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EFFECTS OF REACTION CONDITIONS ON THE FORMATION OF TODOROKITE AT ATMOSPHERIC PRESSURE

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Abstract—Todorokite is a common Mn oxide (with a tunnel structure) in the Earth surface environment, and can be obtained by hydrothermal treatment or refluxing process from precursor buserite with a layered structure. Several chemical reaction conditions for the phase transformation from Na-buserite to todorokite at atmospheric pressure were investigated, including temperature, pH, crystallinity of precursor Na-buserite, the amount of the interlayer Mg^{2+} of the Mg-buserite and clay minerals. The results showed that the conversion rate and crystallinity of todorokite decreased with falling temperature, and Mg-buserite could not be completely transformed to todorokite at lower temperatures (40ºC). The poorly crystalline Na-buserite could be converted into todorokite more easily than highly crystalline Na-buserite. Todorokite can be prepared at pH 5–9, but the rate of conversion and crystallinity of todorokite did vary with pH in the order: neutral ≈ alkali > acidic. The conversion rate of todorokite decreased with decreasing interlayer Mg^{2+} content of the Mg-buserite. The presence of montmorillonite or goethite slowed the formation reaction of todorokite in the refluxing process, and the reaction time was prolonged when the amounts of those minerals were increased.

Key Words—Birnessite, Clay Mineral, Mn Oxide, Todorokite, Transformation.

INTRODUCTION

Todorokite is a common Mn oxide (with a tunnel structure) in the Earth surface environment, commonly found in soil, terrestrial Mn ore deposits, and marine Mn nodules. Since todorokite was first found in Todoroki mine (Japan) in 1934, creation of its synthetic counterpart has been used to study its structure, properties and origin (Turner *et al.*, 1982; Golden *et al.*, 1986; Shen *et al.*, 1993; Naoaki *et al.*, 2001; Post *et al.*, 2003; Al-Sagheer and Zaki, 2004; Feng *et al.*, 2004a, 2004b; Liu *et al.*, 2005; Cui *et al.*, 2005). Todorokite was first synthesized by Golden *et al.* (1986) through autoclave treatment of Mg^{2+}-exchanged birnessite (Mg-buserite). Other hydrated inorganic divalent cations, such as Ni^{2+}, Co^{2+} and Cu^{2+}, have been used successfully in templates for the synthesis of todorokites with different physical and chemical properties (Golden *et al.*, 1987; Shen *et al.*, 1993, 1994). More than 25 kinds of ions, including group I/II metals and some other main-group metals, transition metals and lanthanides, have been ion-exchanged into stabilized Na-buserite by the double-ageing method. These stable metal-buserites were used to prepare todorokites by hydrothermal treatment (Luo *et al.*, 1999). During hydrothermal treatment of the buserite, foreign metal cations were incorporated into the Mn oxide layer framework to synthesize todorokites, and the distribution of the foreign cations in framework or tunnel sites was studied (Ching *et al.*, 1999). A nm-sized todorokite with particular characteristics was synthesized by Liu *et al*. (2002) from a layered precursor prepared using a sol-gel process. A microwave-assisted hydrothermal method of synthesis was used to prepare todorokite, which revealed properties superior to those of the conventionally synthesized ones such as greater stability, crystallinity and catalytic activity (Vileno *et al.*, 1999; Malinger *et al.*, 2004). The crystallinity, thermal stability and particle morphology of the synthesized todorokite were related to the crystallinity of the initial Na-birnessite (Liu *et al.*, 2005). However, hydrothermal treatment in those studies needed high temperature and autogenous pressure, resulting in difficulties in controlling the conditions. Although much work has been done on the synthesis of todorokite and its properties, there are few reports on the effects of reaction conditions on the process of todorokite formation.

Feng *et al.* (2004a, 2004b) first synthesized todorokite at atmospheric pressure by refluxing (at 100ºC) Mg-buserite, and found the structure and characteristics of the product were similar to that of hydrothermally synthesized samples. This work could have a significant effect on our understanding of mechanisms of formation of todorokite in the Earth surface environment. The rate of formation and the crystallinity of todorokite decreased with falling reaction temperature when highly crystalline birnessite was used as the precursor. The nature of the interlayer cations of buserites obviously affected transformation from buserite to todorokite, and todorokite could be obtained in a weak alkali medium or

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in a slightly acidic medium (Cui *et al.*, 2005). Natural todorokites typically occur as poorly crystalline nm-sized particles or are present as coatings coexisting with other minerals such as Fe oxides and clay minerals. However, it is not clear whether these minerals affect the formation of todorokite, and if so, what their influence is. Its also important to study the rate of formation and crystallinity of todorokite in alkali or acidic medium. Natural birnessite occurs in poorly crystalline form and the concentration of cations in the natural environment is far smaller than that used for ion exchange with Na-buserite during synthesis of todorokite (~0.5–1 M). In the present paper, the factors that may influence the formation of todorokites were investigated by using poorly crystalline Na-buserite as a precursor at atmospheric pressure.

MATERIALS AND METHODS

Synthesis of goethite

Goethite was synthesized by addition of KOH to an $Fe(NO_3)_3{\cdot}9H_2O$ solution until pH 12, and then ageing the suspension for 24 h at 60ºC (Atkinson *et al.*, 1967). The suspension was washed with distilled deionized water (DDW) until the supernatant solution pH was ~7. The sample was filtered and then freeze dried.

Treatment of montmorillonite

Montmorillonite was purchased from Henan Xinyang Montmorillonite Company. The clay was suspended in DDW and the pH value of the suspension was adjusted to 10 by addition of 0.01 M NaOH. The suspension was dispersed by occasional sonification. The <2 mm fraction was separated by sedimentation. The clay was washed with DDW and ethanol to completely remove Cl^- ions before being air dried.

