

Porous Transition Metal Hexacyanoferrates (II) with High Available Free Volume: Framework Stability

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INTRODUCTION

Transition metals hexacyanomellates have received notable attention as prototype of porous solids for hydrogen storage in the last five years [1–12]. Within this family of coordination compounds for Prussian blue analogues at the cavities surface metal centers with open coordination sites, six per $[M(CN)_6]$ vacancy, are available for a specific interaction with the hydrogen molecule. At low pressure these sites determine the amount of H_2 molecules that can be adsorbed. At high pressures (above atmospheric conditions) the H_2 storage capacity would be determined by the available free volume. From this fact, an evaluation on the porous framework topology and its stability under vacuum and heating of PB analogues with extremely high free volume is recommended. During the sample preparation for H_2 storage evaluation the structure free volume must be liberated from crystal water molecules and then H_2 is adsorbed under cryogenic conditions, usually using N_2 bath. In this activity report the results obtained on that subject are summarized. In PB analogues the porosity is related to the amount of $[M(CN)_6]$. In PB, $Fe_4[Fe(CN)_6]_3$ the available free volume is due to 1/4 of vacant $[Fe(CN)_6]$ sites. For M^{III} and T^{2+} combinations compounds of formula unit $T_3[M(CN)_6]_2$ are formed with 1/3 of building block vacancies. For M^{II} and T^{2+} in principle $T_2[M(CN)_6]$ with an extremely high porosity could be formed. To the best of our knowledge, before this study, except for $T = Mn, Cd$ [13], the preparation and characterization of such materials have not been reported.

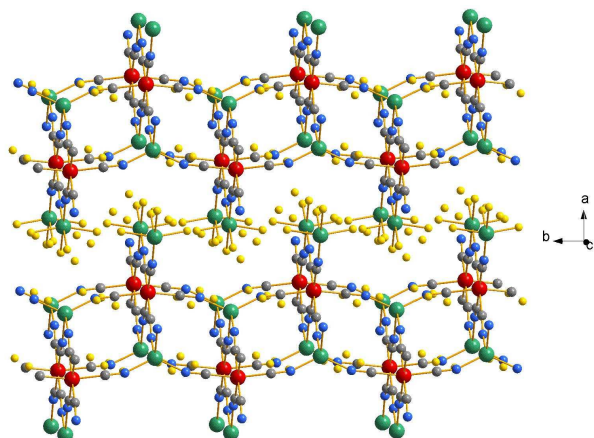


FIG. 1: Structure of stacked layers for $Co_2[Fe(CN)_6].xH_2O$. These layers remain linked through a network of hydrogen bonding interactions between coordinated and weakly bonded water molecules.

EXPERIMENT

$T_2[Fe(CN)_6]$ with $T = Co, Ni, Cu, Zn$ were prepared by the precipitation method from T^{2+} and $[Fe(CN)_6]^{4-}$ solutions. As source of the $[Fe(CN)_6]^{4-}$ anion, ferrocyanic acid, $H_4[Fe(CN)_6]$ prepared in situ was used. When the solids are precipitated from solutions containing an alkaline ion, non-porous materials are formed. The obtained powders were characterized by chemical analyses, and IR, Mössbauer, TG and XRD data. Their crystal structures were solved and refined from XRD powder patterns. The materials behavior on heating for the crystal water removal and on cooling under vacuum was study from HR-XRD data collected at XPD-10B beam line of the LNLS synchrotron radiation facility. The structural study was complemented with H_2 adsorption isotherms collected at 75 K.

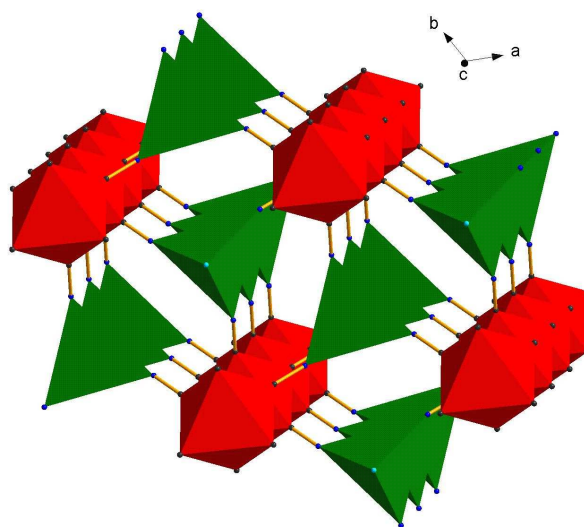


FIG. 2: Porous framework for $Zn_2[Fe(CN)_6].2H_2O$

RESULTS AND DISCUSSION

Figures 1-3 show the refined framework, as hydrated phases, for the materials under study. $Co_2[Fe(CN)_6].xH_2O$ crystallizes with a layered structure with the Co atom in both octahedral, $CoN_2(H_2O)_4$, and tetrahedral, CoN_4 , coordination. Neighboring layers remain through a network of hydrogen bonding interaction of weakly bonded water molecules with the coordinated ones. $Zn_2[Fe(CN)_6].xH_2O$ crystallizes