

Porous hexacyanocobaltates(III): Role of the metal on the framework properties

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Abstract

The extended porous framework of divalent transition metal hexacyanocobaltates(III) was studied from the refined crystal structures and adsorption isotherms of H₂O, CO₂ and N₂. From the obtained adsorption data the pore accessibility, pore volume, adsorption potentials and nature of the guest–host interactions were evaluated. The properties of the porous framework are modulated by the metal used to form the 3D framework from the elemental building block, the hexacyanocobaltate(III) ion. From that fact, this family of microporous compounds can be considered as tunable zeolites, with a pore volume and a system of pore windows appropriate for separation and storage of small molecules. The adsorption isotherms also reveal that the electric field gradient at the pore surface and the pore accessibility are determined by the metal linked at the N end of the CN groups. These compounds are usually obtained as hydrates. The dehydration process and the thermal stability were studied from thermo-gravimetry combined with X-ray diffraction. The crystal water is lost below 100 °C and then the anhydrous structure remains stable, preserving its porous features, up to 250 °C. Upon water removal a progressive cell contraction which amounts 4% of cell volume reduction was observed.

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1. Introduction

Divalent transition metal hexacyanocobaltates(III) form an interesting family of porous molecular materials, with a pore volume and pore windows appropriate for separation and storage of small molecules [1–3]. In this sense, recent studies have evaluated the molecular hydrogen storage in their porous framework [4–6]. Hexacyanometallates can be considered as a 3D assembling of a molecular block, the hexacyanometallate anion, [M(CN)₆]^{m−}, through a tran-

sition metal cation (T^{m+}), in the following the metal, which links the N ends of neighboring blocks. Within hexacyanometallates, cobalticyanides of divalent cations (T²⁺), (T₃[Co(CN)₆]₂·xH₂O), are particularly attractive as microporous materials. The Co(III) ion in low spin state has six electrons in the *t*_{2g} orbitals. These orbitals are filled. This provides a high stability to the building block ([Co(CN)₆]). No obvious participation of the hexacyanocobaltate(III) anion in oxidation or reduction processes is expected. The reported hydrogen adsorption isotherms in this family of compounds show certain dependence on the metal involved [4,5], an effect that deserves to be studied since it could be used as a tuning way for the properties of these materials.

Porous cyanometallates are light weight crystalline solids, with a relatively high free volume and with intermediate to

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