

Contents lists available at ScienceDirect

### Journal of Solid State Chemistry



journal homepage: www.elsevier.com/locate/jssc

# Conditions for the formation of pure birnessite during the oxidation of Mn(II) cations in aqueous alkaline medium



Hella Boumaiza<sup>a,b,c</sup>, Romain Coustel<sup>b</sup>, Ghouti Medjahdi<sup>d</sup>, Christian Ruby<sup>b,\*</sup>, Latifa Bergaoui<sup>a,c</sup>

<sup>a</sup> Laboratoire de Chimie des Matériaux et Catalyse, Faculté des Sciences de Tunis, Université El Manar, Tunisia

<sup>b</sup> Laboratoire de Chimie Physique et Microbiologie pour l'Environnement (LCPME)-UMR 7564, CNRS-Université de Lorraine, 405, rue de Vandœuvre, 54600

Villers-lès-Nancy, France

<sup>e</sup> Département de Génie Biologique et Chimique, Institut National des Sciences Appliquées et de Technologies (INSAT), Université de Carthage, Tunis, Tunisia

<sup>d</sup> Institut Jean Lamour, Centre de Compétences Rayons X et Spectroscopie (X-Gamma), UMR 7198 CNRS-Université de Lorraine, France

#### ARTICLE INFO

Keywords: Birnessite Hausmannite Redox synthesis Dissolved oxygen XPS

#### $A \ B \ S \ T \ R \ A \ C \ T$

Birnessite was synthetized through redox reaction by mixing  $MnO_4^-$ ,  $Mn^{2+}$  and OH<sup>-</sup> solutions. The Mn(VII): Mn(II) ratio of 0.33 was chosen and three methods were used consisting in a quick mixing under vigorous stirring of two of the three reagents and then on the dropwise addition of the third one. The obtained solids were characterized by XRD, FTIR and XPS spectroscopies. Their average oxidation states were determined from ICP and CEC measurements while their surface properties were investigated by XPS. This study provides an increased understanding of the importance of dissolved oxygen in the formation of birnessite and hausmannite and shows the ways to obtain pure birnessite. The role of counter-ion *ie.* Na<sup>+</sup> or K<sup>+</sup> was also examined.

#### 1. Introduction

Birnessite is a mixed Mn(III)-Mn(IV) oxide constituted by layers of edge-sharing MnO<sub>6</sub> octahedra separated by planes of hydrated cations (e.g. Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>) and water molecules. It was found to be one of the most common and active occurring Mn oxide in soils and sediments [1,2]. Jones and Milnes [3] proposed the formula  $Na_{0.7}Ca_{0.3}Mn_7O_{14}$ , 2-8H<sub>2</sub>O. This natural form presents a disordered structure [2,4,5]. Thereby, many studies were focused on ways to obtain birnessite. Besides the existing biogenic ways, the chemical methods could be divided in four groups based on the mechanism involved.

The first method is based on the Mn(II) oxidation in alkali media producing Mn(OH)<sub>2</sub> and its oxidation by O<sub>2</sub> bubbling to form buserite, the hydrated form of birnessite [6,7]. To avoid hausmannite formation as by-product many authors studied the mechanism involved. Intriguingly, Yang and Wang [8] prepared pure birnessite by O<sub>2</sub> oxidation of Mn(OH)<sub>2</sub> precipitate that was prepared from deoxygenated NaOH and MnCl<sub>2</sub> solutions. They suggested that the use of deoxygenated water prevented the presence of Mn(III) responsible of the hausmannite formation. Feng et al. [9] showed that the formation of hausmannite was avoided when NaOH and MnCl<sub>2</sub> were mixed below 10 °C; this study also showed that an oxygen flow rate of 5 L min<sup>-1</sup> during 5 h is required to produce pure birnessite. Cai et al. [10] proposed a variant of Giovanoli's method by replacing O<sub>2</sub> by air and they pointed that, in that case, a flow rate of  $24 \text{ Lmin}^{-1}$  is essential to avoid hausmannite formation. Pure birnessite was also obtained by using H<sub>2</sub>O<sub>2</sub> instead of O<sub>2</sub> as oxidant [11,12].

The second way to obtain birnessite relies on the reduction of  $MnO_{4}^{-}$  in concentrated HCl medium [13,14]. Numerous organic reducing agents were used such as fumaric acid [15], sugars [16,17], alcohols [12,18], ethylene glycol [19] and more recently epoxypropane [20] and lactate [21]. This method could be constraining as it involved a relatively long time aging step [12,18], a calcination step at temperature above 400–450 °C [16,17] or a hydrothermal treatment [20].

The third method is based on a direct conversion of hausmannite to birnessite involving a dissolution/recrystallization mechanism [22] in alkaline medium. Birnessite was obtained for concentrations of OH<sup>-</sup> above 2 mol L<sup>-1</sup>. The reaction required several weeks to be complete and the dissolution of hausmannite was found to be the rate-limiting step in this reaction.

