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 ($Co^{+2}Fe^{III}$) in an ozone flow. The CN stretching bands occur at 2085 cm^{-1} for $Co^{+2}Fe^{II}$ and at 2160 cm^{-1} for $Co^{+2}Fe^{III}$. 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 cobalti 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 $M_j^A[M^B(CN)_6]_k mH_2O$ 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 complexs 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