MÖSSBAUER AND INFRARED SPECTROSCOPIC STUDIES OF NOVEL MIXED VALENCE STATES IN COBALTOUS FERROCYANIDES AND FERRICYANIDES

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Novel mixed valence states have been obtained by the treatment of cobaltous ferrocyanides (Co^{2+}Fe^{II}) and ferricyanides (Co^{3+}Fe^{III}) in an ozone flow. The CN stretching bands occur at 2085 cm^{-1} for Co^{2+}Fe^{II} and at 2160 cm^{-1} for Co^{3+}Fe^{III}. After the ozonization process of Co^{2+}Fe^{II}, an intense band approximately at 2125 cm^{-1} is detected. This intermediate band must correspond to a mixed valence state of the type:

Fe^{II} – CN – Co^{2+} – NC – Fe^{III}

Mössbauer spectra recorded “in situ” during the ozonization of Co^{2+}Fe^{II} show the presence of two components: a doublet with isomer shift and quadrupole splitting values close to the cobalt ferricyanide and a very broad line for the mixed valence state. From the Mössbauer and infrared spectra of the aged samples of the Co^{2+}Fe^{II} after ozonization, a relaxation process to the initial state of the samples is observed but the mixed valence state is stable.

1. Introduction

Cobalt ferrous and ferricyanides are analogs of Prussian Blues, with a general formula $M^A_j[M^B(CN)_6]_k mH_2O$ where $M^A$ and $M^B$ are the transition metal cations, $j$ and $k$ are the stoichiometric numbers which depend on the oxidation states A and B, and $m$ is the degree of hydration [1]. They crystallize in a cubic system with a unit cell of fcc symmetry and $a_0$ close to 10 Å [2]. The $M^A$ and $M^B$ atoms are octahedrally coordinated to N and C ends of the CN ligand respectively. The strong crystal field at $M^B$, produces a low spin state while $M^A$ is in a high spin state. The water molecules occupy the cubic voids in the network, being of a zeolitic nature.

The ferrous and ferricyanide complexes as well as the Co^{2+} salts have been used as catalysts in oxidation-reduction processes. We are not aware of previous studies of the interaction of the cobalt hexacyanoferrates with ozone. These compounds could be used as catalysts for ozone decomposition. Furthermore, the