

MÖSSBAUER AND INFRARED SPECTROSCOPIC STUDIES OF NOVEL MIXED VALENCE STATES IN COBALTOUS FERROCYNANIDES AND FERRICYNANIDES

E. REGUERA, J.F. BERTRÁN, C. DÍAZ, J. BLANCO

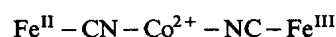
National Center for Scientific Research, P.O. Box 6990, Havana, Cuba

and

S. RONDÓN

Applied Study Center for Nuclear Energy, 5ta y 30, Miramar, Havana, Cuba

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



Mössbauer spectra recorded “in situ” during the ozonization of $\text{Co}^{+2}\text{Fe}^{\text{II}}$ 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 $\text{Co}^{+2}\text{Fe}^{\text{II}}$ 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 $\text{M}^{\text{A}}_j[\text{M}^{\text{B}}(\text{CN})_6]_k m\text{H}_2\text{O}$ 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