Synthesis of Na-buserite

Na-buserite was prepared in alkali media by modifying Giovanoli's procedure (Feng *et al.*, 2004c). 250 mL of 5.5 M NaOH solution (<5ºC) were added quickly to 200 mL of 0.5 M $MnCl_2$ solution to form a white $Mn(OH)_2$ precipitate, and O_2 was immediately bubbled through the solution at rate of 1.5 L/min. The temperature was controlled at 5±1ºC by an ice-water bath thermostat. After being oxidized for 5 h, the black precipitate was washed by centrifugation until the pH was ~7.

Synthesis of Na-buserite with different crystallinity

Highly crystalline Na-buserite (HC-Na-bus) was obtained using the above method at 25±1ºC. Various poorly crystalline birnessites were prepared by fixing the time of bubbling of O_2 at 1 h, 3 h and 5 h at 5±1ºC. All products were washed with DDW until the pH was ~7. The washed samples are referred to in this paper as Na-bus-1h, Na-bus-3h and Na-bus-5h, respectively.

Preparation of Na-buserite-coated montmorillonite and goethite

Na-buserite-coated montmorillonite and goethite were prepared using the same method as the above synthesis of Na-buserite, except that 4 g of montmorillonite or 1 g, 4 g or 8 g of goethite were dispersed into $MnCl_2$ solution. The washed samples are referred to in this paper as Mon-Na-bus and Goe1-Na-bus, Goe4-Na-bus and Goe8-Na-bus, respectively. For example, Goe1-Na-bus equates to 1 g of goethite coexisting with synthesized Na-buserite.

ION EXCHANGE OF Na-BUSERITES AND CONVERSION TO TODOROKITES

About 10 g of purified Na-bus-5h (wet) were dispersed in each of 0.01, 0.05, 0.1 and 1 M $MgCl_2$ solutions (500 mL) with mild stirring for 24 h to prepare different Mg-buserites (0.01M-Mg-bus, 0.05M-Mg-bus, 0.1M-Mg-bus and 1M-Mg-bus) at room temperature. All the other Na-buserites in this work were ion exchanged with a 1 M $MgCl_2$ solution. Mg-buserites were dispersed in water to prepare the suspension; then the suspension was heated at 100ºC(refluxing), 90ºC, 80ºC and 40ºC with stirring at atmospheric pressure. The pH values of the systems were adjusted to 5.0, 7.0 and 9.0 using HCl or NaOH solutions, respectively. Two grams of montmorillonite or 2 g of goethite were dispersed in the Mg-buserite suspension (Mg-bus-Mon and Mg-bus-Goe), and then converted to todorokite by refluxing. The intermediate products at the different stages of the conversion were obtained for characterizing the effects of these factors on the formation of todorokites.

CHARACTERIZATION OF THE SAMPLES

X-ray diffraction (XRD) was carried out at ambient temperature, using a D/Max-3B diffractometer equipped with monochromated FeKα radiation. The diffractometer was operated at a tube voltage of 40 kV and a tube current of 30 mA, and a step scanning rate of 0.04º s^{-1}. Both Mg-buserites and todorokite have basal spacings of 1 nm. Mg-buserites are not stable and can be transformed into 0.7 nm manganate by heating or dehydrating. However, todorokite has a relatively high thermal stability. To eliminate the interference of diffraction peaks of Mg-buserite in the identification of todorokite, the oriented slides for the intermediate products were heated for 12 h at 140ºC before the XRD analyses (Feng *et al.*, 2004a).

The Mg-buserites were analyzed for their elemental contents using a Varian Vista-MPX inductively coupled plasma-optical emission spectroscope. Approximately 150 mg of the sample were dissolved in 50 mL of aqua regia and diluted to 1000 mL. Samples were analyzed to determine the concentration of Mn, Mg and Na at wavelengths of 260.568 nm, 280.270 nm and

589.592 nm, respectively. Three duplicate measurements of each ion were taken and the averages calculated.

Transmission electron microscopy (TEM) analysis was carried out using a JEM 2010 TEM operated at 200 kV. The samples were crushed gently to powder, and then dispersed in absolute alcohol for sonification. The sample was deposited on a holey copper grid and dried in air.

RESULTS AND ANALYSIS

Effects of temperature

Figure 1 shows the XRD patterns of intermediates heat treated (at 140ºC) at different stages when Mg-buserite was treated at different temperatures. When Mg-buserite was refluxed at 100ºC for 2 h, only the characteristic peaks of todorokite appeared in the XRD pattern of the product, indicating that Mg-buserite had been converted completely to todorokite. At a prolonged refluxing time of 24 h, the intensity of the XRD peaks was similar to that at a time of 2 h (Figure 1a). When the temperature was reduced to 90ºC, the intensity of the characteristic peaks of todorokite was similar to that of birnessite (product of Mg-buserite dehydrated) obtained after 6 h of treatment indicating that only some of the Mg-buserite had been converted to todorokite. At a heating time of 18 h, the characteristic diffraction peak of birnessite almost disappeared, and the characteristic diffraction peak became strong, indicating that Mg-buserite had been converted completely. When the treatment time was prolonged to 84 h, the characteristic peaks of todorokite became stronger, indicating that the crystallinity of the product was further enhanced (Figure 1b). When Mg-buserite was treated at 40ºC for 8 days (Figure 1c), the intensity of characteristic peaks of todorokite was similar to that of birnessite, indicating that only some of the Mg-buserite converted into todorokite. When the treatment time was prolonged to 35 days (Figure 1c), the intensity of characteristic peaks of todorokite was still similar to that of birnessite. This showed that no more Mg-buserite was converted to todorokite during this process. These results suggest that the transformation from Mg-buserite to todorokite takes

