Materials for Hydrogen Storage: Low temperature Structural Transformation in Pillared 2D Solids, T[Ni(CN)$_4$].2pyz, T =Mn, Zn, Cd

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INTRODUCTION

The incorporation of pillars in 2D solids allows the preparation of 3D porous materials with tailored cavity size and shape. In this sense, planar coordination polymers based on tetracyanometallates, T[M(CN)$_4$] with T = Mn, Fe, Co, Ni, Cu, Zn, Cd; M = Ni, Pd, Pt, appear as an ideal prototype of 2D solids to be considered. The metal centers at their surface contain available coordination sites which can be used as anchoring positions for the ligands to be used as pillars. Under certain preparative conditions, a fraction of the available metal coordination sites could be maintained free of ligands to allow their interaction with the guest molecule within the cavities. Such possibility provides an ideal system of porous 3D solids for studies related with the hydrogen storage in nanocavities; in fact, two studies in that sense has already been reported [1, 2]. All the studies related with the hydrogen storage in porous solids are carried out under cryogenic conditions, usually at 77 K. For some cyanometallates negative thermal expansion behavior has been reported [3], which could be interpreted as evidence of charge redistribution within the T-N-C-M-C-N-T chain on the temperature change, particularly under cryogenic conditions. This suggests that in 2D pillared solids low temperature structural transformation could be present, particularly for pillars of certain flexibility and where the electronic structure of layers and pillars remains strongly coupled. Such possibility is explored in this contribution. As prototype of pillared 2D solids T[Ni(CN)$_4$].2pyz, with pyz = Pyrazine were used.

EXPERIMENT

The layered solids T[Ni(CN)$_4$] were obtained when mixing diluted aqueous solutions of the tetracyanonickelate ion, $[Ni(CN)_4]^{2-}$, and of divalent transition metals (T= Mn, Zn and Cd). The layers are exfoliated in a 0.3M solution of citric acid followed by addition of a pyrazine (0.07M) solution. The formation of the pillared solid is achieved when the solution pH is adjusted to be in the 4-5 range, by adding the appropriate amount of diluted citric acid. The HR-XRD powder patterns were collected at the XPD-10B beamline at the LNLS synchrotron radiation facility. The wavelength used was 1.549950 Å (7.9998 keV).

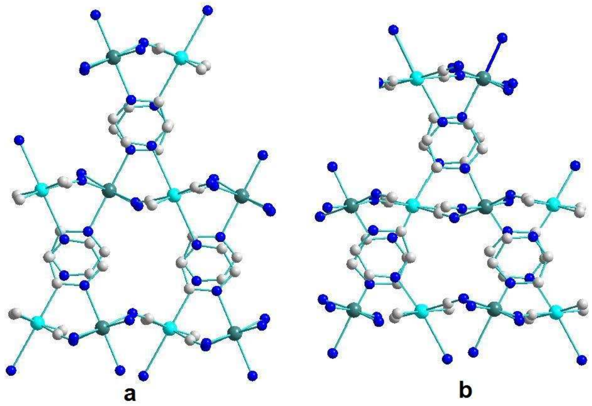

FIG. 1: Atomic packing within the a) orthorhombic, b) monoclinic unit cell for the series T[Ni(CN)$_4$].2pyz with T= Mn, Zn, and Cd.

RESULTS AND DISCUSSION

The crystal structures and related properties for the materials to be studied were already reported in a recent paper [4]. These solids crystallize with an orthorhombic unit cell (Pnc2 space group) with two molecules per unit cell (Z = 2). All the available metal coordination sites on neighboring layers are occupied by pyrazine molecules, which form T-pyz-Ni bridges, adopting a crossed configuration along the c axis (Figure 1). This configuration for the T-pyz-Ni bridges is related with the positions for Ni and T metals on the layers. Due to the non-equivalence for the T-pyz and Ni-pyz interactions, in the pillared solids the layers appears as rippled sheets (Figure 1). When HR-XRD powder patterns were recorded at 77 K and compared with those obtained at room temperature, the occurrence of a structural transformation was noted. This is illustrated in Figure 2, Inset, where certain splitting for several peaks is observed. The new pattern was indexed with a monoclinic unit cell (Pc space group). From HR-XRD powder patterns recorded at different temperatures above 77 K, the temperature of transformation was found to be in the 180-200 K range. This is reversible process. The patterns corresponding to temperatures above 200 K belong to the room temperature phase. The structural study was complemented with measurements of the involved change for the specific heat capacity at constant pressure (Cp). From the Cp vs T curves the transformation temperature was found to be: Mn: 192K, Zn: 185K, Cd: 198K. Such structural transformation was attributed to a change for the electronic configuration within the layers