

SYNTHESIS OF BIRNESSITE FROM THE OXIDATION OF Mn^{2+} BY O_2 IN ALKALI MEDIUM: EFFECTS OF SYNTHESIS CONDITIONS

XIONG HAN FENG¹, FAN LIU^{1,*}, WEN FENG TAN¹ AND XIANG WEN LIU²

¹ College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, PR China

² Testing Center, China University of Geosciences, Wuhan 430074, PR China

Abstract—An O_2 oxidation and freeze-dry procedure has been used to synthesize birnessite through the oxidation of Mn^{2+} in alkali media. The effects of O_2 flow rate, the fluxion velocity of reaction suspension, the reaction temperature, pretreatment the reaction solutions with N_2 , and the hydration conditions on the purity of birnessite, the crystallinity, the ion-exchange properties, and the phase transformation of intermediate phases were examined. Buserite with a 1 nm basal spacing, produced after the oxidation, is transformed to 0.7 nm Na birnessite by complete freeze drying. Increasing the fluxion velocity of the reaction suspension and the O_2 flow rate facilitated oxidation of $Mn(OH)_2$. Prephase I (a phase related to hausmannite, γ - Mn_3O_4 (Luo and Suib, 1997; Luo *et al.*, 1998), and feitknechtite (β - $MnOOH$) were formed as intermediates during the synthesis. Mechanical stirring was used to change the fluxion velocity of the reactive suspension. When the speed of stirring and the O_2 flow rate were raised to 250 rpm and 3.0 L/min, respectively, or 450 rpm and 2.0 L/min, respectively, birnessite was the only phase in the final product. Irrespective of temperature in other reactions, pure birnessite was synthesized as long as the temperature during the initial mixing of the reaction solutions was maintained below 10°C. Increasing the reaction temperature led to a larger crystal size, better crystallinity and lower surface area. The pretreatment of solutions with N_2 or O_2 had little effect on the synthesis; synthesized birnessites had the same purity (100%) as, and similar crystallinity to, that of the no-pretreatment control. Dehydration of the buserite by freeze drying and heating at 60°C did not affect the production of birnessite; however, the latter caused partial loss of ion-exchange capacity with Mg^{2+} . The pathways of the birnessite formation in this study might be:

(1) $Mn(OH)_2$ (amorphous) \rightarrow feitknechtite \rightarrow buserite \rightarrow birnessite, and

(2) $Mn(OH)_2$ (amorphous) \rightarrow prephase I \rightarrow feitknechtite \rightarrow buserite \rightarrow birnessite

$Mn(OH)_2$ existed in an X-ray amorphous state, not in the form of ‘pyrochroite’, during the synthesis.

The adopted conditions for synthesis of pure birnessite were NaOH to Mn molar ratio of 13.7, O_2 flow rate of 2 L/min and oxidation for 5 h during vigorous stirring at 450 rpm at room temperature. The birnessite synthesized had a hexagonal platy morphology with good crystallinity, an average composition of $Na_{0.25}MnO_{2.07} \cdot 0.66H_2O$, and a surface area of 38 m²/g.

Key Words—Buserite, Birnessite, Fluxion Velocity, Hausmannite, Oxidation, Synthesis.

INTRODUCTION

Manganese oxide and hydroxide minerals are important constituents in soils and sediments. They are important sources of Mn for plant nutrition, and participate readily in redox and cation-exchange reactions. To a large extent they influence and control the behavior and availability of many other elements, heavy metals and organic contaminants in soils and sediments (Oscarson *et al.*, 1981; Huang, 1991; Post, 1999). The term birnessite refers to a group of Mn oxides that have layer structures, first described by Jones and Milne (1956) as a natural phase with a chemical formula of $Na_{0.7}Ca_{0.3}Mn_7O_{14} \cdot 2.8H_2O$. It is one of the most common, naturally occurring Mn oxide minerals in soils, sediments and ocean Mn nodules (Chukhrov and Groshkov, 1981; Siegel and Turner, 1983; Paterson *et al.*, 1986; McKenzie, 1989), and is of great interest to many investigators studying redox chemistry (Oscarson

et al., 1981; Kim *et al.*, 2002) and sorption-desorption reactions (Feng *et al.*, 1995; Violante and Pigna, 2002; Lanson *et al.*, 2002a; Drits *et al.*, 2002). The formations of many other Mn oxides have close relations with birnessite. Most of these oxides are formed directly or indirectly from birnessite (Golden *et al.*, 1987; Shen *et al.*, 1993; Mandernack and Tebo, 1993; Tu *et al.*, 1994; Feng *et al.*, 1995). However, because of the easily changeable valence state, low contents in soils, co-existence of different species, and finely crystalline or poorly ordered forms, the identification and characterization of naturally occurring Mn oxides are difficult (Paterson *et al.*, 1986; Brown, 1984; Post and Veblen, 1990). Furthermore, the crystal structure and characters of many Mn oxides are only partly known (McKenzie, 1989; Post, 1992). The preparation of many Mn oxides begins with a synthesis of birnessite; this is accepted as an important means by which to study the crystal structures, chemical and physical properties of many Mn oxide minerals, and the relationships and transformations between them (Wadsley, 1950a; McKenzie, 1971; Golden *et al.*, 1987; Shen *et al.*, 1993; Mandernack and

* E-mail address of corresponding author:

liufan@mail.hzau.edu.cn

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Tebo, 1993; Tu *et al.*, 1994; Feng *et al.*, 1995; Chen *et al.*, 2002).

