Synthesis of todorokite-type manganese oxide from Cu-buserite by controlling the pH at atmospheric pressure

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ABSTRACT

A todorokite-type manganese oxide molecular sieve material was successfully synthesized at atmospheric pressure by refluxing treatment of Cu²⁺ exchanged Na-buserite (named as Cu-OMS-1). TEM (transmission electron microscope) and HRTEM (high resolution transmission electron microscope) images revealed that this material has a needle-phase crystal morphology with thickness 0.1–1 μm, and the lattice fringes spacing 1.0 nm corresponding to the [100] plane of the todorokite structure. Such morphological and intergrowth characteristics were similar to those of hydrothermally synthesized todorokites. The Cu-OMS-1 with a chemical composition of Cu_{0.34}MnO_{2.19} · 1.11H₂O, was stable below 400 °C. The BET surface area was found to be 62.5 m²/g, and a major micropore size distribution peak centered at 0.70 nm for Cu-OMS-1 by the Horvath–Kawazoe (HK) method. As determined by the *t*-plot method, 31% of the surface area was contributed by micropores. The pH of reaction solution plays an important role in the sub-structure modification of formed Cu-buserites and the formation of todorokite at atmospheric pressure. A mechanism for the influence of pH on the transformation is discussed.

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1. Introduction

Manganese oxide materials are a family of microporous transition metal oxides and can form mixed-valent semiconducting octahedral molecular sieves (OMS) with tunnel structures of various sizes [1–6]. Todorokite-type manganese oxide (OMS-1) is one group in the OMS family, containing 3 × 3 tunnel structure with a pore size of 6.9 Å [7]. The OMS-1 materials have been found to have a wide variety of applications as catalysts, absorbents, and battery materials due to their unique structures and physical and chemical properties [7–10]. Todorokite was firstly synthesized by Golden et al. through autoclave treatment of Mg²⁺ exchanged birnessite (Mg-buserite) under hydrothermal conditions [11]. Other hydrated inorganic divalent cations, such as Ni²⁺, Co²⁺, Cu²⁺, have successfully been used as templates for the synthesis of todorokites with different physical and chemical properties [12–14]. Over 25 ions, including group I/II metals and other main-group metals, transition metals, and lanthanides, have been ion-exchanged into stable Na-buserite by double-aging method, and todorokites have been made from these stable metal-buserites by hydrothermal treatment [15].

Low productivity, difficulties in controlling the reaction, and the high costs of hydrothermal synthesis in a volume limited autoclave

container obstruct further fundamental studies and extensive applications of todorokite. Feng et al. synthesized todorokite at atmospheric pressure by refluxing (100 °C) Mg-buserite, and the structure and properties of this product were similar to hydrothermally synthesized samples [16]. Ni²⁺, Cu²⁺, Co²⁺, Co(NH₃)₃³⁺ and La³⁺ were also used as templates to prepare precursor buserite. Todorokites can be synthesized by refluxing Ni-buserite, Co(NH₃)₆-buserite and La-buserite. However, no todorokite was obtained after refluxing of Cu-buserite and Co-buserite [17].

The features of extended X-ray absorption fine structure spectra (EXAFS) for Cu²⁺ in the Cu-buserite indicated that Cu²⁺ could replace Mn²⁺ that is located above or below octahedral vacancies in the interlayer, and Cu²⁺ could bond tightly with MnO₆ layers via shorter bonds (Cu–O) because of the unsymmetrical electron configuration and the difference in radius between the two cations [18,19]. The amount of migration or disproportionation of Mn³⁺ and formation of vacancies in Na-rich buserite depended on the solution pH, and more vacancies were produced at low solution pH (pH 2–5) [20,21]. Consequently, the amount of Cu²⁺ that located above or below the octahedral layer vacancy sites by replacing Mn²⁺ would also increase with decreasing pH value.

