BEHAVIOUR OF PRUSSIAN BLUE DURING ITS INTERACTION WITH OZONE

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Received 27 January 1992; accepted 3 April 1992

The interaction of ozone with Prussian Blue has been studied by Mössbauer, infrared and XRD techniques. All spectral results reveal a reversible conversion of ferrocyanide to ferricyanide with preservation of the crystal skeleton. Ferric ferricyanide obtained by ozonization of ferric ferrocyanide has Mössbauer parameters different to those of an ordered Prussian Brown, which has been attributed to secondary reaction products located at the zeolite voids of the former compound.

1. Introduction

In previous papers, we have reported the occurrence of mixed valence states when cobalt ferrocyanide is ozonized [1] or cobalt ferricyanide is reduced tribochemically [2]. We have now carried out a systematic study of the interactions of ozone with hexacyanometallates. In this paper, we present our results on the ozonization of ferric ferrocyanide (Prussian Blue) followed by Mössbauer, infrared and XRD techniques. For comparison, a study of ferric ferricyanide (Prussian Brown, PBr) has been included.

As Prussian Blue (PB) are designed four different types of ferric ferrocyanides [3]: Insoluble Prussian Blue (IPB), $Fe_4[Fe(CN)_6]_3 . nH_2O$; Soluble Prussian Blue (SPB), $KFe[Fe(CN)_6] . nH_2O$; Turnbull's Blue (TB), $MFe_3[Fe(CN)_6]_2 . nH_2O$, where M is an appropriate anion; and that derived on aging of PBr (APBr), $(H_3O)Fe[Fe(CN)_6] . nH_2O$. All these compounds crystallize in the cubic system and are members of a family of compounds named Prussian Blue analogous [4,5]. The structure of SPB and APBr can be described as a cubic network of $Fe^{II}-C-N-Fe^{3+}$ with low-spin Fe^{II} coordinated to six CN ligands at the C end and the high-spin Fe^{3+} similarly coordinated to six CN ligands at the N end. The K^+ and H_3O^+ cations are located in the Fe^{3+} environment. In IPB and TB there is an exces of Fe^{3+} over Fe^{II} cations due to vacancies created by the omission of $[Fe(CN)_6]^{4-}$ anions in the cubic lattice, in order to maintain charge neutrality. The place of the missing N atoms as ligands of Fe^{3+} cations is taken over by water molecules [6]. Additional water molecules have a zeolite character.

Different analytical methods can be used to monitor the ozone interaction with PB. Mössbauer spectroscopy is especially suited, since it can detect valence