Birnessite is generally prepared by reduction of permanganate or oxidation of pyrochroite ($\text{Mn}(\text{OH})_2$) with different reducing or oxidizing agents (Stähli, 1968; Giovanoli *et al.*, 1970a, 1970b; McKenzie, 1971; Drits *et al.*, 1997; Yang and Wang, 2002; Cai *et al.*, 2002). The former method is usually conducted in hydrochloric acid media (McKenzie, 1971, 1989; Tu *et al.*, 1994), or adopts a sol-gel synthetic route with different kinds of sugars or polyalcohols as the reducing reagent (Witzemann, 1915, 1917; Ching *et al.*, 1997). The latter is carried out in alkali media, the product is well crystallized with typically platy crystal morphology, but it is difficult to obtain pure birnessite because of a side reaction, in which hausmannite is produced (Giovanoli *et al.*, 1970a, 1970b; McKenzie, 1971, 1989; Golden *et al.*, 1986a, 1986b, 1987; Paterson, 1986; Yang and Wang, 2002; Cai *et al.*, 2002). Though birnessite is easy to prepare in acid media, the product has the crystal morphology of balls of needles with poor crystallinity (known as $\delta\text{-MnO}_2$) (McKenzie, 1971, 1989), or it may not have the layer structure of phyllophanates but a tunnel structure similar to that of cryptomelane (Yang and Wang, 1991; Tu *et al.*, 1994).

Over the past decade, Suib and co-workers developed a method for the synthesis of birnessite by oxidizing pyrochroite using permanganate (known as the OPP method, Yang and Wang, 2002) instead of O_2 in alkali media (Shen *et al.*, 1993; Luo and Suib, 1997; Luo *et al.*, 1998; Ma *et al.*, 1999); however, the OPP method always requires much longer for the reaction and ageing process than the other method. Hence it is common to prepare birnessite by oxidation of $\text{Mn}(\text{OH})_2$ to 1 nm buserite with O_2 in alkali media (known as the OPO method) followed by dehydration to 0.7 nm birnessite (McKenzie, 1971; Paterson *et al.*, 1986; Cornell and Giovanoli, 1988; Yang and Wang, 2002). The preparation of many other Mn oxide minerals from birnessite synthesized using the OPO method was achieved successfully (Wadsley, 1950a; McKenzie, 1971; Giovanoli *et al.*, 1973; Golden *et al.*, 1986a, 1987; Duncan *et al.*, 1998). Wadsley (1950b) and Buser *et al.* (1954) first prepared birnessite by bubbling air or oxygen through a mixture of Mn hydroxide and sodium hydroxide, but during the synthesis uncertain impurities were produced.

In order to obtain pure birnessite, many investigators tried modified versions of that method (Stähli, 1968; Giovanoli *et al.*, 1970a, 1970b; McKenzie, 1971; Golden *et al.*, 1986a, 1986b, 1987; Yang and Wang, 2002), *e.g.* the reactive temperature was controlled at 5°C because a low temperature in alkali media favored the formation of birnessite, or buserite (Levinson, 1962; Bricker, 1965; Stähli, 1968; Giovanoli *et al.*, 1970a, 1970b; McKenzie, 1971). When the flow rate of O_2 was increased to a certain value, pure birnessite could be obtained (Stähli, 1968; Golden *et al.*, 1986a, 1986b, 1987; Yang and

Wang, 2002; Cai *et al.*, 2002). The MnCl_2 and NaOH solutions were pretreated with N_2 before they are mixed to avoid production of a hausmannite impurity (Yang and Wang, 1991, 2002). However, it is not easy to prepare birnessite of good crystallinity, but without impurity, using the OPO method (Post and Veblen, 1990; Lanson *et al.*, 2002b).

In previous studies, the effects of individual preparation conditions on the synthesis of birnessite were emphasized and discussed; there is no agreement on how these parameters influence the synthesis of birnessite collectively. The pathways and mechanism of the birnessite formation are not fully established. In this study the effects of these factors on the synthesis of birnessite using the OPO method were determined systematically and the process of birnessite formation is also illustrated.

EXPERIMENTS

Syntheses of birnessite

In this study, birnessite was synthesized using a modified version of Stähli's (1968) procedure in alkali media. Anti-alkali materials were selected to prepare the experiment device. Distilled deionized water (DDW, 18 M Ω , from Labconco Water Pro Ps), after boiling for 1 h to remove the dissolved air, was used to prepare 200 mL of 0.5 M MnCl_2 and 250 mL of 5.5 M NaOH. These two solutions were then pretreated by bubbling N_2 (>99.9%) or O_2 (>99.99) at a flow rate of 1 L/min for 30 min. In addition, untreated DDW was used to prepare other MnCl_2 and NaOH solutions with the same concentrations and used throughout the other experiments. For typical syntheses, the cool solution of NaOH ($<5^\circ\text{C}$) was added quickly to the solution of MnCl_2 , and the oxygen was bubbled through the mixture solution via a plastic porous jet at a set rate. Concurrently, mechanical stirring at the required speed was used to change the flow velocity of the suspension. During the mixing of the two solutions, the temperature was kept below 10°C . After 5 min of mixing, the temperature was controlled at $5\pm 1^\circ\text{C}$ or $25\pm 1^\circ\text{C}$ in an ice-water bath and water bath thermostat. After oxidation for 5 h, the precipitate was centrifuged (2.54×10^4 g) and washed with DDW until the pH value of the supernatant liquid was <9.0 . The precipitate was then dialyzed electrically at a voltage of 150–220 V until the conductivity of the supernatant liquid was $<2.0\ \mu\text{S cm}^{-1}$, and its pH was <5.0 . The precipitate was finally freeze dried at -40°C or heated at 60°C to form Na birnessite (NaBi) from buserite (Giovanoli *et al.*, 1970a, 1970b; Golden *et al.*, 1986a, 1986b, 1987), and stored in an air-tight bottle for further analysis.

Characterization

X-ray diffraction (XRD) analysis was performed with a D/Max-3B diffractometer equipped with monochro-

mated FeK α radiation. The monochromated radiation had a tube voltage of 40 kV, a tube current of 20 mA and the count time of 0.5 s per 0.02°. To examine the phases formed during the synthesis, an aqueous slurry of the precipitate produced was washed, filtered and spread onto a glass slide, and XRD analysis conducted immediately. Powder samples were used for powder XRD to identify various species in the final products.

