

Behavior of transition metals ferricyanides as microporous materials

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Abstract

The properties of divalent transition metal ferricyanides as microporous materials remain poorly documented. This family of compounds crystallizes with a cubic cell (Mn, Co, Ni, Cu, Zn, Cd) and also in a rhombohedral (R-3c) modification (Zn). The porous nature of the cubic complexes is related to the occurrence of systematic vacancies of the octahedral building unit $[\text{Fe}(\text{CN})_6]$. The system of vacancies forms a porous framework with polar surface. The rhombohedral modification for the zinc complex salt also has a porous structure but free of vacancy and with a practically non-polar surface. Such structural information was complemented with adsorption isotherms of H_2O , N_2 and CO_2 , which were evaluated according to Dubinin model for the volume pore filling. For CO_2 the maximum adsorbed amount was calculated using the Langmuir–Freundlich isotherm. From these adsorption data, a characterization of the studied ferricyanides according to pore volume, pore accessibility and guest–host interactions is given. Information on the guest–host interaction was also derived from Mössbauer spectra recorded on samples with N_2 , CO_2 , ethanol, methanol and water as adsorbed species. The quadrupole splitting (Δ) of the Mössbauer spectrum appears as an excellent sensor for the interaction between the adsorbed species and the metal at the pore surface. The Mössbauer spectra were also used as sensor for the pore accessibility to light hydrocarbons. The surface properties of the studied ferricyanides result modulated by the metal used to form the 3D structure from the octahedral block. In this sense, the studied materials behave as tunable zeolites. The materials behavior during the dehydration process and their thermal stability were evaluated from X-ray powder patterns, thermogravimetric and spectroscopic (IR and Mössbauer) data. For all the studied compositions the crystal structure was refined from the corresponding X-ray powder patterns using the Rietveld method.

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1. Introduction

It is well-known that many hexacyanometallates have an open-channel structure with potential applications as molecular sieving [1,2], absorbents [3–7], in catalysis [8] and ionic exchange [9]. The first studies on cyanometallates as microporous materials [1–6] were limited by the poor state of the art concerning the available information on

their crystal and electronic structure. In fact, the surface properties of porous cyanometallates remains poorly documented, nevertheless they offer a high flexibility to change the geometry, size and physical properties of the pores system [1,7,10]. Such features could support some attractive applications, including hydrogen adsorption and storage [11,12]. This contribution forms part of a systematic study of this family of coordination complexes as microporous materials [7,10,13].

Hexacyanometallates can be considered as molecular materials formed by the assembling of the octahedral block $[\text{M}(\text{CN})_6]^{n-}$ through an appropriate transition metal (T^{m+}). The metal links neighboring blocks at N ends. The charge

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