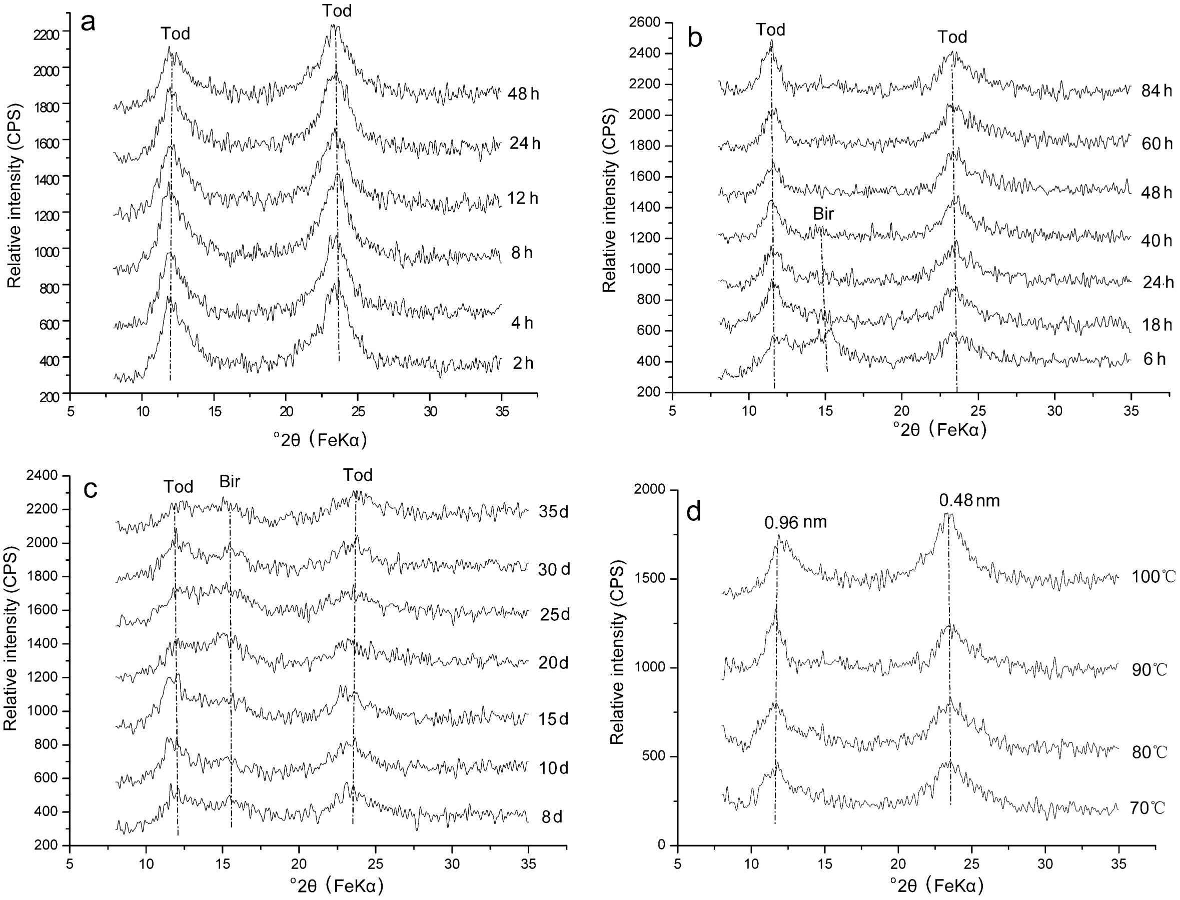

Figure 1. XRD patterns of the intermediates at different stages when Mg-buserite was treated at different temperature (a) heated at 100ºC; (b) heated at 90ºC; (c) heated at 40ºC; and (d) XRD patterns of todorokites synthesized at different temperature. Tod, todorokite; Bir, birnessite. (Na-bus-5h, pH 7, 1 M $MgCl_2$).

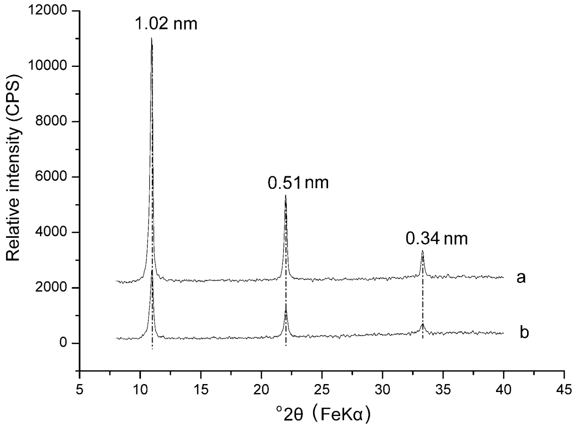

Figure 2. XRD patterns of Na-buserites synthesized at (a) 25ºC; (b) 5ºC.

longer at lower reaction temperatures, and Mg-buserite could not be transformed completely into todorokite at a relatively lower temperature. The XRD patterns of todorokites synthesized at different temperature are shown in Figure 1d. The intensity of the 0.96 nm and 0.48 nm characteristic diffraction peaks decreased slightly with reduction in temperature, indicating that the products became less crystalline.

Effects of crystalline of Na-birnessite

The main precursor to todorokite is Na-birnessite, and it affects the physical and chemical properties of the synthesized todorokite (Liu *et al.*, 2005). The structure and characteristics of synthesized birnessites are different when they are prepared using different methods (Feng *et al.*, 1999, 2004c). Figure 2 shows the XRD patterns of the products at two different oxidation temperatures. The peak intensities in the XRD pattern of Na-buserite prepared at 25ºC were much stronger than those of the Na-buserite prepared at 5ºC. Transmission electron microscopy bright-field images of the two Na-buserites are shown in Figure 3. The crystallites of birnessite prepared at 25ºC consisted mainly of well stacked hexagonal plates, while birnessite prepared at 5ºC had a thin and random stacked platy morphology. When using the former as the precursor, the highly crystalline Mg-buserite was converted completely to todorokite after it was treated at 80ºC for 7 days (Figure 4a). However, the poorly crystalline Mg-buserite was completely transformed to todorokite when it was treated at the same temperature for 48 h (Figure 4b) showing that the crystallinity of birnessites as a precursor was not only related to the morphology and characteristics of synthesized todorokites, but was also responsible for the conversion rate of todorokite. The poorly crystalline birnessite is more easily transformed than the highly crystalline one.