Transmission electron microscopy (TEM) analyses were carried out using a Philips-CM12 TEM operated at 120 kV. The pure birnessite samples used for XRD were crushed gently to powder, then dispersed in absolute alcohol and sonicated prior to deposition on a holey carbon film.

After the XRD, pure birnessite was subjected to chemical analysis to determine the general molecular formula. Samples were analyzed using Varian Vista-MPX ICP-OES. Approximately 150 mg of sample were dissolved in 50 mL of aqua regia, and the volume increased to 1000 mL. Samples were analyzed for Na at 589.592 nm and Mn at 293.931 nm. The average oxidation state (AOS) of Mn was determined from the result of the titration method as follows (Kijima *et al.*, 2001). About 0.1 g of the sample were dissolved into an excess of 10 mL of 0.5 M H₂C₂O₄ solution and 10 mL of 0.5 M H₂SO₄ to reduce all the manganese to Mn²⁺. The excess C₂O₄²⁻ was determined by back titration at ~60°C with standardized 0.02 M KMnO₄ solution. The water percentage was calculated from weight difference.

Specific surface area measurements were carried out using an ST-08 Surface Area Analyzer. The adsorbate was nitrogen, the carrier gas was hydrogen, and the BET method was used to calculate the specific surface area.

RESULTS AND DISCUSSION

The effects of alkalinity on the synthesis of birnessite using the OPO and OPP methods were investigated in detail in previous studies; increasing the alkalinity of the reaction media improved the crystallinity of the product (Luo *et al.*, 1997, 1998; Yang and Wang, 2002; Cai *et al.*, 2002). In the two methods, alkalinity influenced the synthesis in a similar way. Lowering the concentration of the NaOH solution led to a decrease in the crystallinity of the synthetic birnessite; a low-valence phase (such as hausmannite) was produced when the concentration of the initial NaOH solution was <1.3 M (data not shown). A slightly more crystalline birnessite could be obtained in a more concentrated NaOH solution (8 M, OH/Mn = 20) than that in the typical synthesis, but it would take much longer to rinse the product to approach neutrality after oxidation. To simplify the experiments, the regular and more suitable initial concentration of NaOH solution (5.5 M, OH/Mn = 13.8) was used throughout this study as reported in the literature (Giovanoli *et al.*, 1970a, 1970b; Golden *et al.*, 1986b, 1987; Paterson *et al.*, 1986). After the 5 h of oxidation,

ageing the suspension without stirring at room temperature for 2 weeks did not change the final product and the crystallinity of the final product almost remained the same, so the ageing process was not included in the synthesis procedure.

Effects of pretreatment of the solutions with N₂ or O₂

Before mixing the MnCl₂ and NaOH solutions, pretreatment of the solutions with N₂ to remove the dissolved oxygen in them was proposed, to avoid the yield of hausmannite in the synthesis (Yang and Wang, 1991, 2002). In the present study, two different pretreatments, one with N₂, the other with O₂, were compared to examine the effects on the synthesis under the experimental conditions. Meanwhile, the control treatment was included without any pretreatment of the solutions. When the syntheses were carried out at 25°C with a stirring speed of 450 rpm and an O₂ flow rate of 2 L/min in the three comparative experiments, the characteristics of the products in the three experiments with different pretreatments or without pretreatment were very similar, including their XRD patterns. The XRD pattern of the product obtained in the experiment with pretreatment of the solutions with O₂ and with mechanical stirring is shown in Figure 1A,B. Birnessite was the only phase (JCPDS 23-1046) in the products; its strong peaks were at *d* spacings of 0.712, 0.358, 0.252, 0.244, 0.223, 0.216, 0.186, 0.182, 0.171, 0.163, 0.148 and 0.145 nm. When three comparative experiments were carried out with no mechanical stirring and the other parameters remained the same as above, very similar products were also obtained, but there was a great deal of hausmannite (JCPDS 24-734) and a little feitknechtite (JCPDS 18-804) mixed with the birnessite in the final products. The XRD pattern of the product obtained in the experiment without pretreatment of the solutions and without mechanical stirring is shown in Figure 1C. Thus, under the conditions in this study, pretreatment of the solutions with N₂ or O₂ had no apparent influence on the synthesis of birnessite. In the following context, birnessite was synthesized without pretreatment of the solutions to examine the effects of other synthesis conditions.

Effects of the O₂ flow rate

The O₂ flow rate was varied from 1 to 4 L/min to study its effect on the synthesis of birnessite at 25°C. Mechanical stirring at 450 rpm was used and when the O₂ flow rate was 2 L/min, the product was pure birnessite, as described above. Its average composition was Na_{0.25}MnO_{2.07}·0.66·H₂O with the Mn average oxidation state of 3.89. Apart from the greater oxidation state of Mn, probably due to the greater oxidation caused by the vigorous stirring, the chemical composition was similar to the synthesized samples reported by other researchers (Giovanoli *et al.*, 1970a, 1970b; Post and Veblen, 1990; Duncan *et al.*, 1998). When the O₂ flow