Liu et al. have reported that the reaction temperature significantly influenced the formation of todorokite under the hydrothermal condition [22]. Todorokite could be easily obtained by hydrothermal treatment of Cu-buserite at high temperature (150–170 °C) [13,23]. However, the transformation from Cu-buserite to

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todorokite was interrupted at lower pH by increased Cu^{2+} located at vacancy sites, because the dissociation of the strong Cu–O bond was difficult during refluxing at atmospheric pressure [17]. Therefore, Cu-buserite may transform to todorokite under refluxing conditions, if the amount of Cu^{2+} located above or below the vacancy sites is reduced by controlling pH at higher values (pH 4.5 in present work).

2. Experimental section

2.1. Preparation of Na-buserite

Na-buserite was prepared as follows: 250 mL of 5.5 mol/L NaOH solution ($<0^\circ\text{C}$) was added to 200 mL of 0.5 mol/L MnCl_2 solution quickly to form a white $\text{Mn}(\text{OH})_2$ precipitate, and O_2 was bubbled immediately at a rate of 1.5 L/min. After oxidation for 5 h, the black precipitate was washed with distilled deionized water (DDW) until the pH was approximately 7 [24].

2.2. Preparation of Cu-buserite at uncontrolled pH

Ten grams of purified Na-buserite (still wet) was dispersed in a 300 mL solution containing 0.5, 1, 2, 3, 4, 5 or 6 mmol of CuCl_2 at room temperature. After stirring at a mid-speed for 12 h, the suspensions were centrifuged and the supernatants were analyzed for Cu^{2+} , Mn^{2+} , Na^+ and pH. The solids were washed 3–5 times with DDW. The treated buserites were labeled as 0.5Cu-buserite, 1Cu-buserite, 2Cu-buserite, 3Cu-buserite, 4Cu-buserite, 5Cu-buserite and 6Cu-buserite.

2.3. Preparation of Cu-buserite at pH 4.5

This treatment was similar to that of the uncontrolled pH treatment, but the CuCl_2 solution was added dropwise into the suspension of Na-buserite at pH 4.5 using pH stat titration. The treated buserites were labeled as 0.5Cu-buserite (pH 4.5), 1Cu-buserite (pH 4.5), 2Cu-buserite (pH 4.5), 3Cu-buserite (pH 4.5), 4Cu-buserite (pH 4.5), 5Cu-buserite (pH 4.5) and 6Cu-buserite (pH 4.5).

2.4. Treatment of Cu-buserites by refluxing

The above treated Cu-buserites were dispersed in 400 mL of DDW, and the suspensions were transferred to a flask and refluxed (100°C) with stirring for 24 h at atmospheric pressure. The refluxed products were washed 3–5 times with DDW and then dried at 110°C .

2.5. Chemical analysis

The chemical compositions of the buserites and the elemental contents of exchanged solution were analyzed by a Varian Vista-MPX ICP-OES (ICP). Approximately 100 mg of sample was dissolved in 50 mL of aqua regia and diluted to 1000 mL. The concentration of Cu, Mn, and Na was analyzed at wave lengths of 224.70, 260.568 and 589.592 nm, respectively. All chemical analyses were replicated three times and the means were recorded. The average manganese oxidation state (AOS) was obtained using a oxalic acid-permanganate back-titration method that has been described in detail elsewhere [16].

2.6. Physical analysis

X-ray powder diffraction (XRD) was carried out using a D/Max-3B diffractometer equipped with a monochromated Fe K α radiation. The diffractometer was operated at a tube voltage of 40 kV

and a tube current of 20 mA, and a step scanning rate of 0.02° per 0.5 s.

