



Behavior of Microporous Nitroprussides in Presence of Ammonia

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Abstract. The behavior of microporous nitroprussides in the presence of ammonia, both in anhydrous and hydrated states, was studied using ammonia adsorption isotherms and IR, Mössbauer and XRD techniques. In their anhydrous state these materials behave as a zeolite for ammonia adsorption, however when structural water is present a decomposition process was observed. The crystallization or adsorbed water is used by ammonia to form NH_4^+ and OH^- , creating basic conditions where the structural building unit $[\text{Fe}(\text{CN})_5\text{NO}]$ loses the NO group to form a pentacyano complex. This leads to the formation of mixed salts, $\text{M}(\text{NH}_4)[\text{Fe}(\text{CN})_5] \cdot x\text{H}_2\text{O}$. For ferrous nitroprusside the formed OH^- ion competes with the complex anion for the iron(2+) cation which is removed, then oxidized and finally observed as a ferric oxyhydroxide, FeOOH .

Keywords: adsorption, microporous, nitroprusside, pentacyanide, ammonia, Mössbauer, infrared

1. Introduction

Nitroprussides are salts of the pentacyanonitrosylferate (II) anion, $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$. They form a family of microporous molecular materials, particularly the salts of divalent transition metal cations [1]. In their crystal structure the NO ligand at the O end remains always unlinked. This leads to materials with a system of channels appropriate for small molecules separation [2]. The octahedral coordination sphere of the cation is commonly completed with removable water molecules which leads to other system of small pores. Some nitroprussides show an additional system of bigger and

interconnected pores, which is related to the occurrence of structural vacancies of both, the complex anion and the assembling cation [3]. The structural micropores are usually filled with zeolitic waters which are hydrogen bonded to the coordinated ones [3–10]. When both, coordinated and zeolitic waters, are removed the available pore volume significantly increases. Nitroprussides have also attracted certain attention in the last years as novel materials, mainly due to its potential applications in molecular devices development [11–15]. These perspectives are supported by the existence of photo-induced long-life meta-stable electronic states generated via metal (Fe) to ligand (NO) charge transfer [12, 13]. The small free space around the unlinked NO groups “absorbs” the change in both, the iron ionic radius and inter-atomic N-O distance, induced by the

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