

Mixed valences system in cobalt iron cyanide. Microporous structure stability

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Abstract Divalent transition metal hexacyanoferrates(III) have a microporous framework appropriate for separation and storage of small molecules. The nature of such porous framework is found in the existence of systematic vacancies of the building unit, the hexacyanoferrate octahedral block, $[\text{Fe}(\text{CN})_6]$, in the material structure. The relatively low thermal stability appears to be the main limitation of these materials for such applications. In the as-synthesized material the available free volume is occupied by water which, can be removed by moderated heating but always involving decomposition of at least a small sample fraction. For cobalt a unique behavior has been observed. The heating of cobalt(2+) hexacyanoferrate(III) leads to an inner charge transfer to form the mixed valences $\text{Co}(2+)\text{Co}(\text{III})$ hexacyanoferrate(II,III) system.

Since this inner oxidation–reduction reaction does not modify the coordination environments for the involved metals, the porous nature of the parent compound could be preserved and at the same time with a higher thermal stability related to the formation of the most stable ferrous species. The porous structure of the obtained material was evaluated from CO_2 adsorption, X-ray diffraction, thermogravimetric, and infrared and Mössbauer spectroscopic data. The heat-induced charge transfer is accompanied of a progressive fracture of the material crystallites and also of a decrease for the pore volume as detected by the CO_2 adsorption. For comparative purposes, a parallel study on a porous Prussian blue (ferric hexacyanoferrate(II)) species was carried out. The porous framework of this last material is also related to systematic vacancies of the hexacyanoferrate building block but without the mentioned heat-induced charge transfer effect. In this case the sample heating has no effect on the material porous properties.

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1 Introduction

The studied materials belong to a family of molecular structures known as Prussian blue (PB) analogues. Such structures result from the assembling of the octahedral anionic block, $[\text{M}^n(\text{CN})_6]^{n-6}$, through a transition metal cation (T^{m+}) which forms relatively strong bonds at the N ends of the CN groups. The assembling process is usually carried out through soft chemical methods. The free space (porosity) of the obtained 3D network is related to the existence of systematic absence of the building block in the material structure or to the coordination adopted by the