The samples for TEM (transmission electron microscopy) were gently crushed to powder, then dispersed in anhydrous alcohol and sonicated prior to deposition on holey C-substrate on a Cu-grid where they were dried in air. The TEM images and electron diffraction patterns were obtained by a JEM 2010 TEM at an accelerating voltage of 200 kV. The HRTEM was performed on sample suspensions dried on a holey carbon grid with a JEOL JEM 2010 FEF electron microscope operated at 200 kV. SEM (scanning electron microscopy) images were obtained with a Quanta200 emission scanning electron microscope. Infrared spectra (IR) were obtained with a Bruker Equinox 55 model spectrophotometer by making pellets with KBr. The resolution was set at 4 cm^{-1} with a scan number of 15. TGA (thermogravimetry analysis) was carried out on a NET-ZSCH TG 209 thermogravimetric analyzer with a 20 mL/min N_2 flow from 37 to 800°C at a heating rate of $10^\circ\text{C}/\text{min}$. A Quantachrome Autosorb-1 instrument was used to measure the surface areas and micropore size distributions of the materials. Samples were degassed in a vacuum at 250°C for about 10 h to remove water and other physically adsorbed species. The N_2 isothermal adsorption and desorption experiments were performed at relative pressures (P/P_0) from 10^{-6} to 0.9916 and from 0.9916 to 0.047, respectively.

3. Results

3.1. Transformation of Cu-buserites to todorokite prepared at uncontrolled pH

3.1.1. XRD analyses

Fig. 1a shows the XRD patterns of products (Cu-buserites) that were produced by ion-exchanged of Na-buserite at different concentrations of CuCl_2 and uncontrolled pH. The basal d-spacing of Cu-buserites decreased gradually from 1.020 nm of Na-buserite to 0.956 nm of 6Cu-buserite with increasing Cu^{2+} from 0 to 6 mmol (Fig. 1a). Fig. 1b shows the XRD patterns of products with refluxing for different Cu-buserites. The intensity of 0.96 and 0.48 nm diffraction peaks of todorokite increased gradually upon changing the amount of Cu^{2+} from 0.5 to 3 mmol, indicating that Cu^{2+} addition increased the formation of todorokites. However, above 4 mmol of Cu^{2+} treatment, the intensity of characteristic diffraction peaks became weaker or even disappeared, indicating that the formation of todorokites was interrupted.

3.1.2. TEM studies

TEM bright-field images and electron diffraction (ED) patterns obtained from the refluxed products of 3Cu-buserite are shown in Fig. 2. The matrices were actually formed by fibrous crystals twinned with each other at 120° , which was the typical characteristic of todorokite (Fig. 2a). The ED pattern of the trilling crystal matrix of the todorokites showed that diffraction spots were linked by streaks to one another to construct a hexagonal net, equivalent to overlapping of three [001] ED patterns of single fibrous with each other at 120° (Fig. 2b). The present results are in agreement with those todorokite synthesized by hydrothermal treatment and reflux method [7,16].

3.1.3. Elemental analyses

Table 1 shows the elemental composition of Cu-buserites prepared at uncontrolled pH. The quantity of Cu^{2+} in Cu-buserites increased gradually with increasing Cu^{2+} concentration in the reaction solution, but the amount of interlayer Na^+ decreased until the interlayer Na^+ exchanged completely with Cu^{2+} and H^+ . The Mn content in Cu-buserites decreased during the ion-exchange

Fig. 1. XRD patterns of different Cu-buserites (a) and corresponding refluxed (100 °C for 24 h) products (b) (Re stands for refluxing).

Fig. 2. TEM images (a) and ED patterns (b) of refluxed product of 3Cu-buserite.

Table 1

Elemental composition of the different Cu-buserites prepared at uncontrolled pH

Sample	Na (mmol/0.1 g)	Cu (mmol/0.1 g)	Mn (mmol/0.1 g)	Cu/Mn (molar ratio)
Na-buserite	0.279	0	1.106	0
0.5Cu-buserite	0.171	0.022	1.010	0.022
1Cu-buserite	0.133	0.042	1.005	0.042
2Cu-buserite	0.064	0.086	0.974	0.088
3Cu-buserite	0.022	0.111	0.931	0.119
4Cu-buserite	0	0.162	0.822	0.197
5Cu-buserite	0	0.181	0.817	0.222
6Cu-buserite	0	0.203	0.812	0.250

process, and the ratio of Cu/Mn increased gradually with increasing Cu^{2+} concentration in the reaction solution.

