



Behavior of Prussian blue-based materials in presence of ammonia

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Abstract

Prussian blue and related materials, usually considered that behave as a zeolite for ammonia adsorption, when hydrated are unstable in the presence of this gaseous species. They remain stable only in the anhydrous form. In the decomposition products ammonium hexacyanometallates and an XRD amorphous iron(III) oxyhydroxide are detected. The crystallization and adsorbed water present in these solid materials participates in a decomposition reaction to give NH_4^+ and OH^- . The very basic OH^- anion removes the iron(III) cations from the complex to form $\text{Fe}(\text{OH})_3$ and finally FeOOH , while the formed NH_4^+ appears as the salt of the complex anion. As reference reactions, the interaction of ammonia with ferrocyanic acid and ferric chloride, both in solid state, were studied where crystalline ammonium ferrocyanide and ammonium chloride, respectively, are formed.

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1. Introduction

Perhaps the oldest application of Prussian blue (PB) or ferric ferrocyanide was as a pigment for paints, printing inks, laundry dye, and other color-related uses [1]. The microporous character of PB and its analogues find applications as adsorbent, as sieves for molecular separation [2–5] and for some catalytic processes [6,7]. Their high insolubility and ion exchange properties have found applications for ^{137}Cs removal from radioactive waste solutions [8,9], in humans and animals therapy affected by nuclear accidents [10,11], as an alternative to the use of silver halide in the development process in the photographic industry [12] and in heavy metal ions removal during wine production [13,14]. Electrochemical application as battery building is another field where PB has found promising uses [15]. PB and its analogs also find applications as electronic switching and electrochromic devices [16,17]. However, the field of molecular magnets is the subject that has prompted the major research activity on PB and its analogues in the last years [18–31]. These

compounds are playing a main role in the field of molecular materials that show magnetic order at high temperatures [22–31] and also in those where the magnetic order can be induced by an external stimuli [28,30]. In this last sense the photoinduced magnetization in cobalt iron cyanide has received particular attention [28,29,31–38]. All these applications of PB-based materials presuppose a high stability and longevity of their properties.

PB is the best known member of hexacyanometallates, a well-documented family of coordination compounds [39–41]. PB also serves as structural prototype of many transition metal hexacyanometallates, which adopt an fcc crystal cell during their crystallization [41–43]. As PB are known four slightly different compositions of ferric ferrocyanide, depending on the starting reagents used in their preparation [6,44,45]: insoluble PB (IPB), $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$, soluble PB (SPB), $\text{FeK}[\text{Fe}(\text{CN})_6] \cdot x\text{H}_2\text{O}$, and Turnbull's blue (TB), $\text{Fe}_3\text{A}[\text{Fe}(\text{CN})_6]_2 \cdot x\text{H}_2\text{O}$ where A is a compensating anion. On aging, ferric ferrocyanide (Prussian brown, PBr) reduces to ferric ferrocyanide and also adopts the same deep blue color. From the abundant structural and spectroscopic data on these compounds, it is known that they are modifications of ferric ferrocyanide where Fe^{II} ion is found coordinated to six CN ligands at C end

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