Three kinds of poorly crystalline Na-buserites were also used to prepare todorokite under refluxing condition (Figure 5a), and the powder XRD patterns of the intermediates heat treated (at 140ºC) at different stages are shown in Figure 5. After 2 h of refluxing, almost all Mg-birnessites have been transformed to todorokites, and the crystallinity of the synthesized todorokite depended on that of the initial Na-buserite (Figure 5b–d). At a refluxing time of 8 h, the intensity of the characteristic peaks of the synthetic todorokite increased, using the most poorly crystalline Na-birnessite as precursor, indicating that the crystallinity of the

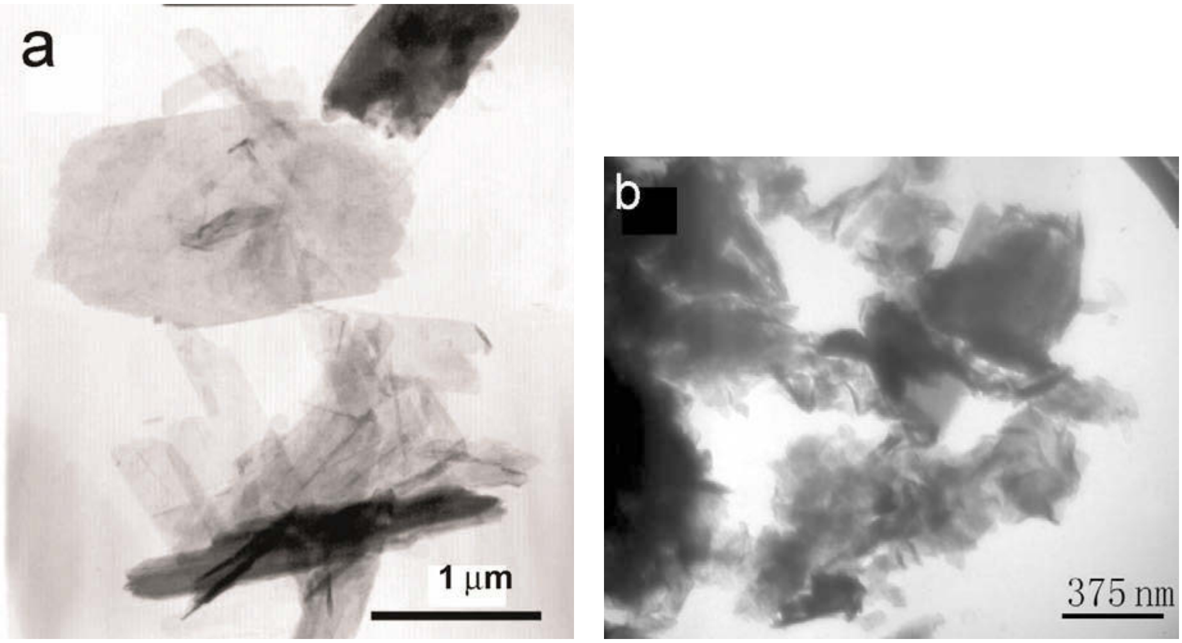

Figure 3. TEM images of Na-buserite synthesized at (a) 25ºC; (b) 5ºC.

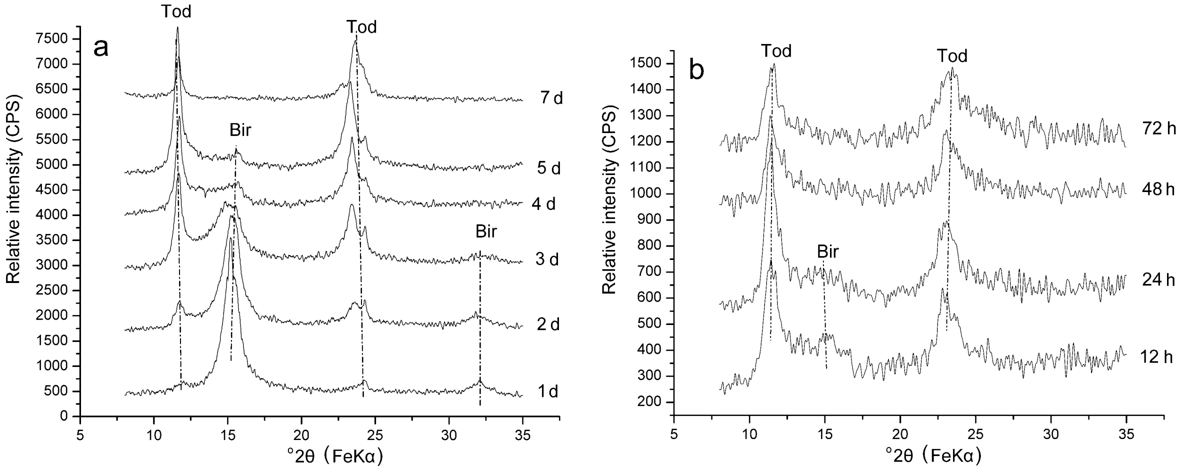

Figure 4. XRD patterns of the intermediates at different stages when Na-buserites of different crystallinities as precursors were treated at 80ºC: (a) Na-buserite synthesized at 25ºC; (b) Na-buserite synthesized at 5ºC. (pH 7, 1 M $MgCl_2$)

product was enhanced. When the refluxing time was prolonged to 12 h, the characteristic diffraction peaks became stronger, and were similar to that of todorokite synthesized using two other more crystalline Na-buserites as precursors, indicating that the crystallinity of the todorokite was further enhanced (Figure 5b). When the two Na-buserites treated for longer periods were converted completely to todorokite, the intensity of

