Hydrogen Storage in Copper Prussian Blue Analogues: Evidence of H₂ Coordination to the Copper Atom

L. Reguera,[†] C. P. Krap,[‡] J. Balmaseda,^{||} and E. Reguera^{*,‡,§}

Facultad de Química, Universidad de La Habana, La Habana, Cuba, Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada-Unidad Legaria, Instituto Politécnico Nacional, México, D.F., Departamento de Polímeros, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, México, D.F. C.P. 04510, and Instituto de Ciencia y Tecnología de Materiales, Universidad de La Habana, La Habana, Cuba.

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The hydrogen adsorption in porous Prussian blue analogues shows the highest value for copper, suggesting the possibility that a direct interaction between the copper atom and the hydrogen molecule is established. The bonding of copper (2+) to the CN group of cyanometallates shows a unique behavior. The trend of copper to receive electrons in its 3d hole to adopt an electronic configuration close to $3d^{10}$ is complemented by the ability of the CN group to donate electrons from its 5σ orbital, which has certain antibonding character. Because of this cooperative effect, the electronic configuration of the copper atom at the cavity surface is close to Cu(+). The resulting large availability of electron density on the copper atom favors its interaction with the antibonding σ^* orbital of the hydrogen molecule. The charge removed from the metal t_{2g} orbitals is compensated (donated) by H₂ through a side-on σ interaction. From these combined mechanisms, where H₂ behaves as an acceptor-donor ligand for the copper atom, the high ability that copper hexacyanometallates show for the hydrogen storage could be explained. This hypothesis is supported by the obtained hydrogen adsorption data for Cu₃[Ir(CN)₆]₂, Cu₃[Fe(CN)₆]₂, Cu₂[Fe(CN)₆], Cu[Pt(CN)₆], and Cu_{3-x}Mn_x[Co(CN)₆]₂, where $0 \le x \le 3$, and also by the estimated values for the involved adsorption heats. The studied samples were previously characterized using X-ray diffraction, thermogravimetry, and infrared and Mössbauer spectroscopies.

1. Introduction

Hydrogen, because of its large heat combustion, 572 kJ/mol, and environmentally compatible byproduct, water, is being considered as an alternative to fossil fuel derivatives in mobile applications. However, molecular hydrogen has a low critical temperature (32.7 K) to be handled in liquid state for practical applications as fuel. Thereby, one of the challenges for the development of an energetic technology based on hydrogen is the availability of an appropriate method for hydrogen storage. The established target (2010 DOE targets) in that sense is 6 wt %, for a reversible process and relatively short storage-release times.¹ To date, the highest hydrogen storage capacity in materials has been reported for chemical and metal hydrides,² and for some cases, above that target.³ However, the desorption process of hydrogen stored as hydrides usually requires relatively high temperatures of heating (>500 K), and this storage process is not always reversible.⁴ An attractive option in order to have a reversible process is the storage through physical adsorption in porous materials; however, to date, the reported gravimetric density of hydrogen adsorbed at atmospheric pressure remains well below that target of 6 wt %.5 From these facts, the development of new porous solids with high potential for hydrogen adsorption and an appropriate understanding on the driving forces that determine the stability of the hydrogen molecule within nanometric size cavities are among the main research subjects related to hydrogen storage.

Related to its physical properties, H₂ storage in porous solids through purely physical interactions, at least up to the technologically required gravimetric density, represents a huge challenge. The paradigm for the hydrogen storage is probably found in the H₂ coordination chemistry.⁶ The H₂ binds side-on to the metal center through σ -donation to a vacant metal d orbital to form a coordination bond. This interaction is stabilized when a fraction of the metal electrons populates the H₂ σ^* orbital by means of a back-bonding interaction. The hydrogen molecule behaves as a donor–acceptor ligand. From this fact, the H₂ adsorption in porous materials with open metal sites has received notable attention.^{7–19} The metal hydride formation could be considered a limited case of that coordinating interaction where a progressive weakening for the H····H bond leads to the hydrogen molecule dissociation.⁶

Several types of porous solids with open transition metal sites located at the channels and/or cavities surface have been evaluated for the hydrogen storage, among them, metal–organic frameworks (MOFs)^{7–13} and cyanometallates.^{14–19} In practically all these materials, the metal is found in the divalent state. This could favor the side-on σ -donation to the metal from the hydrogen molecule but not the related stabilizing metal-to-ligand back-bonding interaction. The existence of an excessively high positive charge on the metal does not favor the back-bonding charge donation to the ligand. For copper in porous Prussian blue (PB) analogues, a unique scenario is found because the valence for the copper atom located at the cavity surface is close to Cu(+).²⁰ The copper (2+) atom has a certain trend to receive electrons in its 3d hole in order to reach an electronic

^{*} To whom correspondence should be addressed. E-mail: ereguera@ yahoo.com.

[†] Facultad de Química, Universidad de La Habana.

[‡] Instituto Politécnico Nacional.

Universidad Nacional Autónoma de México

[§] Instituto de Ciencia y Tecnología de Materiales, Universidad de La Habana.