

Prussian Blue Analogues: Prototype of Porous Solids for H₂ Storage and of Tunable Molecular Magnets

Reguera, E.,¹ Rodriguez-Hernandez, J.,¹ and R. Martínez-García¹

¹Universidad de la Havana - C. Havana Havan Cuba

INTRODUCTION

The non-availability of an appropriate storage medium for hydrogen is probably the main challenge for a hydrogen-based energetic technology development. The hydrogen oxidation produces 572 kJ/mol (three times the energy obtained from gasoline), with water as by-product. However H₂ has an extremely low critical temperature (32.9 K) to be handled in liquid phase. The option of high pressure vessel also appears to be impractical, for a pressure of 345 atm, a storage density of 15 g/L is obtained, well below the value of 71 g/L corresponding to the liquid state. From these facts, the storage in porous solids is being evaluated due to its high reversibility. Among the considered materials in that sense, Prussian blue (PB) analogues have been considered in that sense due to the availability of metal center with open coordination sites on the cavities surface [1, 2]. These sites are available for a specific interaction with the hydrogen molecule [3, 4]. In this contribution we are reporting the behavior of PB analogues on heating for the water removal from the porous framework and then during their cooling for the hydrogen storage ability evaluation. The changes observed in the materials electronic structure on their dehydration also shed light on the possibility of magnetic properties modulation in porous solids through adsorbed species.

EXPERIMENT

The materials to be studied, T₃[Co(CN)₆]₂.xH₂O with T = Mn, Co, Ni, Cu, Zn, Cd were prepared using a previously reported procedure [5]. All the samples were characterized from chemical analysis, X-ray diffraction (XRD), infrared (IR) and thermogravimetric (TG) data. XRD powder patterns were recorded under vacuum and at different temperatures of heating until to obtain an anhydrous solid and then on cooling down to 12 K. From the recorded XRD patterns the structural stability and the evolution of the cell edge were evaluated and the results used to understand the H₂ adsorption data for analogue compositions, and also to explain the modulation of the magnetic properties through adsorbed species.

RESULTS AND DISCUSSION

When the samples are submitted to vacuum, without heating, a fraction of the crystal water evolves and it is detected as a slight cell contraction (figure 1). Then, on heating, the

water molecules evolution continues until to obtain an anhydrous solid below 373 K. This process is accompanied of a continuous cell contraction. Within the cavities the available coordination sites for the T metal are occupied by water molecules. The filling of the cavity volume is completed by weakly bonded water molecules stabilized through hydrogen bonding interactions with the coordinated ones. The removal of both weakly bonded and coordinated waters leads to a reduction for the cell size and for the cavity volume (Figure 1). Once the coordinated water molecules are removed, all the T metal interaction is concentrated on the framework CN ligand. This leads to an increase for the metal charge subtraction from the CN group through its 5σ orbital, which has certain anti-bonding character, reducing the T-N distance and at the same time also inducing a greater π-back donation from the inner metal toward the CN group, shortening the Co-C distance. From these combined effects a shorter T-N-C-Co-C-N-T chain length results (Figure 1). This effect depends on the T metal nature. For a metal like Cu (2+), with a 3d⁹ electronic configuration and with a high ability to subtract charge from the CN ligand, the cell contraction on the water removal is the smallest one within the studied series of materials [5]. When the anhydrous sample is cooled certain charge redistribution within the chain takes place and no addition a cell contraction is observed, which is interpreted as a zero thermal expansion behavior. Such mechanism could be used to explain the reported negative thermal expansion in PB analogues [6]. The above discussed mechanism to explain the cell contraction observed on the water removal also explains the modulation for the magnetic properties in PB analogues by adsorbed species [7]. The adsorbed species in this family of materials modifies the electronic structure of the bulk sample and, in consequence, its physical properties, among them, the magnetic order temperature.

CONCLUSION

A mechanism to explain the cell contraction in PB analogues on the water removal is provided. The cell contraction is closely related to the solid electronic structure modification reducing the effective charge on the metal found at the cavity surface. This increases the metal ability to interact with the hydrogen molecule through a coordination bond. That mechanism also explains the modulation for the magnetic properties in PB analogues through the adsorption of guest species within the cavities. The results herein summarized are available from references [3–5, 7].