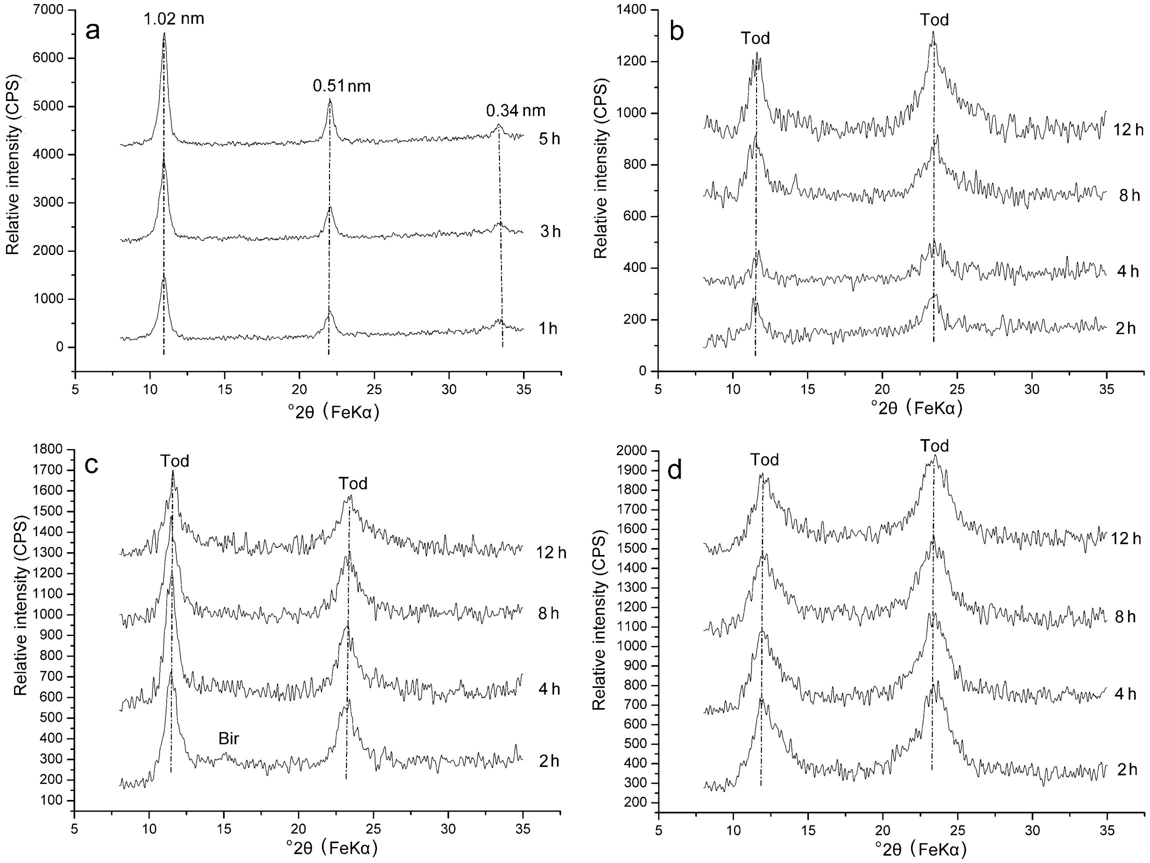

Figure 5. XRD patterns of Na-buserite synthesized with different bubbling O_2 time (a), and intermediates at different stages when Mg-buserites with different crystallinities were refluxed (at 100ºC): (b) Na-buserite-1h; (c) Na-buserite-3h; (d) Na-buserite-5h. (pH 7, 1 M $MgCl_2$).

characteristic peaks of todorokite did not increase when the refluxing time was prolonged (Figure 5c,d).

Effect of pH

The results regarding pH effects on the transformation are summarized in Figure 6. The XRD patterns of the intermediate products at different stages of refluxing process at pH 5 are shown in Figure 6a. A very weak 1.0 nm diffraction peak of todorokite appeared after 2 h of reflux, but the 0.7 nm diffraction peak of birnessite was also strong, indicating that a little Mg-buserite was converted into todorokite. After 8 h of refluxing, the intensity of the 1.0 nm diffraction peak increased, and the intensity of the 0.7 nm peak decreased, indicating that more todorokite was gradually being produced. When the refluxing time was prolonged to 12 h, the characteristic peaks of todorokite and birnessite in the XRD pattern of the products are similar to that for 8 h of reflux time, indicating that some of the Mg-buserite could not be converted to todorokite, and still had a layered structure. However, the intensity of the 1.0 nm diffraction peak was very strong after refluxing for 2 h at pH 7, and the intensity of the 0.7 nm diffraction peak was very weak, indicating that most of the Mg-buserite has been converted to todorokite. After a prolonged reflux time of 8 h, the intensity of the 1.0 nm diffraction peak increased, and the intensity of the 0.7 nm diffraction peak decreased. After 12 h of reflux, the 0.7 nm diffraction peak disappeared, and the Mg-buserite was converted completely to todorokite (Figure 6b). The proportion of the sample converted when refluxed at pH 9 was similar to that at pH 7 (Figure 6c). It is concluded that the phase transformation from Mg-buserite to todorokite was affected by the pH values of the medium, and todorokite could also be formed at a relatively wide range of pH values from 5 to 9 and the rate of formation and crystallinity of todorokite followed the sequence: neutral ≈ alkali > acidic (Figure 6d).

Effects of exchanged ion intensity

The nature and amount of interlayer cations in the buserites had an obvious effect on the stability of the buserites and physicochemical characters of the todorokites synthesized under such hydrothermal conditions (Shen *et al.*, 1994; Giovanoli *et al.*, 1975; Mellin and Lei, 1993; Kuma *et al.*, 1994). After Na-buserite was

