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Communication

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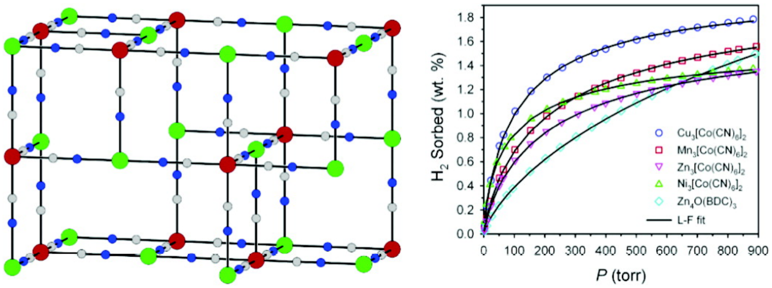

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Hydrogen Storage in the Dehydrated Prussian Blue Analogues $M_3[Co(CN)_6]_2$ (M = Mn, Fe, Co, Ni, Cu, Zn)

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Owing to its clean combustion and high heating value, hydrogen is under consideration as a replacement for fossil fuels in mobile applications. Its success in this role, however, relies in part upon development of an effective means of storage.[1] Although extensive effort has been directed toward storing hydrogen in nanostructured carbon, chemical hydrides, and metal hydrides,[1] such materials still exhibit limitations necessitating further research.[2−4] Recently, Yaghi and co-workers exposed the considerable potential for hydrogen storage in microporous coordination solids with robust three-dimensional frameworks and high surface areas.[5] Specifically, cubic frameworks consisting of tetrahedral $[Zn_4O]^{6+}$ units linked via linear aryldicarboxylates were shown to adsorb significant quantities of hydrogen reversibly, with $Zn_4O(BDC)_3$ (BDC = 1,4-benzenedicarboxylate) adsorbing 1.3 wt % H_2 at 77 K and 1 atm.[5b] This work was followed by reports of hydrogen storage in several different porous frameworks, most of which also contain aryldicarboxylates as the organic linker.[6] In such compounds, the primary interaction with hydrogen is thought to be through van der Waals contact with the framework.[5a] Here, we report the hydrogen storage properties for dehydrated Prussian blue analogues of the type $M_3[Co(CN)_6]_2$, wherein interactions with bridging cyanide ligands and/or coordinatively unsaturated metal centers lead to higher adsorption enthalpies.

Prussian blue analogues possess structures based upon a simple cubic $M[M'(CN)_6]$ framework, in which octahedral $[M'(CN)_6]^{n-}$ complexes are linked via octahedrally coordinated, nitrogen-bound M^{n+} ions. In Prussian blue itself, $Fe_4[Fe(CN)_6]_3{\cdot}14H_2O$, charge balance with the Fe^{3+} ions leads to vacancies at one-quarter of the $[Fe(CN)_6]^{4-}$ sites in the framework.[7] Remarkably, the water molecules (six Fe^{3+}-bound and eight solvate) filling the resulting cavities can be removed upon heating to leave the iron−cyanide framework intact.[8] By combining M^{2+} ions with $[M'(CN)_6]^{3-}$ complexes, one can generate even more porous Prussian blue analogues of formula $M_3[M'(CN)_6]_2{\cdot}xH_2O$, featuring vacancies at one-third of the hexacyanometalate sites. As with aromatic bridges, the polarizable π-electron clouds of the cyanide bridges in these materials can be expected to have some affinity for H_2, assuming porosity is retained upon dehydration. Moreover, H_2 may also be able to interact with the open coordination sites on the M^{2+} ions arising upon removal of the bound water molecules.

In view of their greater stability relative to M′ = Cr, Mn, or Fe,[9] we chose to examine the porosity and hydrogen storage properties of the Prussian blue analogues $M_3[Co(CN)_6]_2$ (M = Mn, Fe, Co, Ni, Cu, Zn). Hydrated forms of the six compounds were synthesized under identical conditions, as detailed in the Supporting Information. The X-ray powder diffraction patterns of the products were fully consistent with the usual Prussian blue structure type, and with the exception of $Ni_3[Co(CN)_6]_2{\cdot}15H_2O$, all displayed sharp, intense peaks. This single exception showed significantly broadened peaks, suggesting a much smaller crystallite size. Elemental analyses confirmed the composition of each compound and indicated the presence of less than 0.1 equiv of potassium per formula unit. The solids were completely dehydrated by heating at 95 °C for 48−60 h under dynamic vacuum. Attempts to dehydrate the compounds more rapidly by heating at higher temperatures resulted in lower gas sorption capacities, presumably as a result of partial framework collapse.