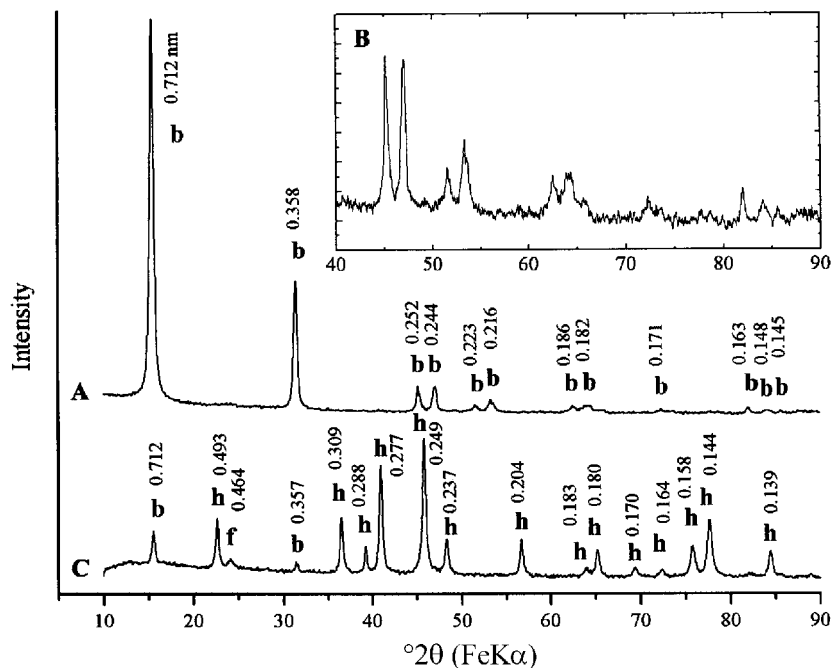


Figure 1. XRD patterns of birnessites synthesized (A) with stirring and with pretreatment of solutions by O_2 ; (B) enlarged XRD pattern of (A) in the 2θ range 40–90°; (C) without stirring and without pretreatment of solutions. b – birnessite; h – hausmannite; f – feitknechtite.

rate was reduced from the typical level of 2 L/min to 1 L/min, the product was a mixture of birnessite and hausmannite as shown in Figure 2. Even if the bubbling of O_2 continued for 10 h, the amount of hausmannite in the product did not reduce much. Transformation of

hausmannite into birnessite in alkaline media is kinetically very slow (Cornell and Giovanoli, 1988); once hausmannite has formed and crystallized during the synthesis it is difficult to convert it to birnessite under subsequent oxidation. Birnessite is the product of the

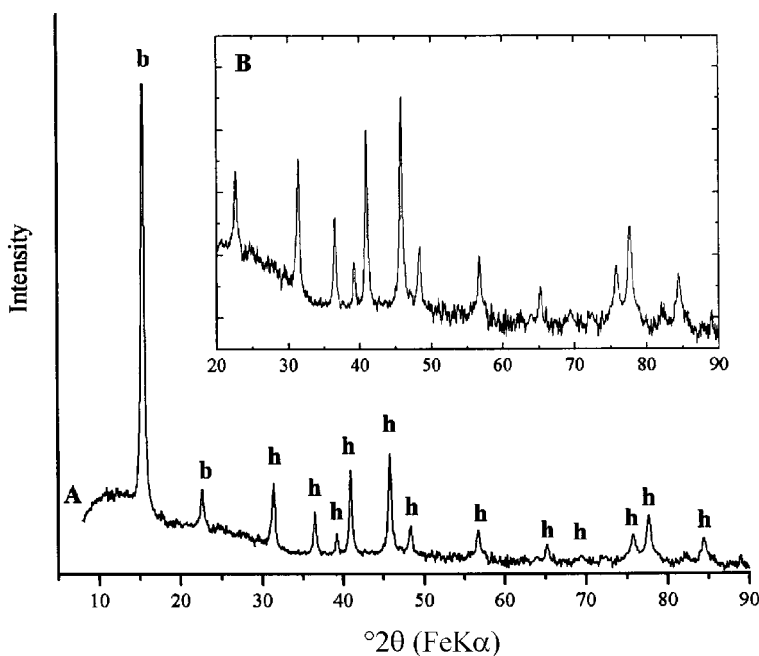


Figure 2. XRD pattern of birnessites synthesized (A) at an O_2 flow rate of 1 L/min and (B) enlarged XRD pattern of (A) in the 2θ range 20–90°. b – birnessite; h – hausmannite.

complete oxidation of $\text{Mn}(\text{OH})_2$; a sufficient concentration of O_2 in the reaction media is necessary, otherwise the low-valence hausmannite would be produced (Giovanoli *et al.*, 1970a, 1970b, Golden *et al.*, 1986b, 1987; Cai *et al.*, 2002). When the O_2 flow rate was increased from 2 L/min to 3 or 4 L/min, the synthesis of pure birnessite was also achieved successfully, and the average oxidation state of Mn in the products increased slightly from 3.89 to 3.90, or 3.92, and there was no notable difference in its degree of crystallinity, indicating that the O_2 flow rate of 2 L/min was sufficient for the synthesis of birnessite.

Synthesis of birnessite at different fluxion velocities of reaction suspension

The effects of the fluxion velocity have not been studied previously in the synthesis of birnessite using the OPO method. The speed of mechanical stirring is the main influence on the fluxion velocity of reaction suspension in the experiments. They were varied from 0 to 100, 250 or 450 rpm in order to determine the dependence of the final products on the fluxion velocity of the reaction suspension. At 450 rpm, the final product prepared at 25°C with an O_2 flow rate of 2 L/min was pure birnessite, as shown by XRD (Figure 3A). The amount of birnessite, demonstrated by the intensity of the diffraction peaks at 0.712 and 0.358 nm in the XRD patterns (Figure 3B,C), decreased with decreasing stirring speed, while the amount of hausmannite, indicated by the intensity of the peaks at 0.277 and 0.249 nm was increased. When the mechanical stirring was removed, a small amount of feitknechtite appeared in the final products (Figure 1C); at this time hausmannite was the main phase instead of birnessite synthesized with mechanical stirring. This suggests that using mechanical

stirring to raise the fluxion velocity of reaction suspension facilitates the synthesis of birnessite.

The bubbling rate of O_2 also played a role in improving the fluxion velocity of the reaction suspension through the agitation of O_2 flow. When the O_2 flow rate increased from the typical 2 L/min to 4 L/min, and the speed of the mechanical stirring was kept at 250 rpm, the final product was birnessite only, similar to the product yielded at the O_2 flow rate of 2 L/min and at the stirring speed of 450 rpm. As mentioned above, an O_2 flow of 2 L/min was enough for the oxidation reaction, so it was the increase of fluxion velocity of the reaction suspension caused by the increase in O_2 flow rate that actually influenced the oxidation and the final products. The results confirm that raising the fluxion velocity of the reaction suspension is essential to the formation of birnessite.