The relations between the concentrations of Cu^{2+} , Mn^{2+} , and Na^+ and pH value in the supernatants after ion-exchange and the amount of Cu^{2+} added are shown in Fig. 3. When 0.5–2 mmol of Cu^{2+} was used for ion-exchange with Na-buserite no Cu^{2+} or Mn^{2+} appeared in the supernatants, and only Na^+ was detected. Moreover, the amount of Na^+ increased and the pH of the supernatants decreased slowly from 7.11 to 6.73 for Cu^{2+} concentrations increasing from 0.5 to 2 mmol. Cu^{2+} and Mn^{2+} were detected when 3 mmol of Cu^{2+} was used for ion-exchange, where the pH dramati-

cally decreased to 4.57. As the amount of Cu^{2+} added exceeded 4 mmol, more Mn^{2+} was released into the solution, but the Na^+ content remained constant; this phase was associated with a slow decrease in pH. The Cu^{2+} and H^+ exchanged mostly with Na^+ in the interlayer of Na-buserite when low concentrations of CuCl_2 (0–2 mmol) were used for ion-exchange, and Mn^{2+} in the interlayer was released into solution when 3 mmol of CuCl_2 or more was used.

3.2. Transformation of Cu-buserites to todorokite prepared at pH 4.5

Fig. 4 shows the XRD patterns of refluxed products for different Cu-buserites prepared at pH 4.5. The intensity of 0.96 nm diffraction peak increased gradually, while the intensity of 0.72 nm diffraction peak decreased with increasing Cu^{2+} from 0.5 to 3 mmol. The 0.72 nm peak disappeared together with an increase in intensity of the 0.96 nm diffraction line for CuCl_2 concentration at 4 mmol and higher. The present results indicated that the formation of todorokite from Cu-buserite prepared at pH 4.5 increased with increasing CuCl_2 from 0.5 to 3 mmol, which was similar to that under uncontrolled pH condition. However, as the amount of CuCl_2 exceeded 4 mmol, there was no interruption in the formation of todorokite and all of the Cu-buserite was converted into todorokite at atmospheric pressure.

Fig. 3. Relations between Cu^{2+} , Mn^{2+} , Na^+ and pH value in the supernatants and amount of Cu^{2+} added.

Fig. 4. XRD patterns of products with different Cu-buserites prepared at pH 4.5 refluxing at 100 °C for 24 h.

Table 2
Elemental composition of the different Cu-buserites prepared at pH 4.5

Sample	Na (mmol/0.1 g)	Cu (mmol/0.1 g)	Mn (mmol/0.1 g)	Cu/Mn (molar ratio)
Na-buserite	0.279	0	1.106	0
0.5Cu-buserite (pH 4.5)	0	0.036	0.984	0.037
1Cu-buserite (pH 4.5)	0	0.051	0.874	0.058
2Cu-buserite (pH 4.5)	0	0.097	0.853	0.114
3Cu-buserite (pH 4.5)	0	0.117	0.800	0.146
4Cu-buserite (pH 4.5)	0	0.165	0.793	0.208
5Cu-buserite (pH 4.5)	0	0.229	0.784	0.292
6Cu-buserite (pH 4.5)	0	0.255	0.766	0.333

The chemical composition of Cu-buserite prepared at pH 4.5 was presented in Table 2. The Na was not detectable and the contents of Mn decreased in the Cu-buserites, and the amount of Cu increased gradually with increasing Cu^{2+} in solution during the ion-exchange process. These were similar to that of Cu-buserites prepared at uncontrolled pH. However, in comparison with that of Cu-buserites prepared at uncontrolled pH, all the interlayer Na^+ was exchanged by Cu^{2+} and H^+ in the solution when lower concentrations of CuCl_2 (0.5–3 mmol) were used for ion-exchange at pH 4.5, and the content of Cu in Cu-buserites prepared at pH 4.5 was greater than that of Cu-buserites prepared at uncontrolled

pH. The higher molar ratio of Cu/Mn in Cu-buserites prepared at pH 4.5 (Table 1) than that of Cu-buserites prepared at uncontrolled pH (Table 2) may be due not only to the release of Mn^{2+} at uncontrolled pH, but also to the higher sorption capacity at a controlled pH of 4.5.