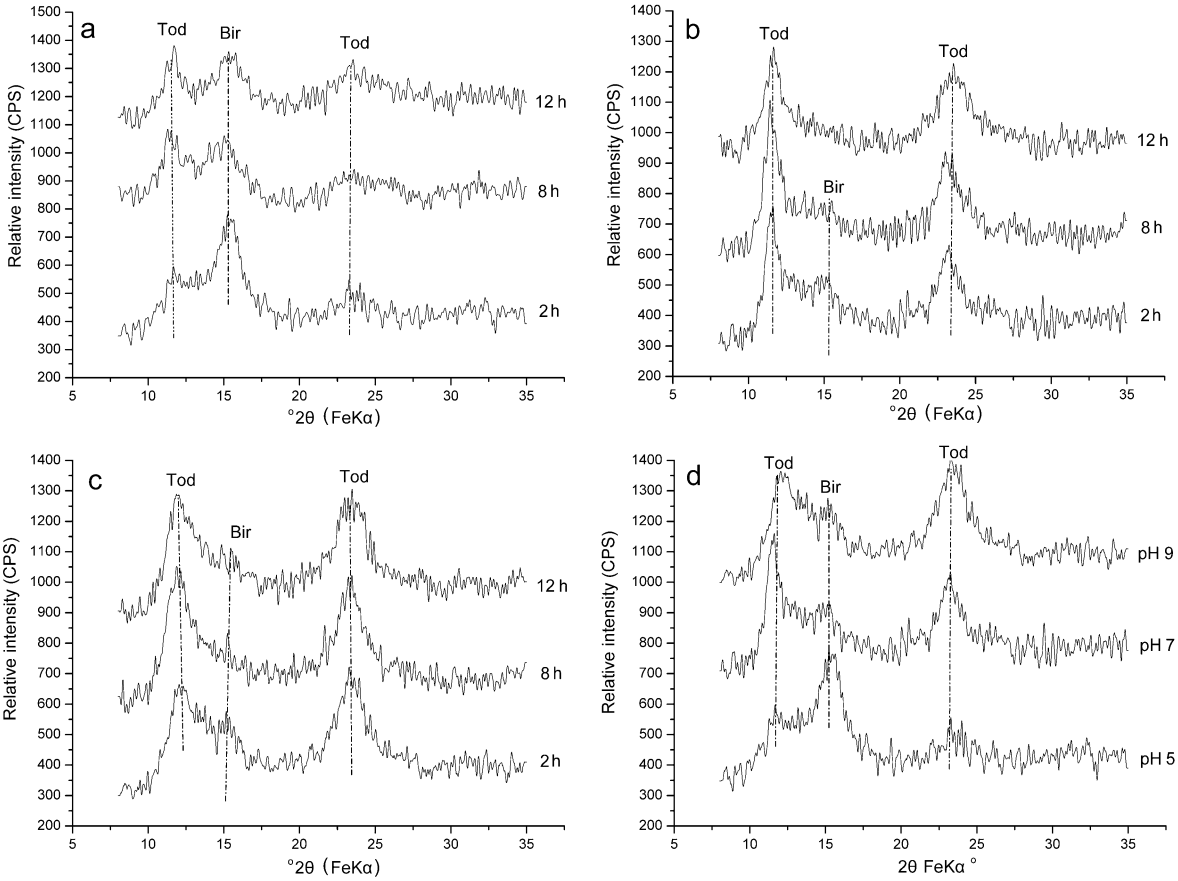

Figure 6. XRD patterns of intermediates at different stages when Mg-buserite was refluxed (at 100ºC) at different pH values. (a) pH 5; (b) pH 7; (c) pH 9; (d) products of refluxing 2 h at different pH values.

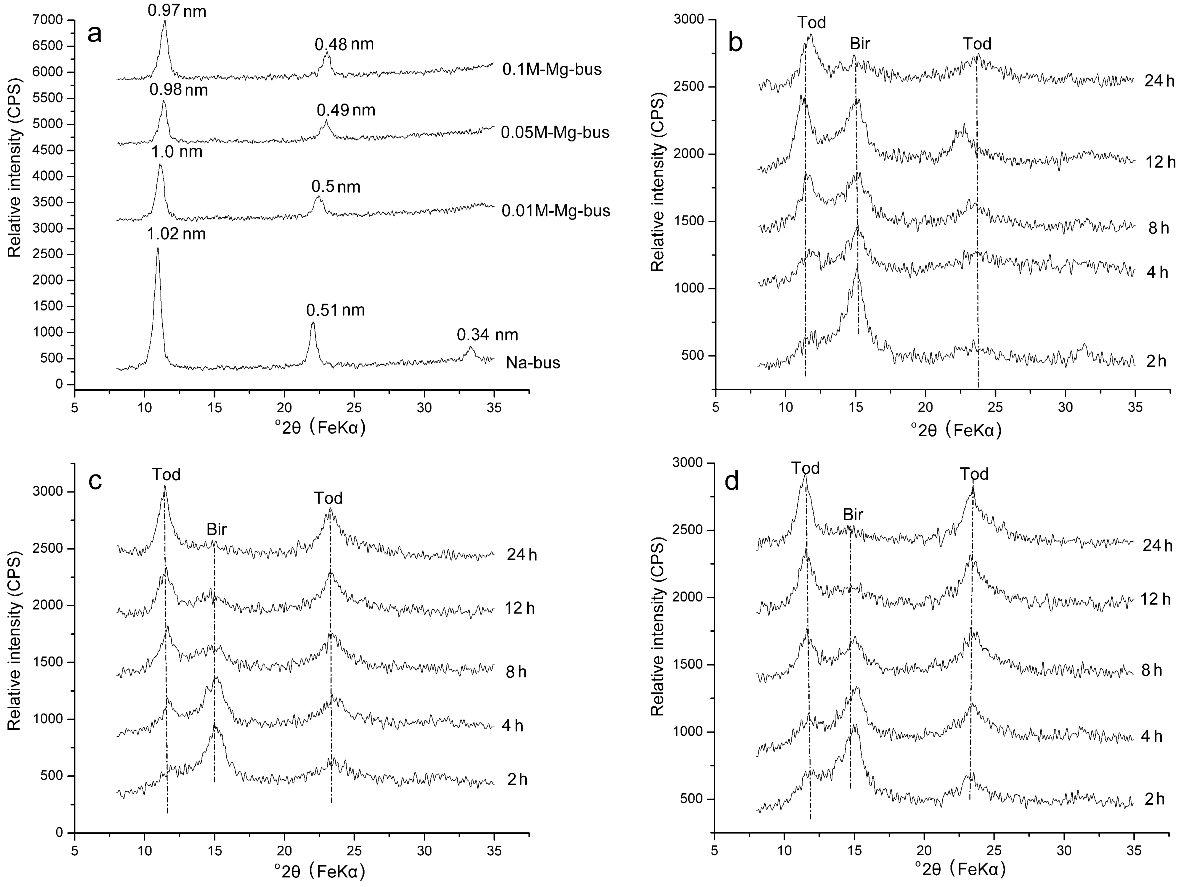

Figure 7. XRD patterns of Mg-buserites with different amounts of Mg^{2+}-templating reaction (a) and intermediates at different stages of reflux (at 100°C): (b) 0.01M-bus; (c) 0.05M-bus; (d) 0.1M-bus. (pH 7).