Effects of the reaction temperature

The reaction temperature was regarded as a key parameter affecting whether pure birnessite could be synthesized. Birnessite was usually synthesized at 10°C or 5°C. At higher reaction temperatures, the rate of the side reaction, hausmannite formation, increased greatly and the side reaction competed strongly with the reaction of birnessite formation (Stähli, 1968; Giovanoli *et al.*, 1970a; Golden *et al.*, 1987; McBride, 1987; Yang and Wang, 2002). As reported in the literature (Yang and Wang, 2002), the temperature at which the NaOH and MnCl_2 solutions were mixing during the initial 5 min (initial temperature) was found to be a decisive factor affecting the final products. When the initial temperature was >20°C, the final products were a mixture of low-valence Mn oxides and birnessite, irrespective of the other parameters. Therefore, throughout this study the initial temperature was maintained below 10°C. This was done by cooling the NaOH solution close to 5°C before pouring it into the MnCl_2 solution.

During the oxidation, the temperatures were controlled at 5°C or 25°C by iced water or water bath to study the effect of the reaction temperature on the synthesis of birnessite and on the properties of products. The O_2 flow rate of 2 L/min and the stirring speed of 450 rpm were kept the same in the experiments. Figure 4 shows the XRD patterns of the products at two different oxidation temperatures; birnessite is the only phase in both products. Peak intensities in the XRD pattern of the birnessite prepared at 25°C were much stronger than those of the birnessite prepared at 5°C. The crystal sizes and relative crystallinities were also increased with increasing reaction temperature from 5 to 25°C. The crystal sizes of the birnessites prepared at 5 and 25°C were 28.8 and 39.4 nm, respectively, measured on the diffraction peaks at 0.712 and 0.358 nm on the Scherrer formula. Particle morphology observed under TEM (Figure 5A,B) also showed that the crystal sizes of birnessite increased when the reaction temperature

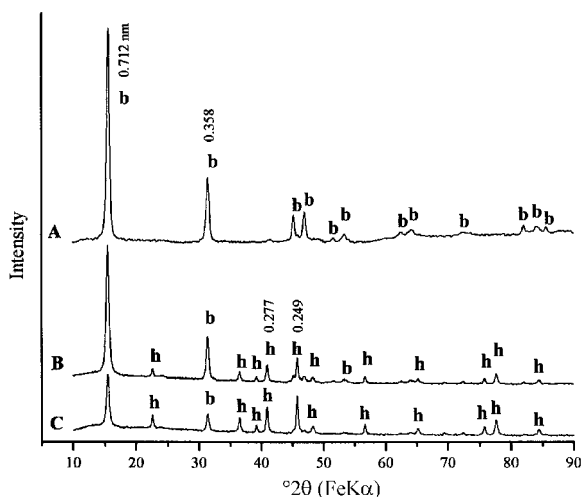


Figure 3. XRD patterns of birnessites synthesized (A) at a stirring speed of 450 rpm, (B) at a stirring speed of 250 rpm and (C) at a stirring speed of 100 rpm. b – birnessite; h – hausmannite.

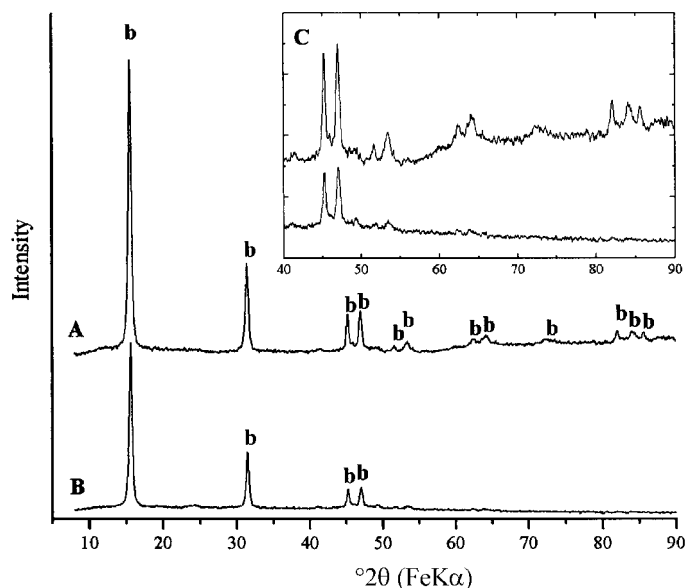


Figure 4. XRD patterns of birnessites synthesized (A) at 25°C; (B) at 5°C and (C) enlarged XRD pattern of A and B in the 2θ range 40–90°. b – birnessite.

increased. The crystallites of birnessite prepared at 25°C mainly consisted of well stacked hexagonal plates along the direction of the (001) plane, $\sim 1 \mu\text{m}$ in size, while birnessite prepared at 5°C had a thin and random stacked platy morphology. The electron diffraction pattern for the synthetic birnessite was indexed successfully assuming a triclinic unit-cell with $a = 2.9573 \text{ \AA}$, $b = 2.9547 \text{ \AA}$, $c = 7.334 \text{ \AA}$, $\alpha = 78.72^\circ$, $\beta = 101.79^\circ$, $\gamma = 122.33^\circ$ (Figure 5C) (Lanson *et al.*, 2002b). This indicated similarity in structure between the synthetic birnessite and those reported in the literature (Giovanoli *et al.*, 1970a; Post and Veblen, 1990; Drits *et al.*, 1997; Lanson *et al.*, 2000; Lanson *et al.*, 2002a, 2002b). For comparison, when calculated from the sum of the areas of the characteristic peaks at 0.71 and 0.36 nm (Luo and Suib, 1997; Luo *et al.*, 1998), the crystallinity of the birnessite prepared at 25°C was assigned to 100%, the calculated relative crystallinity of the birnessite prepared at 5°C was 76%. Better crystallinity and larger crystal sizes at low temperature led to a lower surface area. The BET surface area of the birnessite prepared at 5°C was $52.6 \text{ m}^2/\text{g}$, and $35.8 \text{ m}^2/\text{g}$ at 25°C. The average Mn oxidation state of the birnessite synthesized at 5°C was 3.86, very similar to that of birnessite synthesized at 25°C.