The fourth process is based on a redox reaction between  $MnO_4^-$  and  $Mn^{2+}$  in alkaline conditions. A manganese salt (*i.e.*  $MnCl_2$ ,  $MnSO_4$ ) and sodium or potassium permanganate were generally used as Mn(II) and Mn(VII) suppliers respectively while NaOH or KOH were used to provide alkaline medium. This method was first reported by Murray [23]; it consisted on adding slowly the  $MnCl_2$  solution to NaOH/NaMnO<sub>4</sub> solution. The product presented a poor crystallinity similar to

http://dx.doi.org/10.1016/j.jssc.2017.01.014

<sup>\*</sup> Corresponding author. E-mail address: Christian.ruby@univ-lorraine.fr (C. Ruby).

Received 24 October 2016; Received in revised form 11 January 2017; Accepted 12 January 2017 Available online 16 January 2017 0022-4596/ © 2017 Elsevier Inc. All rights reserved.

natural birnessite. Luo et al., [24] and Luo and Suib [25], studied the influence of many parameters (temperature, basicity,  $MnO_4^-/Mn^{2+}$  ratio, presence of magnesium and anion effect) and showed that pure birnessite could be obtained in strong alkaline conditions with a  $MnO_4^-/Mn^{2+}$  ratio of 0.28–0.36 and at 40–65 °C. The authors also pointed that feitknechtite ( $\beta$ -MnOOH) was an intermediate in birnessite formation. Villalobos et al. [26] followed this work and showed the presence of small amount of manganite ( $\gamma$ -MnOOH) in addition to birnessite.

The redox method gained more interest on the past decades as it overcomes the inconvenient of the other methods such as high consumption of O2, use of boiling solution with concentrated acid and strong oxidant and long reaction times. In spite of an extensive literature [27-30] the role of dissolved oxygen on the redox method remains unclear. Actually a reactive medium with an average oxidation state (AOS) of manganese close to 3.25 (Mn(VII): Mn(II) molar ratio of 0.33) led to birnessite with an AOS of Mn equal to 3.53 [29]. This suggests that the oxidation of Mn(II) leading to birnessite is not related to a unique redox reaction between Mn(II) and Mn(VII) and that dissolved oxygen may intervene in it as already observed in other methods such as Giovanoli's studied by Yang and Wang [8]. Besides, the mixing order of the three solutions generally involved (i.e. manganese salt, permanganate and base) varied from one study to another [23,29,30] and to our knowledge, no study has focused on the influence that could have this order of mixing on the nature of the obtained products. Moreover, the occurrence and possible role of hausmannite (Mn<sub>3</sub>O<sub>4</sub>), which can be observed as a by-product, is not clear.

The goals of this study are: i) to optimize the experimental conditions to obtain pure Na-birnessite or K-Birnessite through the redox method and ii) to get an insight into birnessite formation mechanism. A special attention is paid to the role of dissolved oxygen and to the mixing order of the reagents to prevent the side reaction leading to hausmannite. The X-ray photoelectron spectrometry is used in order to gain a more in-depth understanding of the target reaction mechanism.

#### 2. Materials and methods

#### 2.1. Chemicals

All chemicals were purchased from Sigma-Aldrich. Manganese(II) chloride tetrahydrate (MnCl<sub>2</sub>,4H<sub>2</sub>O, ACS reagent, ≥98%) was used as  $Mn^{2+}$  supplier, sodium permanganate monohydrate (NaMnO<sub>4</sub>,H<sub>2</sub>O, ACS reagent ≥97%) or potassium permanganate (KMnO<sub>4</sub>, ACS reagent, ≥99.0%) as  $MnO_4^-$  supplier and sodium hydroxide (NaOH, BioXtra, ≥98% pellets anhydrous) or potassium hydroxide (KOH, ACS reagent, ≥85%, pellets) to provide alkaline medium. Double distilled water (DDW, 18.2 MΩ cm) was used for all the experiments.

#### 2.2. Synthesis of birnessite

Three solutions were used for the synthesis of Na-birnessite: 125 mL of NaOH (8.8 mol  $L^{-1}$ ), 250 mL NaMnO<sub>4</sub> (0.1 mol  $L^{-1}$ ) and 125 mL MnCl<sub>2</sub> (0.6 mol  $L^{-1}$ ). Some syntheses were performed by using KMnO<sub>4</sub> instead of NaMnO<sub>4</sub> and KOH instead of NaOH. The Mn(VII): Mn(II) ratio of 0.33 was chosen accordingly to a previous study [29]. The typical procedure used in the present work consisted on a quick mixing under vigorous stirring of two of the three reagents and then on the addition of the third in one go (0 h) or during 2, 4 or 8 h. The reaction mixture was then stirred for another 30 min and aged at 60 °C for 14 h. The product was finally centrifuged and washed until the pH of the solution was between 9 and 10 and dried at 60 °C during 16 h. The designation of the three methods refers to the nature of the third reagent added. Thus, the first method, named the "reductant-last method", consists on a dropwise addition of the reductant (MnCl<sub>2</sub>)