exchanged with 0.01 M $MgCl_2$ solution, the basal spacing of the Na-buserite decreased from 1.02 nm to 1.0 nm, and decreased to 0.98 nm when the concentration of $MgCl_2$ was enhanced to 0.05 M, and finally reduced to 0.97 nm when the concentration of $MgCl_2$ was 0.1 M (Figure 7a), close to that of 1 M $MgCl_2$ (0.967 nm) (Feng *et al.*, 2004a). These results indicate that the basal spacing of the Mg-buserites obtained depended on the concentration of Mg^{2+} in solution and would decrease with the increase in Mg^{2+}. Although the Mg/Mn molar ratio remained constant for 0.05M-Mg-bus, 0.1M-Mg-bus and 1M-Mg-bus (Table 1), their basal spacing values were different. This shows that the interlayer Mg^{2+} may occupy different sites in the Mg-buserites.

The XRD patterns of the intermediate products at different stages of refluxing the Mg-buserites above are shown in Figure 7b–d. After 12 h of refluxing, the intensity of characteristic peaks of todorokite was equivalent to that of birnessite in the XRD pattern when 0.01M-Mg-bus was used to prepare todorokite (Figure 7b), suggesting that about half of the Mg-buserite transformed into todorokite. When the refluxing time was increased to 24 h, the intensity of the characteristic peaks of todorokite became strong, but a weak diffraction peak of birnessite remained, showing that Mg-buserite has not been converted completely to todorokite. Under the same conditions, the degree of transformation increased greatly when 0.05M-Mg-bus

Table 1. Chemical compositions (wt.%) of the Na-buserite and Mg-buserites.

Sample	Na (mmol/0.1 g)	Mg (mmol/0.1 g)	Mn (mmol/0.1 g)	Mg/Mn
Na-birnessite	0.294	0	0.879	
0.01M-Mg-bus	0.118	0.074	0.756	0.098
0.05M-Mg-bus	0	0.132	0.818	0.161
0.1M-Mg-bus	0	0.134	0.811	0.165
1M-Mg-bus	0	0.132	0.812	0.162

and 0.1M-Mg-bus were used for refluxing (Figure 7c,d). The two Mg-buserites were largely converted to todorokite after 12 h of reflux, but were not completely converted to todorokite after 24 h of reflux. However, it only needs 2–8 h for 1M-Mg-buserite to convert completely into todorokite under refluxing condition. These results indicate that the conversion rate of todorokite was reduced with the decrease of interlayer Mg^{2+}.

Effects of clay minerals

Natural todorokites are commonly found in Fe-Mn nodules, and typically occur as poorly crystalline nm-sized size particles coexisting with other Mn oxides, Fe oxides and other clay minerals. Figure 8 shows the powder XRD patterns of the products of Mg-buserites with montmorillonite and goethite refluxed for 12 h. The intensity of the characteristic peaks of todorokite was similar to those in all powder XRD patterns of different products. Furthermore, the diffraction peak of birnessite could be observed, indicating that the transformation was incomplete. However, when there was no co-existing clay mineral, Mg-buserite converted completely to todorokite in a short refluxing time (<8 h). These results indicate that the conversion rate of Mg-buserites decreased when the Mg-buserites co-existed with montmorillonite and goethite.

When 1 g of goethite was dispersed into $MnCl_2$ solution, only a diffraction peak for Na-buserite appeared in the XRD pattern of the synthetic product, indicating that the crystalline Mn oxide (Na-buserite) coated goethite completely. When the amount of goethite was increased, the diffraction peaks of goethite started to appear, and gradually became stronger with increase in the goethite content (Figure 9a). The XRD patterns of the intermediate products, obtained after different stages of the refluxing process, show that Goe1-Mg-bus was almost completely converted to todorokite after refluxing for 2 h (Figure 9b), and the intensity of the diffraction peaks of birnessite remained strong after 12 h of refluxing when Goe4-Mg-bus and Goe8-Mg-bus were treated under refluxing conditions (Figure 9 c,d). When the refluxing time was prolonged to 48 h, the characteristic peaks of birnessite in the XRD pattern of the product disappeared for Goe1-Mg-bus and Goe4-Mg-bus, and a very weak diffraction peak of birnessite still appeared for Goe8-Mg-bus (Figure 9b–d). It suggests that the rate of transformation from layered Mg-buserite to todorokite with tunnel structure decreased with increase in the amount of goethite added.

