



Thermodynamic simulation of the reaction mechanism of Mn^{2+} oxidation with an SO_2/O_2 mixture

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ABSTRACT

Manganese oxides are essential in the production of electronic components and batteries. A promising alternative for their production from secondary sources is the leaching of the Mn and later oxidative precipitation of Mn^{2+} by an SO_2/O_2 mixture. The steps involved in this last reaction have not been fully understood. This work presents the reaction mechanism describing the oxidative precipitation of Mn^{2+} by an SO_2/O_2 mixture with MnO_2 and SO_4^{2-} as reaction products. The analysis was supported in thermodynamic simulations in which the formation and effect of the oxidant species was verified. The proposed reaction mechanism was validated with experimental batch tests and it was found that it describes satisfactorily the oxidation reaction. Experimental evidence revealed that this system is efficient at low concentrations of SO_2 in the gas mixture composition; an optimal composition of 7.3% SO_2 of the gas mixture was found.

1. Introduction

The transition metal-catalysed oxidation of sulfur (IV) oxides plays an important role in atmospheric chemistry (e.g. acid rain formation) (Brandt and van Eldik, 1995) as well as in industrial processes (e.g. oxidation of cyanide in alkaline media) (Devuyst et al., 1982). Sulfur dioxide alone is an effective reductant agent used in the leaching of the MnO_2 contained in a low grade ore, dissolving the Mn as soluble sulphate (Naik et al., 2000); however, it has been demonstrated the capability as oxidant of the SO_2/O_2 mixture to precipitate Mn^{2+} producing high purity manganese oxides (Bello-Teodoro et al., 2014). These oxides are essential in the manufacturing of electronic components and batteries. There is a lack of information about the reaction mechanism conducting the Mn^{2+} oxidation by SO_2/O_2 . This work deals with the reaction mechanism of the oxidation of Mn^{2+} by an SO_2/O_2 mixture with MnO_2 and SO_4^{2-} as reaction products.

In the literature, two types of reaction mechanisms have been proposed for the metal-S(IV)- O_2 system: a) a mechanism focused on the S(IV) oxidation catalysed by transition metals, where the reaction products are S(V) and S(VI) species (i.e. the oxidation of SO_2 to $\text{S}_2\text{O}_3^{2-}$ or SO_4^{2-}) without the formation of solid products. Its main objective is to explain the role of the transition metal ions in the oxidation of sulfur (IV) oxides, after SO_2 was identified as one of the major contributors to acid rain; atmospheric chemists suggested metal-catalysed S(IV) oxidation may be a major acid rain production pathway (Kuo et al., 2006).

In this mechanism, the transition metal ions (Fe^{n+} , Mn^{n+}) are reduced and re-oxidised, remaining in ionic state. b) A mechanism focused in the oxidation of the transition metal ions by an SO_2/O_2 gas mixture and in the understanding of the role of the metal ions, due to these acting as catalysts of the oxidation reaction of S(IV) and simultaneously being oxidised, resulting in the formation of high-purity solid products (i.e. metal oxides).

There is a lack of information about the reaction mechanism that operates in the latter system described, because the stage where the solid is formed is not fully understood; one original contribution of this research work is the proposal of the complete reaction path that shows the interaction between the different species in the system and explains how a mixture containing a strong reductant (SO_2) and an oxidant with mild effect in aqueous systems is transformed into a powerful oxidant when it is added to an aqueous solution of Mn. This oxidative system is very important due to its variety of applications in hydrometallurgy, such as the removal of manganese from circuits containing other metals and the processing of secondary sources of manganese to produce high-value products.

2. Background

According to Kuo et al. (2006) the oxysulphur radicals chain model has been most frequently quoted to explain redox the redox chemistry of the metal-S(IV)- O_2 system. The authors also found that most of the

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