From the above results, it was apparent that varying the temperature during the oxidation from 5 to 25°C only influenced the crystallization behavior of the synthetic birnessite. Relatively high temperature (25°C) improved the crystallization of the birnessite but did not affect the formation of hausmannite.

Transformation of busserite into birnessite under different dehydration conditions

In the OPO method, $\text{Mn}(\text{OH})_2$ is oxidized by O_2 or air to form 1 nm busserite which is further transformed into

0.7 nm birnessite under a dehydration condition such as freeze drying or heat drying (Giovanoli *et al.*, 1970a, 1970b; Golden *et al.*, 1986a, 1986b, 1987; Paterson *et al.*, 1986; Cornell and Giovanoli, 1988; Yang and Wang, 2002; Cai *et al.*, 2002). Apart from a slight difference in crystallinity determined from the profiles of XRD patterns, the final products subjected to freeze drying and heat drying were similar in appearance, particle size, crystallinity and morphology. The birnessite formed using freeze drying could be converted completely to a 1 nm Mg birnessite (or Mg busserite) structure after being exchanged with 1 M MgCl_2 solution for 10 h (Figure 6B). However, only part of the birnessite formed by heat drying could be converted into Mg birnessite. Prolonging the exchange period to 10 days did not increase the conversion (Figure 6A). Rearrangement and fixation of Na between interlayers of birnessite caused by heat might account for the partial loss of ion-exchange capacity with Mg^{2+} (Shen *et al.*, 1993; Luo and Suib, 1997). When the freeze drying was carried out for 3 h, the dehydration and conversion process of busserite into birnessite was incomplete; the products were a mixture of busserite (McKenzie, 1989) which showed the major peaks at 1.025, 0.511 and 0.340 nm and birnessite; no other intermediate appeared. If the freeze drying process was continued, the mixture was transformed into pure birnessite (Figure 7).

The pathways and mechanism of the formation of birnessite by O_2 oxidation

In spite of many published works on birnessite, the mechanism and the pathways of its formation in nature have not been elucidated fully. The same is true for the synthetic birnessite using the OPO method. Giovanoli (1970) suggested that the synthetic birnessite retained

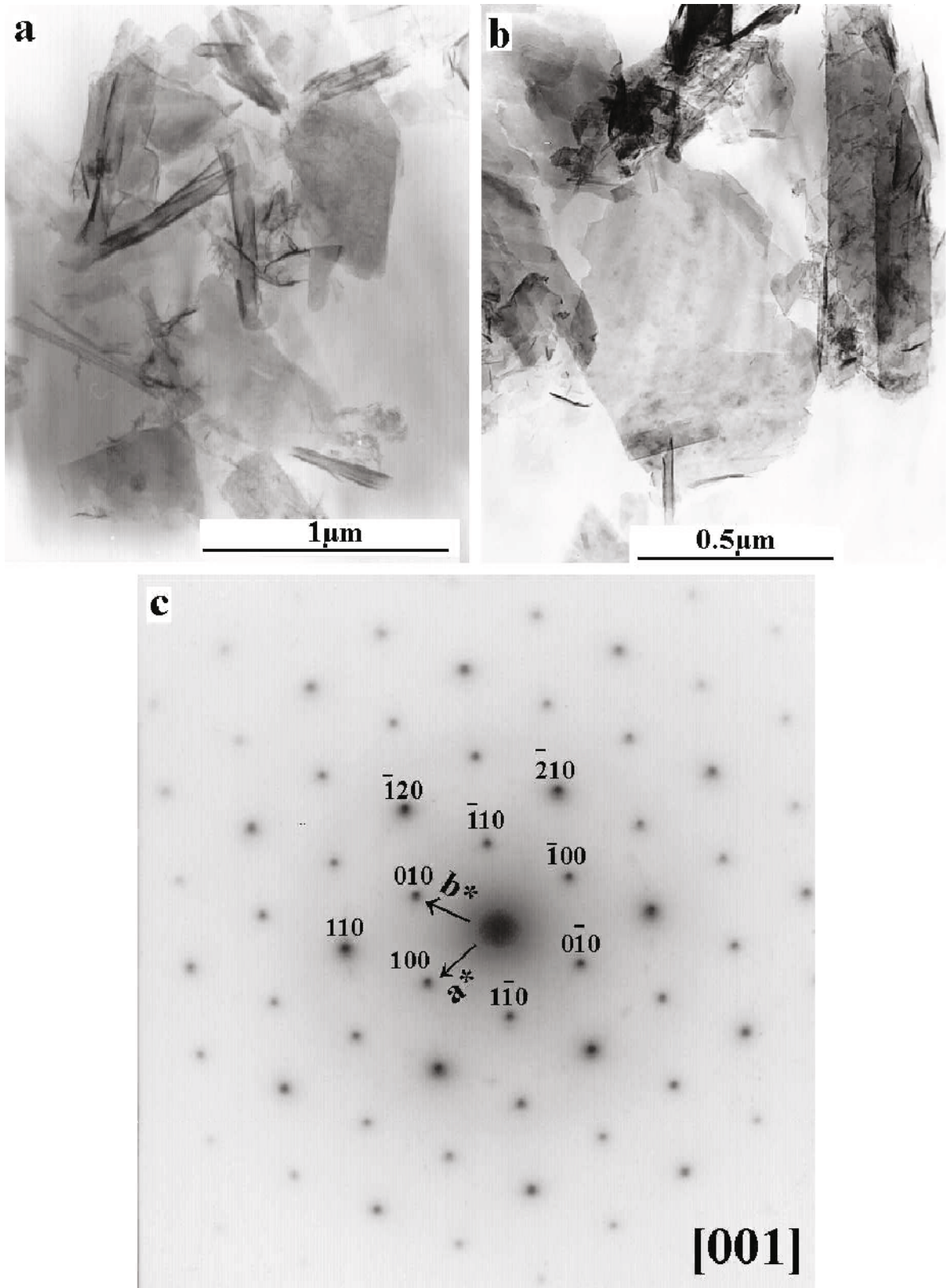


Figure 5. TEM images of (a) birnessite synthesized at 5°C, (b) birnessite synthesized at 25°C, and (c) indexed selected area electron diffraction of birnessite synthesized at 25°C.

