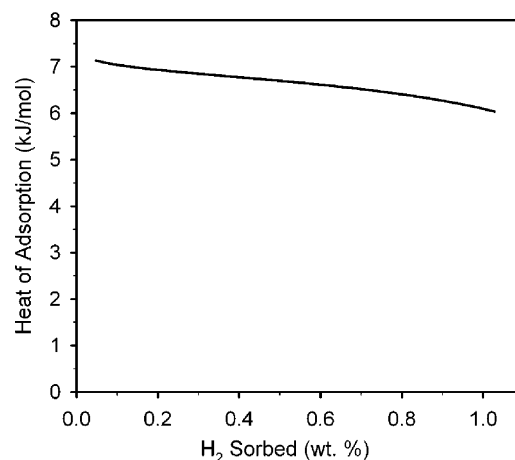


Fig. 7. Enthalpy of H_2 adsorption for $Co_3[Co(CN)_5]_2$.

Disappointingly, the results vary within the range 6.0–7.1 kJ/mol, which is quite comparable to the ranges of 6.3–6.9 kJ/mol measured for $Ga[Co(CN)_6]$ and 6.5–6.8 kJ/mol for $Co_3[Co(CN)_6]_2$ [7]. Thus, the exposed carbon-bound Co^{II} centers within $Co_3[Co(CN)_5]_2$ do not enhance the strength of the H_2 binding interactions.

4. Outlook

The results disclosed are consistent with a correlation between the concentration of framework vacancies and the hydrogen storage capacity of a Prussian blue analogue. The strength of the H_2 binding interaction, however, was not observed to be substantially higher for frameworks containing coordinatively-unsaturated metal centers. Future efforts to increase the adsorption enthalpy will be directed towards synthesizing and characterizing materials containing exposed metal sites of differing electronic character. In particular, we will focus on producing frameworks featuring more electron-rich metal centers, such as Cr^0 and Cu^+ , which are known to have higher affinities for H_2 due to increased π -backbonding into the H_2 σ^* orbital.

Acknowledgements

This research was funded by the Department of Energy. We thank the National Science Foundation for providing S.S.K. with a predoctoral fellowship.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.cattod.2006.09.018](https://doi.org/10.1016/j.cattod.2006.09.018).

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