

Hydrogen Storage in Prussian Blue Analogues: H₂ Interaction with the Metal Found at the Cavity Surface

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In open framework Prussian blue analogues, all of the metal atoms linked at the N end of the CN groups are found at the surface of the cavities with an unsaturated coordination environment. These metal sites are available for a specific interaction with guest species. To shed light on the H₂ interaction with these metal sites, H₂ adsorption isotherms in Ni_{3-x}Mn_x[Co(CN)₆]₂, Ni_{3-x}Co_x[Co(CN)₆]₂, Ni_{3-x}Cd_x[Co(CN)₆]₂, and Co_{3-x}Mn_x[Co(CN)₆]₂ were recorded and evaluated. According to the obtained data for the adsorption heat values, the strongest H₂–metal interaction was found for Ni. The same evidence is obtained from the fitting of the isotherms using the osmotic model, where the value for the osmotic parameter (*g*) senses the strength for the guest–host interaction. The probable origin of that stronger interaction for the Ni atom is discussed. The information derived from these mixed series was complemented with an analogue study for T₃[Co(CN)₆]₂ and T₃[Ir(CN)₆]₂, with T = Mn, Co, Ni, Zn, Cu, and Cd. The strength for the guest–host interaction in these two simple series follows the order: Ni > Cu > Co ~ Cd > Mn ~ Zn. For the series T₃[Co(CN)₆]₂, H₂ adsorption isotherms up to 7600 Torr were recorded, confirming that the strongest H₂–metal interaction corresponds to Ni and Cu. The samples to be studied were characterized from energy-dispersed spectroscopy, X-ray diffraction, infrared, and CO₂ adsorption data.

1. Introduction

Hydrogen, because of its clean combustion (producing water as a byproduct), is being considered as potential replacement for fossil fuel derivatives, particularly for mobile technologies.¹ Fossil fuels are nonrenewable energy resources, and the emission of CO₂, as the main byproduct of their combustion, is responsible for global warming and the related climate changes. In addition, the oxidation of hydrogen liberates a large amount of energy, 142 kJ/g, 3 times the value obtained from gasoline (47.5 kJ/g). The use of hydrogen as an energy bearer involves three challenges: the production from the water splitting, for instance, because it is a secondary bearer and not a primary source, the availability of a safe and economically viable storage method, and its use through appropriate fuel cells. The concerning state of art suggests that a lot of basic research is required to support a hydrogen-based economy realization in the near future. With regard to the storage, all of the reported results remain short with respect to the technological requirements for practical applications. The established target [2015 U.S. Department of Energy (DOE) targets], in that sense, is 9 wt % for a reversible process and relatively short storage-release times.²

The difficulties for the H₂ storage are related to the weak H₂–H₂ intermolecular interactions (mainly of dispersive nature), which result in its low critical temperature (32.97 K). This is quite a low temperature to allow for H₂ handling in the liquid state for massive practical applications as combustible in mobile technologies, even when for years liquid H₂ has been used as fuel in test vehicles. Furthermore, the liquefaction process consumes about 40% of the energy to be generated. The storage in containers at high pressure also appears to be impractical, at least for mobile applications. For a pressure of 345 atm, a density of 22 g/L is obtained, relatively low compared to 71 g/L for the liquid state. From these facts, several routes are being studied to increase the storage density, among them, the physical adsorption in porous solids.^{3–5} This is an attractive H₂ storage method because of its reversibility. However, to date, the reported gravimetric density of hydrogen adsorbed close to the atmospheric conditions remains well below the target of 9 wt %. Several families of porous materials have been evaluated in that sense, among them, carbon-based solids,³ zeolites,⁴ and metal–organic frameworks.^{5–7} Recently, also porous coordination polymers, of Prussian blue (PB) type, have received

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