Reversible hydrogen gas uptake in nanoporous Prussian Blue analogues†

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The family of dehydrated nanoporous Prussian Blue analogues, $M^{II}_3[Co^{III}(CN)_6]_2$ (M^{II} = Mn, Fe, Co, Ni, Cu, Zn, Cd), which contain coordinatively unsaturated divalent metal cations, undergoes reversible sorption of hydrogen gas up to 1.2 wt% (at 77 K, 101.3 kPa), the capacity of which depends on the metal ion.

The safe and efficient storage of hydrogen gas represents a pivotal challenge in the development of hydrogen as an alternative energy carrier.[1] A need to move away from the dangers associated with high pressure and cryogenic methods has pushed attention towards storage by chemisorption into metal hydrides and by physisorption into porous materials.[2,3] Of these two approaches, the physisorption of surface monolayers of dihydrogen has a number of recognised advantages, in particular, the speed of this process and the absence of a long-term decrease in sorption capacity associated, for example, with metal oxidation. Mass storage uptakes equivalent to those of metal hydrides, however, are yet to be achieved. In the past year, particular interest has arisen in the storage capabilities of porous molecular frameworks.[4] In comparison with other nanoporous phases such as zeolites, these materials have lower framework densities and higher surface areas[5] and are, therefore, ideally suited to high hydrogen mass loadings.

† Electronic Supplementary Information (ESI) available: Syntheses, thermogravimetry and adsorption data and analyses. See http://www.rsc.org/suppdata/cc/b5/b502850g/
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Separate to the challenge of maximising surface area per mass is the need to increase the strength of dihydrogen binding, thereby enhancing the efficiency of monolayer formation; the very low mass of the dihydrogen molecule, whilst responsible for its excellent energy density, leads to considerable challenges in maximising the host–guest interaction.

Here we report reversible sorption of hydrogen gas in a family of nanoporous Prussian Blue analogues $M^{II}_3[Co^{III}(CN)_6]_2$ (M^{II} = Mn, Fe, Co, Ni, Cu, Zn, Cd) (A_M) in which the pore walls are lined by bare metal sites capable of interacting with the dihydrogen molecule. The importance of such sites to dihydrogen physisorption is suggested by the absence of loading in related molecular frameworks, $M^{II}Pt^{IV}(CN)_6$ (B_M), which lack these sites.

The Prussian Blue family are amongst the earliest known coordination compounds and their diverse magnetic and electronic properties have been studied extensively.[6] Until now their gas sorption properties have remained largely unexplored.[7] The structural topology characteristic of the Prussian Blues is a simple cubic (α-Po type) network, with linear bridging of the octahedral metal ions by cyanide anions which defines pores within the framework.[8] There are $Co^{III}(CN)_6^{3-}$ lattice vacancies at one third of the Co^{III} sites disordered throughout the structure. In the as synthesised hydrated phase, $M^{II}_3[Co^{III}(CN)_6]_2[H_2O]_6.x\{H_2O\}$ (A'_M, x = 6–8), the coordination sphere of M^{II} ions surrounding vacancies are completed by coordinated water molecules, with non-coordinated guest water molecules located in the pores on two crystallographically distinct sites (see Fig. 1). Coordinated and non-coordinated water can be removed simultaneously by heating at moderate temperatures (350–425 K).†
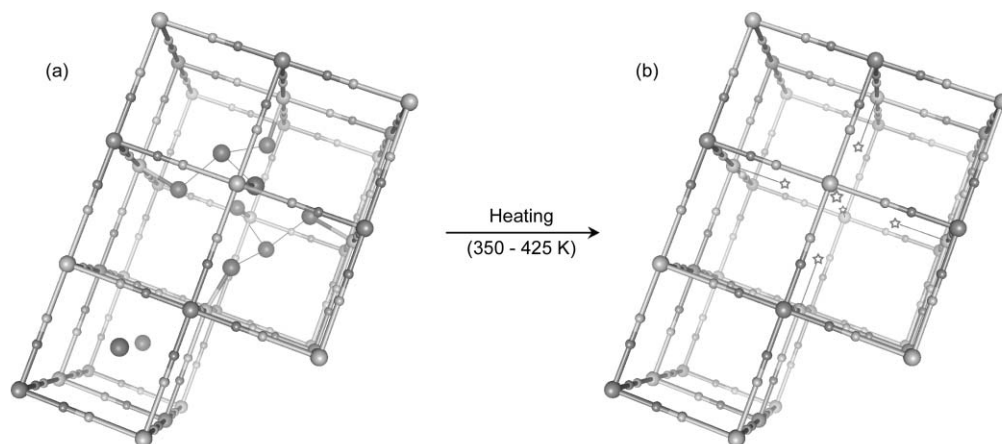