solution to the NaMnO<sub>4</sub>/NaOH mixture. The second one, the "alkalilast method" consists on a dropwise addition of the basic solution (NaOH) to the MnCl<sub>2</sub>/NaMnO<sub>4</sub> mixture. The third one, called the "oxidant-last method", consists on a dropwise addition of the oxidant (NaMnO<sub>4</sub>) solution to the NaOH/MnCl<sub>2</sub> mixture. Samples were denoted  $C_t^m$ : C=Na or K when NaMnO<sub>4</sub> and NaOH or KMnO<sub>4</sub> and KOH were used respectively, m=R, A or O when the reductant-last, the alkali-last or the oxidant-last method was used respectively and t corresponds to the addition time, in hour, of the third reactant. Three extra samples were synthesized using pre-deoxygenated solutions and N<sub>2</sub> bubbling to study the influence of dissolved oxygen. These samples were synthesized following the oxidant-last method and the bubbling was maintained during only the mixture of NaOH and MnCl<sub>2</sub> for the first sample  $(N_2^O - a)$  and during all the reaction time of 2 h for the second one  $(N_2^O$ -b). A sample of hausmannite was prepared by the mixture of 250 mL NaOH (5.5 mol L<sup>-1</sup>) and 200 mL of MnCl<sub>2</sub>  $(0.5 \text{ mol } L^{-1})$  under air bubbling at a flow rate of 2 L min<sup>-1</sup> during 5 h.

#### 2.3. Characterization techniques

The X-ray powder diffraction data were collected from an X'Pert MPD diffractometer (Panalytical AXS) with a goniometer radius 240 mm, fixed divergence slit module (1/2° divergence slit, 0.04 rd Sollers slits) and an X'Celerator as a detector. The powder samples were placed on zero background quartz sample holders and the XRD patterns were recorded at room temperature using Cu  $K_{\alpha}$  radiation  $(\lambda=0.15418 \text{ nm})$ . FTIR analysis was performed using a Bruker Vertex 70 v equipped with a DLaTGS detector. Spectra were recorded in transmission mode using KBr pellets containing 2-5 mg of sample. For each sample, 100 scans were collected in the 5000-220 cm<sup>-1</sup> wavenumber with 4 cm<sup>-1</sup> resolution. The background spectrum of KBr was also recorded at the same conditions. X-ray photoelectron spectra were recorded on a KRATOS Axis Ultra X-ray photoelectron spectrometer with Al Ka source monochromated at 1486.6 eV (spot size 0.7 mm×0.3 mm). Photoelectrons were detected by a hemispherical analyzer at an electron emission angle of 90° and pass energy of 160 eV (survey spectra) and 20 eV (core level spectra). For the core-level spectra, the overall energy resolution, resulting from monochromator and electron analyzer bandwidths, was 800 meV. As an internal reference for the absolute binding energies, the C1s peak of hydrocarbon contamination set at 284.6 eV was used. Total contents of Mn was determined using Inductive Coupled Optical Emission Spectroscopy ICP-AES (Jobin Yvon-Horiba, Ultima) after complete digestion of about 5 mg of birnessite in NH<sub>3</sub>OHCl (0.7 mol L<sup>-1</sup>, pH 1.9). The Cation Exchange Capacity (CEC) was determined following the cobalt-hexamine method [31] in which 150 mg of birnessite were put in 20 mL of 16.67 M Co(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> solution. The mixture was shaken for an hour without temperature regulation and then microfiltered. The cobalt-hexamine concentrations before and after contact with the birnessite were determined by measuring the solution absorption at 472 nm using an UV-visible spectrophotometer, i.e. a Cary 60 (Agilent Technologies).

#### 3. Results and discussion

#### 3.1. Mechanism of birnessite formation

Table 1 gives the nature of the products identified by XRD for all prepared samples.

#### 3.1.1. Comparison of the three used methods

The three different orders of mixing were studied with an identical dropwise addition time (2 h) of the third reactant. The XRD patterns of the samples  $Na_2^R$ ,  $Na_2^A$  and  $Na_2^O$  are shown in Fig. 1. The main product identified for the three methods is Na-birnessite (PDF 00–043–1456) with two main reflections at 7.14 and 3.57 Å corresponding to d<sub>001</sub> and

Download English Version:

## https://daneshyari.com/en/article/5153485

Download Persian Version:

https://daneshyari.com/article/5153485

Daneshyari.com