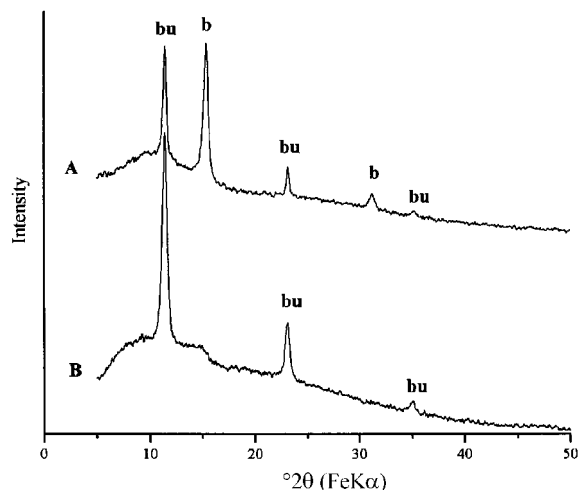


Figure 6. XRD patterns of Mg^{2+} -exchanged birnessites: (A) hydrated by heat drying and (B) hydrated by freeze drying. bu – buserite; b – birnessite.

the parent crystal structure of pyrochroite. He proposed the brief reaction course as: pyrochroite \rightarrow buserite \rightarrow birnessite. The XRD patterns of the oxidation products in wet state at different reaction times are shown in Figure 8. From the different products formed during the course of the oxidation, the formation process of the buserite can be divided into three stages: (1) prephase I (a phase related to hausmannite, $\gamma\text{-Mn}_3\text{O}_4$ (Luo and Suib, 1997; Luo *et al.*, 1998)) and feitknechtite formation period; (2) transformation of prephase I and feitknechtite into buserite period; and (3) buserite-crystal growing period.

In the prephase I and feitknechtite formation period (0–15 min), prephase I and feitknechtite were formed

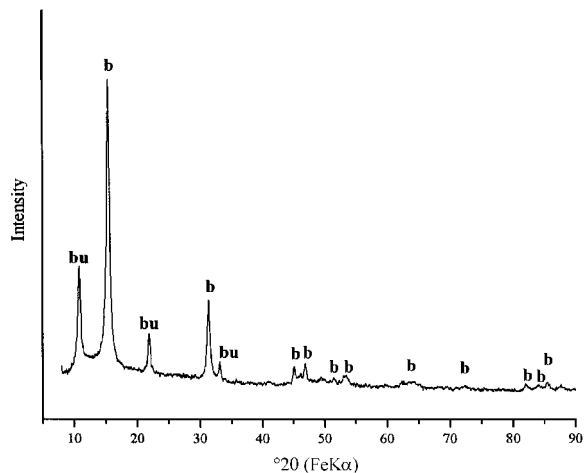


Figure 7. XRD pattern of birnessite dehydrated by freeze drying for 3 h. bu – buserite; b – birnessite.

within the initial 5 min of the oxidation after NaOH and MnCl_2 solutions were mixed (Figure 8A). After that, feitknechtite increased slightly while prephase I decreased gradually, determined from their diffraction-peak intensities (Figure 8B). There were no apparent pyrochroite peaks in the XRD patterns, indicating that $\text{Mn}(\text{OH})_2$ existed mainly in an X-ray amorphous state during the reaction. The characteristic diffraction peaks of pyrochroite are at 0.472 and 0.245 nm (JCPDS 18-787; Bricker, 1965), labeled in Figure 8. Subsequently, buserite appeared and increased slowly after oxidation for 15 min while prephase I had disappeared after 20 min (Figure 8B,C). Meanwhile, feitknechtite reached a maximum and then decreased until it had disappeared after 1 h (Figure 8D). These

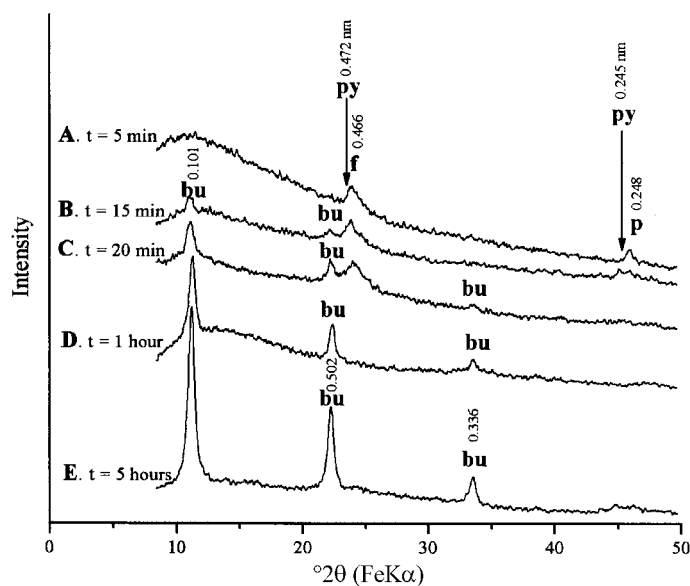


Figure 8. XRD patterns of intermediates synthesized over different time periods at 25°C. bu – buserite; f – feitknechtite; p – prephase I; py – pyrochroite.

were the characteristics of the transformation of prephrase I and feitknechtite into buserite (over 15–60 min). The transformation of hausmannite, the crystalline form of prephrase I, into birnessite, takes place very slowly at 25°C (Cornell and Giovanoli, 1988). It may be that a little of prephrase I transformed directly into buserite. Therefore, in the first hour of the reaction, prephrase I might be converted into feitknechtite which, in turn, was transformed into buserite. Buserite was the only phase in the XRD patterns after 1 h of oxidation. The intensities of the buserite peaks increased continuously at an almost stable rate and eventually approached a steady state (buserite crystal-growing period, 1–5 h) (Figure 8E). More crystalline buserite would be transformed into birnessite with higher crystallinity after freeze drying, or *vice versa*. Accordingly, two pathways of birnessite formation can be established as follows: (1) $\text{Mn}(\text{OH})_2$ (amorphous) \rightarrow feitknechtite \rightarrow buserite \rightarrow birnessite, and (2) $\text{Mn}(\text{OH})_2$ (amorphous) \rightarrow prephrase I \rightarrow feitknechtite \rightarrow buserite \rightarrow birnessite.

