

Study of the interaction of ozone with solid ferrocyanides

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ABSTRACT.-The interaction of ozone with solid ferrocyanides has been studied by means of XRD and Mössbauer and Infrared spectroscopies. Ozone oxidizes ferrocyanides to ferricyanides and the oxidation products have a pronounced trend to reduce on aging. The reversibility of the oxidation process is closely related with the crystal structure of reduced and oxidized states of the complexes.

Introduction

Ozonization processes are normally carried out in gaseous or liquid phases. We have studied ozone interactions with solid ferrocyanides in which the O_3 diffuses through the porous material oxidizing the ferrocyanides to ferricyanides [1,2]. These ferricyanides are less stable than the normal products obtained by wet synthesis and return spontaneously to the starting ferrocyanide on aging. The speed of the reduction process is strongly dependent on the nature of the outer cation. This difference in chemical behaviour, which must be associated to slight differences in constitution, is not detected by IR spectra or XRD patterns [1,2]. The Mössbauer spectrum is sensitive enough to detect the difference, particularly through the quadrupole splitting (Δ) of the low spin Fe^{III} complexes formed by ozonization. The Δ values are normally higher than for the standard ferricyanides. The results of ozonization of Prussian Blue were interpreted by the presence of active species formed during the ozonization process [2]. Another possibility is the consumption of water of crystallization by reaction with ozone [3].

In this communication we present a comprehensive study of ozonization of solid ferrocyanides including alkaline, alkaline-earth, transition metal and rare-earth cations. The reactions are followed by IR and Mössbauer spectroscopies and, in specific cases, additional information is obtained by XRD.