Fig. 1 The cubic network structure of the Prussian Blue analogues in the hydrated phase A'_M (a) showing coordinated and hydrogen bonding guest water molecules and the dehydrated phase A_M (b) showing coordinatively unsaturated metal sites (stars) surrounding the $Co^{III}(CN)_6^{3-}$ lattice vacancies.
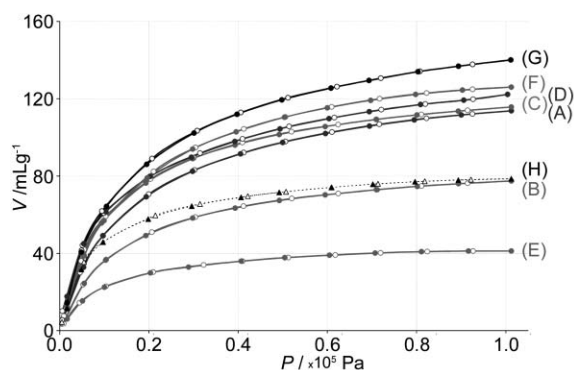
Fig. 2 Hydrogen sorption (closed circles) and desorption (open circles) isotherms in nanoporous Prussian Blue analogues, $\mathbf{A_M}$, M = Mn, Fe, Co, Ni, Cu, Zn, Cd (A–G), at 77 K. Sorption volumes are given for STP. Data for the zeolite H-ZSM-5 (H) are shown for comparison.

The robust nature of the framework, facilitated by the short, rigid connectivity and three-dimensionality, enables the open pore structure defined by the framework to be retained in the absence of guests to leave coordinatively unsaturated metal centres.

The sorption and desorption of hydrogen gas (99.999% purity) were determined volumetrically on freshly dehydrated samples of $\mathbf{A_M}$ at 77 K (see Fig. 2). The isotherms showed fully reversible hydrogen gas sorption resembling an IUPAC type Ib isotherm, typical of a microporous material.[9] There was no evidence of hysteresis. Hydrogen sorption at $P \approx 1.01 \times 10^5$ Pa ranged between 40 and 140 mL g^{-1}, the maximum uptake observed for $\mathbf{A_{Cd}}$ corresponding to a 1.24 wt% loading. The validity of these data was verified by the correspondence of measured hydrogen sorption with reported values for the high surface area zeolite, H-ZSM-5,[3] to eliminate the possibility of systematic errors in sorption measurement associated with gas impurities.

Sorption capacities for $\mathbf{A_M}$ decrease approximately in order M^{II} = Cd > Zn, Ni > Mn, Co > Fe > Cu.[10] This trend in hydrogen sorption correlates well with micropore volumes extracted from nitrogen sorption isotherms with the exception of Fe, for which considerably lower nitrogen sorption was observed.

As the measurements were undertaken away from critical conditions, the maximal sorption quantities at $P \approx 1.01 \times 10^5$ Pa do not represent saturation loadings. Sorption isotherms were fitted with the generalised-Freundlich model,[11] which yielded limiting sorption capacities of between 58.9 and 172.8 mL g^{-1}.† The maximum capacity for $\mathbf{A_{Cd}}$, which exceeds 1.6 wt%, corresponds to approximately 1 dihydrogen molecule per pore or bare metal site, or 6 dihydrogen molecules per formula unit. The rate of saturation obtained from this modelling also yields an indication of the relative favourability of the host–guest interaction, which decreases in the order Zn ≈ Co > Cd > Ni > Fe ≈ Mn > Cu.

In comparison to $\mathbf{A_M}$, no hydrogen gas sorption was evident in corresponding measurements on the related, robust nanoporous phase, Cd^{II}Pt^{IV}(CN)$_6$, $\mathbf{B_{Cd}}$, which shares the cubic lattice and pore structure but lacks lattice vacancies and bare metal sites. This observation suggests two possible causes for the favourable hydrogen sorption into the $\mathbf{A_M}$ phase: the existence of larger pores and/or pore windows associated with the vacancy sites; and/or the ability of the coordinatively unsaturated metal centres

to interact favourably with the dihydrogen molecule. The potential importance of bare metal sites in dihydrogen physisorption has also recently been put forward for zeotype materials.[12] We do not discern a notable trend between hydrogen uptake and total pore volume or d-electron configuration. This is not unexpected as we believe the total hydrogen uptake to be a combined function of surface area and enthalpy of sorption, the latter of which is influenced both by surface chemistry and the pore geometry which best complements the hydrogen dimensions (0.41 nm diameter). Spectroscopic and structural studies are planned to probe the nature of the dihydrogen binding interaction in these Prussian Blue phases.

In conclusion, we show that the vacancy-containing Prussian Blues, $\mathbf{A_M}$, are able to adsorb significant volumes of molecular dihydrogen reversibly at moderate pressures and at temperatures well above the hydrogen boiling point (20.5 K). Although the current materials are not directly applicable for hydrogen storage with respect to the US Department of Energy guidelines (6 wt% target),[13] the broad and versatile nature of this family makes this a model system for investigating the nature of the dihydrogen physisorption interaction, including for decoupling the influences of pore size and surface functionality to dihydrogen binding. We note here the potential for increasing the hydrogen sorption in these phases through modification of the framework structure and composition, and, further, for extending the incorporation of bare metal sites into other nanoporous molecular phases.

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10 Sorption at 1.01×10^5 Pa: $\mathbf{A_{Cd}}.4.8\{H_2\} > \mathbf{A_{Zn}}.3.5\{H_2\}$, $\mathbf{A_{Ni}}.3.3\{H_2\} > \mathbf{A_{Mn}}.3.0\{H_2\}$, $\mathbf{A_{Co}}.3.1\{H_2\} > \mathbf{A_{Fe}}.2.1\{H_2\} > \mathbf{A_{Cu}}.1.1\{H_2\}$.

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