3.3. Characterization of Cu-todorokite prepared by controlling the pH at 4.5

3.3.1. Crystal structure analysis

TEM and HRTEM images of the refluxed products of 6Cu-buserite prepared at pH 4.5 (named as Cu-OMS-1) are shown in Fig. 5. Cu-OMS-1 contain mostly plate-shaped crystallite with the thickness of 0.1–1 μm (Fig. 5a). Fig. 5b is a typical HRTEM images obtained from Cu-OMS-1. The spacing of the lattice fringes is 1.0 nm, which is 3 MnO_6 octahedral chain widths [16], corresponding to the [100] planes of the todorokite structure. SEM photograph is shown in Fig. 6. Cu-OMS-1 clearly contains both needle and plate-shaped crystallites. Needles are well shaped with lengths of about 0.5–1 μm , and the shapes of the plates of Cu-OMS-1 are irregular.

3.3.2. IR results

The IR spectra of Cu-OMS-1 and hydrothermally synthesized Cu-todorokite, which was obtained by autoclaving the Cu-buserite for 24 h at 170 °C are shown in Fig. 7. The IR spectrum of Cu-OMS-1 (Fig. 7a) was generally in agreement with that of the hydrothermally synthesized Cu-todorokite (Fig. 7b). In the IR spectrum of Cu-OMS-1, the bands at 3395 and 1633 cm^{-1} can be assigned to stretching and bending vibrations of –OH groups of crystal and adsorbed water molecules, respectively. Cu-OMS-1 had a stronger band at $\sim 3400 \text{ cm}^{-1}$ than the hydrothermally synthesized Cu-todorokite, indicating that Cu-OMS-1 might possess more disordered water in the tunnel than the hydrothermally synthesized Cu-todorokite. The bands at 433, 504 and 763 cm^{-1} can be assigned to Mn–O stretching vibrations, and the absorbed band around 763 cm^{-1} can be assigned to the characteristic adsorbent of manganese oxides with tunnel structure [12].

3.3.3. Thermal properties

The results of TGA analyses of Cu-OMS-1 and hydrothermally synthesized Cu-todorokite are shown in Fig. 8. From TGA profiles, Cu-OMS-1 shows thermal behavior similar to that of hydrothermally synthesized Cu-todorokite except for an about 5% difference in weight loss. Cu-todorokite showed four major weight losses between 35 and 800 °C. The first weight loss was before 205 °C owing to desorption of physisorbed H_2O (Fig. 8). The second significant weight loss occurred between 205 and 400 °C, which could be due to the loss of lattice oxygen species and loss of the water bound in the tunnel [25]. The second weight loss indicated that the octahedral framework started to break down and the tunnel structure of the Cu-todorokite was not stable any more. The last two steps of weight loss could be attributed to for their destruction and collapse of the tunnel structure, respectively.

3.3.4. Surface area, porosity, and chemical composition

The results of surface area and micropore size of Cu-OMS-1 are shown in Fig. 9. The Brunauer–Emmett–Teller (BET) surface area of Cu-OMS-1 is 62.5 m^2/g . The inset of Fig. 9 shows a micropore size distribution calculated by the Horvath–Kawazoe (HK) method. The HK plot shows a major pore size distribution peak centered at 0.70 nm for Cu-OMS-1, which is agreement with the tunnel size of todorokite (0.69 nm $\times$ 0.69 nm). As determined by the t -plot method, 31% of the surface area was contributed by micropores. The chemical composition of Cu-OMS-1 was determined using ICP-OES. The AOS of Cu-OMS-1 is about 3.69. The composition of

Fig. 5. TEM and HRTEM images of Cu-OMS-1.

Fig. 6. SEM photographs of Cu-OMS-1.

Fig. 7. IR spectra of Cu-OMS-1 (a) and hydrothermally synthesized Cu-todorokite (b).

