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Oxidation of synthetic hausmannite (Mn_3O_4) to manganite (MnOOH)

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Abstract

The oxidation of aqueous solutions of manganese (II) chloride by hydrogen peroxide leads to the mixture of hausmannite (Mn_3O_4) with manganite (MnOOH). Being air dried, this mixture undergoes slow oxidation at room temperature during which the content of manganite is rising, and an equilibrium molar ratio Mn_3O_4:MnOOH reaches 1:3 in approx. 1 year of storage. In terms of reversible first order reactions, rate constants for the forward and reverse reactions are 2.62×10^{-1} and 8.75×10^{-2} month^{-1}, respectively. In the course of oxidation, additional IR adsorption bands emerge in the region of vibrations of physisorbed water molecules at 3160 and 3300 cm^{-1}. These bands are absent in IR spectra of equilibrium mixtures and disappear after treatment of samples with Sr^{2+} ions as a result of ion exchange. This finding enables one to suggest that adsorbed water forms cation exchangeable surface groups —Mn═$(OH)_2$ whose transformation into MnOOH is a step determining the oxidation rate. On the other hand, these data may be considered as the first spectroscopic evidence of sorption of spherical cations onto the surface of hydrous oxides.

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Keywords

Hausmannite; Manganite; Oxidation; Sorption

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