Luo *et al.* (1998) also proposed three stages for the synthesis of birnessite using the OPP method according to the crystallization of birnessite, and gave the possible route of birnessite formation: pyrochroite \rightarrow prephrase I (MnO_x) \rightarrow feitknechtite \rightarrow birnessite. It would take a much longer time (>45 days) to complete the entire three stages at 27°C, and birnessite appeared throughout the three stages, but the pathway of the birnessite formation in the OPP method is similar to that observed in this study using the OPO method.

Yang and Wang (2002) also found two similarities in the ODP method (modified OPO method) and the OPP method: the basicity effects on the synthesis, and the morphology of the products synthesized at high or low basicity. By increasing the basicity, the oxidation of $\text{Mn}(\text{OH})_2$ was promoted. The product prepared at low basicity has a flower-like, platy morphology with low crystallinity, whereas that prepared at high basicity has a hexagonal platy morphology with high crystallinity (Luo *et al.*, 1998; Yang and Wang, 2002). Furthermore, the reaction temperature used in the OPP and OPO methods had similar effects (although to a different extent) on the synthesis of birnessite and some properties of the synthetic birnessite such as crystal size and crystallinity. These similarities indicate that syntheses of birnessite in alkali media, whatever method used, may have the same pathways of birnessite formation or at least similar reaction mechanisms (Yang and Wang, 2002).

The redox reaction between $\text{Mn}(\text{OH})_2$ and O_2 occurs in a heterogeneous system. The diffusion of O_2 molecules in the solution to the surface of $\text{Mn}(\text{OH})_2$ and maintaining a high concentration of O_2 around the surface of $\text{Mn}(\text{OH})_2$ and intermediate phases were the key steps for the reaction. With increasing fluxion velocity of the reaction suspension, the thickness of the diffusion boundary layer through which O_2 was diffused

onto the surface of $\text{Mn}(\text{OH})_2$ and intermediate phases decreased, and thus the concentration gradient of O_2 between bulk solution and the surface of $\text{Mn}(\text{OH})_2$ and intermediate phases increased. On the basis of the Diffusion Law, the velocity of diffusion of O_2 was improved as a result, thus facilitating the formation of buserite or transformation of intermediate phases into buserite during the oxidation. Otherwise, the concentrations of O_2 or the Eh values on the surface of $\text{Mn}(\text{OH})_2$ and intermediate phases were not high enough to complete oxidation of $\text{Mn}(\text{OH})_2$ and intermediate phases, or oxidation of $\text{Mn}(\text{OH})_2$ and intermediate phases at a necessary rate. Consequently, the side reactions (Bricker, 1965; Giovanoli *et al.*, 1970a, 1970b; Golden *et al.*, 1986b, 1987; Yang and Wang, 2002; Cai *et al.*, 2002) took place as follows: $\text{Mn}(\text{OH})_2$ (amorphous) \rightarrow prephrase I \rightarrow (recrystallization) \rightarrow hausmannite.

Therefore, the final products in the synthesis depended on the velocity of diffusion of O_2 to the surfaces of $\text{Mn}(\text{OH})_2$ and intermediate phases if the O_2 flow rate was sufficient for the oxidation reaction. In other words, the diffusion of O_2 was the controlling step of the entire reaction.

CONCLUSIONS

Increasing the fluxion velocity of the reactive suspension and O_2 flow rate enhanced the velocity of O_2 diffusion to the surfaces of $\text{Mn}(\text{OH})_2$ and intermediate phases, and thus facilitated the synthesis of birnessite. Pretreatment of the NaOH and MnCl_2 solutions with N_2 or O_2 had little effect on the synthesis. Birnessite could be synthesized at room temperature and at a low temperature as long as the temperature during mixing the reaction solutions was maintained below 10°C. Increasing the reaction temperature led to a larger crystal size, better crystallinity and lower surface area. Both freeze drying and heating at 60°C, to dehydrate the buserite, produced birnessite, but drying the buserite by heating causes partial loss of ion-exchange capacity.

Prephrase I and feitknechtite were formed as intermediates and $\text{Mn}(\text{OH})_2$ existed in an X-ray amorphous state, *i.e.* not in the form of 'pyrochroite', during the synthesis. The process of buserite formation in the course of oxidation could be divided into three stages: (1) prephrase I and feitknechtite formation period; (2) transformation of prephrase I and feitknechtite into buserite period; and (3) buserite crystal-growing period. The diffusion of O_2 was the controlling step of the entire reaction. Two pathways of the birnessite formation might be:

(1) $\text{Mn}(\text{OH})_2$ (amorphous) \rightarrow feitknechtite \rightarrow buserite \rightarrow birnessite, and

(2) $\text{Mn}(\text{OH})_2$ (amorphous) \rightarrow prephrase I \rightarrow feitknechtite \rightarrow buserite \rightarrow birnessite

The synthesized birnessite was pure and well crystal-

lized with a hexagonal platy morphology. Its average composition was $\text{Na}_{0.25}\text{MnO}_{2.07} \cdot 0.66\text{H}_2\text{O}$, and BET surface area was $37.8 \text{ m}^2/\text{g}$.

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