Fig. 8. TGA curves for Cu-OMS-1 (a) and hydrothermally synthesized Cu-todorokite (b).

Cu-OMS-1 is $\text{Cu}_{0.34}\text{MnO}_{2.19} \cdot \text{H}_2\text{O}_{1.11}$ as determined by ICP-OES combined with the AOS results.

4. Discussion

4.1. Effect of pH on sub-structure of Cu-buserite

Silvester et al., Drits et al. and Lanson et al. have reported that the Na-buserite synthesized at high pH consists of vacancy-free Mn bearing octahedral layers [20,26,27]. However, the replacement of one type of interlayer cation by another may be accompanied by the appearance of layer vacancies [26], and the formation of vacancies would increase markedly during the Na-buserite to H-exchanged hexagonal birnessite transformation at low pH (pH 5–2) [20,21].

When a low quantity of CuCl_2 (0.5–2 mmol) was used for ion-exchange with Na-buserite, the initial Na^+ in the interlayer of Na-buserite was firstly replaced by Cu^{2+} and H^+ in the CuCl_2 solution, and the pH of the supernatants decreased slowly at this stage (Fig. 3). Some Mn^{3+} migrated from the layer of Na-buserite forming layer vacancies during the ion-exchanging process. The migrated Mn^{3+} or Mn^{2+} that appeared to originate from a partial disproportionation of Mn^{3+} occupied above or below the layer vacancy sites in the interlayer, and the negative layer charge was mostly compensated by the

Fig. 9. (A) N₂ adsorption/desorption isothermal plot of Cu-OMS-1 and (B) the micropore size distribution plot by the HK method.

presence of interlayer Mn³⁺, Mn²⁺, Na⁺ and H⁺ cations. The Na⁺ contained in the Na-buserite decreased gradually with the increase in CuCl₂ (2–4 mmol), and the pH of the supernatants decreased dramatically, resulting in more Mn³⁺ migration into the interlayer and disproportionation to Mn²⁺ and Mn⁴⁺ and the concomitant formation of new layer vacancies. The Cu²⁺ and H⁺ in the reaction solution began to replace Mn²⁺ in the interlayer at this stage, leading Mn²⁺ to release into the reaction solution (Fig. 3). As the concentrations of CuCl₂ increased to 4–6 mmol, more Cu²⁺ replaced the Mn²⁺ ion that occupied above or below layer vacancy sites in the interlayer even as the pH of the supernatant decreased slowly in the uncontrolled pH experiment. The disproportionation of Mn³⁺ would release protons and consequently resulted in a greater decrease in pH in the supernatants than in pure CuCl₂ solution (Fig. 10).

Na-buserite released Mn²⁺ into the solution when a low quantity of CuCl₂ (0.5–3 mmol) was used for ion-exchange at pH 4.5, and the quantity of Mn²⁺ released into the reaction solution varied linearly with the amount of Cu²⁺ added (Fig. 11). However, the quantity of Mn²⁺ released became constant with further increase in CuCl₂ (4–6 mmol) concentrations at a controlled pH of 4.5. The amount of Mn²⁺ released was similar to that of Mn²⁺ released using 3 mmol CuCl₂ at an uncontrolled pH (pH 4.57) (Fig. 11). These results indicated that the formation of layer vacancies by the migration of Mn³⁺ from the layer into the interlayer or the disproportionation of Mn³⁺ to Mn²⁺ and Mn⁴⁺ were interrupted at the controlled pH of 4.5. In

Fig. 10. pH of the solution versus the added CuCl₂ concentration.

Fig. 11. Relation between amounts Mn²⁺ released in to the reaction solution and the CuCl₂ added.

other words, the amount of Cu²⁺ that occupied above or below layer vacancies sites by replacing a corresponding Mn²⁺ at the controlled pH of 4.5 was less than that of the uncontrolled pH samples when a large amount of CuCl₂ (4–6 mmol) was used for ion-exchange. The results from the pH controlled and uncontrolled experiments show that the quantity of Mn³⁺ that migrated into the interlayer and disproportionated to Mn²⁺ and Mn⁴⁺ depended on the solution pH during Na-buserite ion-exchanging with Cu²⁺ cation.

