

THERMAL EVOLUTION OF MICROPOROUS NITROPRUSSIDES ON THEIR DEHYDRATION PROCESS

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Divalent transition metal nitroprussides form a family of microporous materials which lose their crystallization water (coordinated and zeolitic) below 100°C and then remain stable up to above 150°C. The dehydration process of representative samples in their stable phases was studied by thermo-gravimetry (TG) and differential scanning calorimetry (DSC). The copper complex dehydrates in a single step through a practically irreversible process. For cadmium and cobalt complexes the water evolution on heating takes place in two stages. The first one, where only zeolitic waters are removed, is dominated by a diffusion mechanism while, during the loss of the strongly bonded waters (second stage) the material framework effect is added. The involved activation energy and its dependence on the conversion degree were estimated evaluating the thermo-gravimetric data according to an isoconversion model.

Keywords: dehydration kinetics, Hi-Res TGA, nitroprussides, thermal analysis, TMDSC

Introduction

Insoluble transition metal nitroprussides can be considered as a tridimensional assembling of the pentacyanonitrosylferrate(II) anion, $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$, through an appropriate cation of transition metal (Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} or Cd^{2+}). They can be obtained as single crystals [1–3] or as polycrystalline powders [4–7] with a crystal structure and hydration degree which depend on the preparation method. However, when both polycrystalline and single-crystal samples are aged in air at room temperature, they adopt, with the exception of the copper complex, the same crystal structure [5, 8]. These stable phases have an open framework with a system of channels suitable for small molecules storage [9] and/or separation [10]. In this sense, cobalt and nickel nitroprussides have showed relatively high hydrogen adsorption capacity [11]. These nitroprussides have a channel topology and specific adsorption sites similar to those found in hexacyanocobaltates where hydrogen storage has also been studied [12]. The adsorption of molecules on channels modifies the electronic structure of the host solid and this can be used to introduce changes in its electronic structure and as modulation way for the material properties and functionality. The studied complexes show interesting properties as holographic information storage materials [13] and for the nickel compound, a photo-induced magnetic order has been reported [14]. The

framework outgassing is an essential step in the applications of porous materials and nitroprussides are not an exception in that sense. However, the dehydration process of these porous molecular materials remains poorly documented [1–4, 8, 9]. Thermal analysis has been widely used to study solid-state reactions [13, 14] and particularly the dehydration reactions [15–19]. The aim of this paper is to shed light on thermo-kinetic aspects of the water desorption process in polycrystalline nitroprussides by means of thermogravimetric and calorimetric experiments. The copper, cadmium and cobalt complexes were studied. They are representative of all the reported stable phases in this family of compounds.

Experimental

Sodium nitroprusside, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$, was used as source of the molecular block, $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$. The assembling metal was provided by a soluble salt, in this case chloride, of divalent transition metals (Co^{2+} , Cu^{2+} and Cd^{2+}). The assembling process was carried out mixing aqueous solutions (0.01 M) of sodium nitroprusside and metal chloride. The formed precipitate was isolated and washed several times with distilled water to obtain a filtrate free of the starting anions and cations. The resulting solids were air-dried at room temperature until reaching constant mass. The chemical nature and

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