The porosity of the dehydrated samples was probed via argon sorption measurements performed at 87 K. To our knowledge, these are the first gas sorption measurements reported for any Prussian blue analogue, with the exception of Prussian blue itself.[10] All compounds showed Type I sorption isotherms characteristic of microporous materials (see Figures S13−S18 in the Supporting Information). The surface areas, calculated by applying the BET model to the data, are listed in Table 1 and range from 560 m^2/g for $Ni_3[Co(CN)_6]_2$ to 870 m^2/g for $Mn_3[Co(CN)_6]_2$. With the exception of the former compound, which exhibited broadened X-ray diffraction peaks, the variations in surface area are only slight and are likely due to differences in the unit cell volumes and perhaps the degree of framework collapse. Note that these are very high surface areas, much higher than the 49 m^2/g estimated for dehydrated Prussian blue,[10] suggesting that the metal−cyanide frameworks remain largely intact upon dehydration. Indeed, the results are comparable to the 904 m^2/g measured for zeolite Y, the highest surface area observed for any known zeolite.[11]

Using the same volumetric apparatus, H_2 sorption isotherms were collected at 77 K for the six dehydrated Prussian blue analogues and $Zn_4O(BDC)_3$ (see Figure 1). Significant differences are apparent in both the shapes of the isotherms and the amounts of H_2 adsorbed. Table 1 lists the storage capacities at the maximum attainable pressure of 890 Torr. The values for the cyano-bridged frameworks compare favorably with the 1.5 wt % adsorbed by $Zn_4O(BDC)_3$, varying from 1.4 wt % in $Zn_3[Co(CN)_6]_2$ to a maximum of 1.8 wt % in $Cu_3[Co(CN)_6]_2$. Assuming no reduction in the unit cell dimensions as a result of dehydration, this gives a minimum storage density of 0.025 kg H_2/L for $Cu_3[Co(CN)_6]_2$, compared to just 0.0092 kg H_2/L for $Zn_4O(BDC)_3$. Hydrogen uptake was found to be fully reversible for all of the compounds, and $Cu_3[Co(CN)_6]_2$

Table 1. Sorption Properties of Dehydrated Prussian Blue Analogues and $Zn_4O(BDC)_3$

compound	SA[a] (m^2/g)	wt % H_2[b]	kg H_2/L[b,c]	ΔH_{ads}[d] (kJ/mol)
$Mn_3[Co(CN)_6]_2$	870	1.6	0.019	5.3−5.9
$Fe_3[Co(CN)_6]_2$	770	1.4	0.017	6.3−6.6
$Co_3[Co(CN)_6]_2$	800	1.5	0.019	6.5−6.8
$Ni_3[Co(CN)_6]_2$	560	1.4	0.018	6.9−7.4
$Cu_3[Co(CN)_6]_2$	730	1.8	0.025	6.7−7.0
$Zn_3[Co(CN)_6]_2$	720	1.4	0.018	6.3−6.5
$Zn_4O(BDC)_3$	3400	1.5	0.0092	4.7−5.2

[a] Surface area calculated using the BET model. [b] Measured at 77 K and 890 Torr. [c] Calculated assuming no reduction in unit cell size upon dehydration. [d] Determined using the method described in the Supporting Information.

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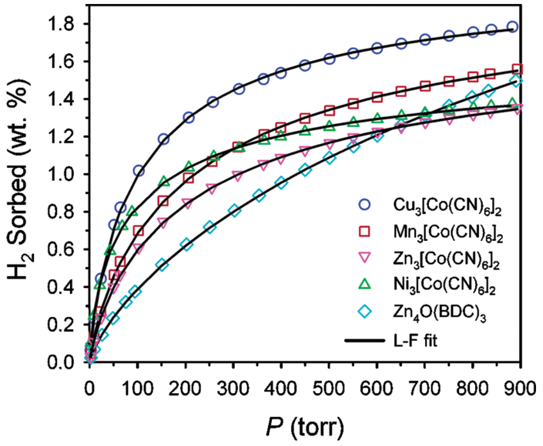

Figure 1. Hydrogen sorption isotherms for the Prussian blue analogues $M_3[Co(CN)_6]_2$ (M = Mn, Ni, Cu, Zn) and $Zn_4O(BDC)_3$. Isotherms for $Fe_3[Co(CN)_6]_2$ and $Co_3[Co(CN)_6]_2$ are not shown for clarity, but are similar to those of $Zn_3[Co(CN)_6]_2$ and $Mn_3[Co(CN)_6]_2$, respectively. Solid lines represent the best fit of the Langmuir−Freundlich (L−F) equation to the data.

showed no detectable loss in capacity after five adsorption/desorption cycles.