4.2. Effects of species and amount of interlayer Cu²⁺ on the formation of todorokites

Copper (II) was incorporated into the interlayer sites and occupied mainly interlayer sites by two chemical species. One was hydrated species when Cu²⁺ was exchanged with interlayer Na⁺ and H⁺. The other was bound to unsaturated O of three MnO₆ adjacent to the octahedral vacancy by a Cu–O bond and three interlayer H₂O molecules when it replaced the Mn²⁺ that originally occupied above or below the layer vacancy sites. The effects of the two chemical species of Cu²⁺ in the interlayer on the formation of todorokite by refluxing of Cu-buserite at atmospheric pressure were different. The hydrated form was favorable to the transformation from Cu-buserite to todorokite, but the Cu²⁺ located above or below the octahedral vacancy sites seemed to be unfavorable to the formation of todorokite because of tightly Cu–O bond during refluxing process at atmospheric pressure [17].

When low concentration of Cu²⁺ (0.5–3 mmol) was used for ion-exchanging with Na-buserite at uncontrolled pH, no vacancies formed and little Mn³⁺ migrated into the interlayer because of the high solution pH and Cu²⁺ mainly being exchanged with interlayer Na⁺ of Na-buserite. At this stage, the hydrated species of interlayer Cu²⁺ was dominant; Cu-buserite could convert into todorokite, and more todorokite was obtained with increasing of the percentage of the hydrated species.

With the increase of CuCl₂ (4–6 mmol) and the concomitant decrease in solution pH, more Mn³⁺ migrated from MnO₆ layers into the interlayer and disproportionated into Mn²⁺ and Mn⁴⁺, which led to more Cu²⁺ replacing interlayer Mn²⁺. Thus the Cu²⁺ occupancy above or below the layer vacancy sites gradually became dominant, and these Cu²⁺ are unfavorable to the formation of todorokite by refluxing method at the atmospheric pressure. Moreover, when Na-buserite ion-exchanged with Cu²⁺, some Na-buserite may have converted into H-birnessite. This change includes the migration of Mn(III) from octahedral layers to the interlayer and the partial disproportionation of Mn(III). As a result, the transformation from Na-buserite to todorokite was restricted to some extent.

However, the migration and the disproportionation of Mn^{3+} was restrained when the solution pH was controlled at 4.5, and the Cu^{2+} located above or below the octahedral vacancy sites by replacing Mn^{2+} was subsequently restricted. The hydrated species of inter-layer Cu^{2+} would increase with the CuCl_2 added, but Cu^{2+} ions located above or below the octahedral vacancy sites remained constant. So the controlled pH conditions were conducive to the formation of todorokite at the atmospheric pressure.

5. Conclusions

We have successfully synthesized Cu-todorokite (Cu-OMS-1) from Cu-buserites, which were prepared at a controlled pH of 4.5 and by a refluxing method at atmospheric pressure. The chemical composition of the Cu-OMS-1 was $\text{Cu}_{0.34}\text{MnO}_{2.19} \cdot 1.11\text{H}_2\text{O}$. The crystallinity of Cu-OMS-1 exhibited needle-phase with thickness 0.1–1 μm . The micropore size distribution was mainly at 0.7 nm. The Cu-OMS-1 exhibited the same structural characteristics to that of hydrothermal products, and it is stable below 400 °C. The sub-structure of Cu-buserites depended on the solution pH during Na-buserite ion-exchanging with Cu^{2+} cation. The amount of Cu^{2+} that occupied above or below layer vacancies sites by replacing Mn^{2+} at a controlled pH of 4.5 was less than that of the uncontrolled pH samples when a large amount of CuCl_2 (4–6 mmol) was used for ion-exchange. The above modification of sub-structure determined the transformation from Cu-buserite to todorokite under refluxing condition at atmospheric pressure.

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