Fits to the hydrogen sorption data employing the Langmuir equation[12] showed large deviations at both low and high pressures. In contrast, fits utilizing the Langmuir−Freundlich equation[13] were accurate over the entire measured pressure range (see Figure 1). By extrapolating the results to infinite pressure, reliable estimates could be obtained for the maximum hydrogen uptake in the Prussian blue analogues. The predicted maximum storage capacities range from 1.7 wt % for $Ni_3[Co(CN)_6]_2$ to 2.1 wt % for both $Mn_3[Co(CN)_6]_2$ and $Cu_3[Co(CN)_6]_2$.[14] There is no apparent correlation between these values and the surface areas of the metal−cyanide frameworks. For example, $Zn_3[Co(CN)_6]_2$ and $Cu_3[Co(CN)_6]_2$ have nearly identical surface areas of 720 and 730 m^2/g, but are predicted to saturate at 1.8 and 2.1 wt % H_2, respectively. The latter corresponds to a storage density of at least 0.029 kg H_2/L, or 8.7 H_2 molecules per face-centered cubic unit cell. This, together with the availability of eight Cu^{2+} binding sites per unit cell, suggests that hydrogen may indeed be interacting with the coordinatively unsaturated metal centers within these frameworks.

The strength of the interaction with the framework was probed by measuring a second hydrogen sorption isotherm for each compound at 87 K. Taking both the 77 and 87 K data, a variant of the Clausius−Clapeyron equation was then used to calculate the enthalpy of adsorption as a function of the quantity of hydrogen adsorbed (see Figure 2).[12] To our knowledge, these represent the first experimental assessments of H_2 binding enthalpies for any microporous coordination solid. While each compound displays a relatively narrow range of enthalpies, noticeable differences arise as the M^{2+} cation is varied in the $M_3[Co(CN)_6]_2$ frameworks. With the exception of M = Ni, the observed trend matches the Irving−Williams stability order.[15] The larger enthalpy of adsorption for $Ni_3[Co(CN)_6]_2$ is, again, likely associated with a smaller crystallite size. Importantly, the enthalpies of adsorption for the Prussian blue analogues are all significantly higher than the 4.7−5.2 kJ/mol observed for $Zn_4O(BDC)_3$, with $Cu_3[Co(CN)_6]_2$ being ∼2 kJ/mol greater over the measured pressure range.[16] Thus, the cyano-bridged frameworks can be expected to store hydrogen at higher temperatures and lower pressures.

Future work will focus on increasing the hydrogen storage capacity of these materials through the synthesis of cyano-bridged frameworks incorporating lighter, main group metal ions. In addition, the introduction of metal centers with higher H_2 binding affinities will be investigated as a means to further increase the temperature at which hydrogen can be stored.

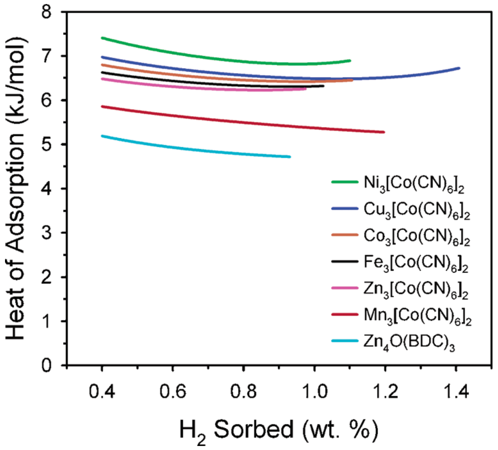

Figure 2. Enthalpy of H_2 adsorption for $M_3[Co(CN)_6]_2$ (M = Mn, Fe, Co, Ni, Cu, Zn) and $Zn_4O(BDC)_3$.

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Supporting Information Available: Detailed experimental procedures, the method used to calculate H_2 adsorption enthalpies, powder X-ray diffraction patterns, thermogravimetric analyses, argon sorption data, and additional hydrogen sorption data. This material is available free of charge via the Internet at http://pubs.acs.org.

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