DISCUSSION

The transformation from layered structure to tunnel structure is a complicated process, involving solid and solid, solid and solution, and redox reactions. During the hydrothermal heating, some of the Mn(III) octahedra from the layers of the precursors may migrate into the interlayer region and become corner-sharing octahedra that assist in the formation of the ‘walls’ of the tunnels (Liu *et al.*, 2002). Mellin and Lei (1993) suggested the interlayer Mn^{2+} ions were slowly oxidized to Mn^{4+} accompanied by a concomitant change of their OH^- ligands to O^{2-}, and these combined interlayer processes gradually stabilized some ‘tunnel’ walls, creating a stable todorokite-like structure. The average oxidation state of Mn of the products would be maintained or enhanced during the above two processes. However, the average oxidation state of Mn of todorokite synthesized by the refluxing method is 3.86, which is a little less than that of the starting Na-birnessite (3.92) (Feng *et al.*, 2004b). This indicated that the percentage of lower-valence Mn cations (Mn^{2+}, Mn^{3+}) increased and that of

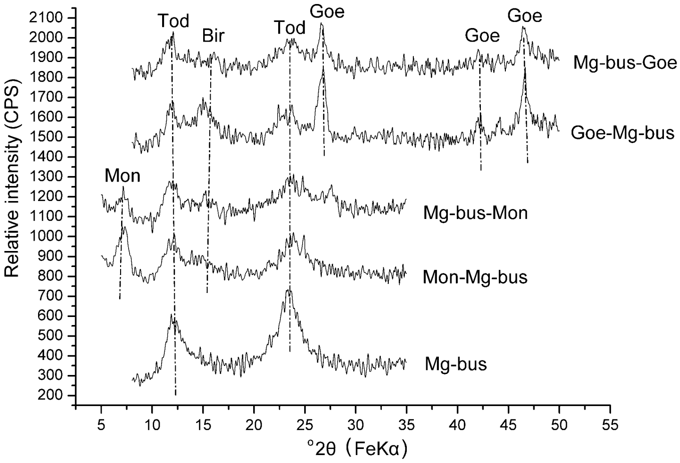

Figure 8. XRD patterns of products after different Mg-buserites were refluxed (at 100ºC) for 12 h (pH 7). (Mg-bus-Goe = Mg-buserite co-existing with goethite; Goe-Mg-bus = goethite co-existing with prepared Na-buserite and then ion-exchanged with Mg^{2+}. The treatment of montmorillonite (Mon) is same to that of goethite (Goe).

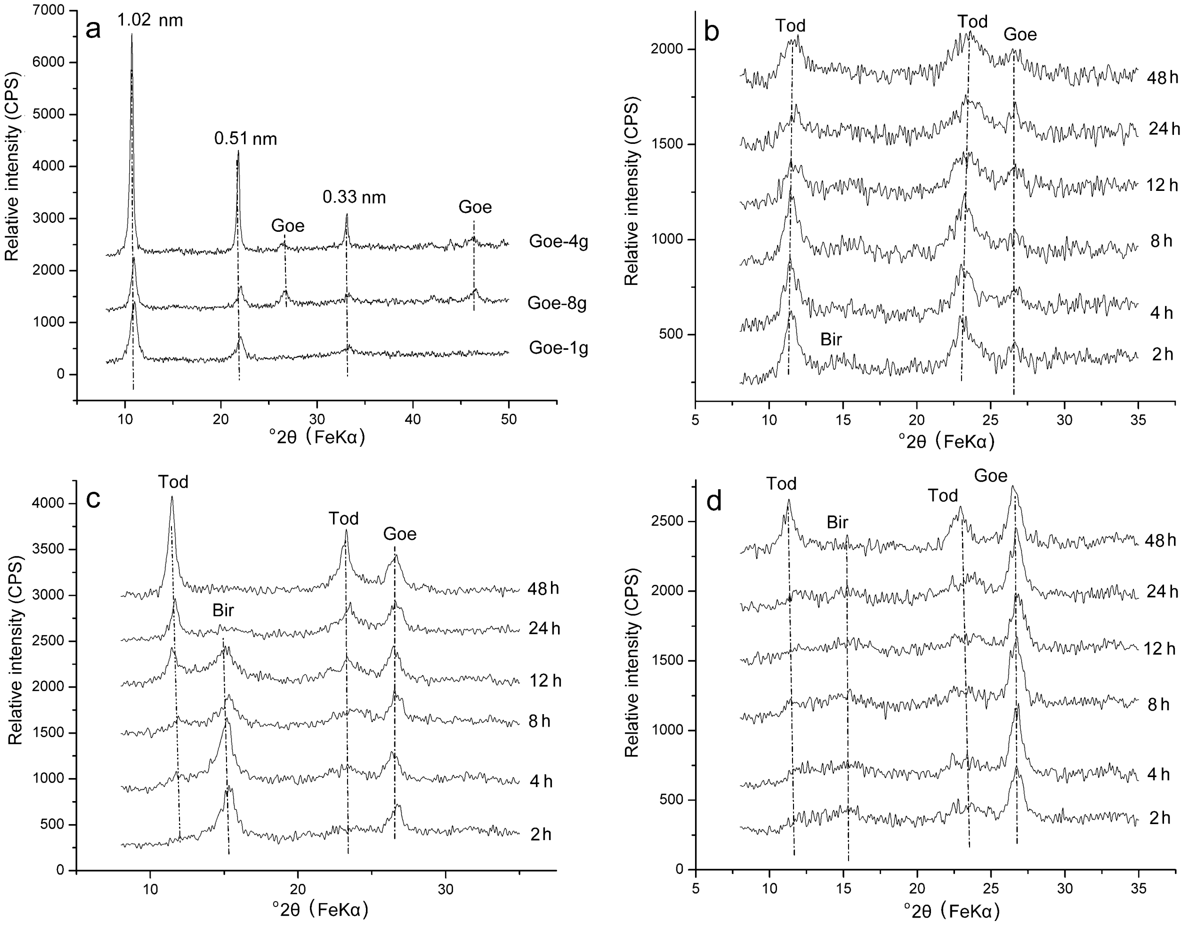

Figure 9. XRD patterns of Mg-buserites co-existing with different amounts of goethite (a) and intermediates at different stages of reflux (at 100ºC): (b) Goe1-buserite; (c) Goe4-buserite; (d) Goe8-buserite. (pH 7).

the higher-valence Mn cation (Mn^{4+}) decreased during the course of transformation. During the transformation process, the Mn(IV) $-$O$-$$M$ (M = Mn^{2+}, Mn^{3+}, Mn^{4+}) bridge may be broken, and several other processes may take place with concomitant release of H^{+}. These H^{+} together with Cl^{-}, may dissolve extraframework MnO$_2$, leading to a lower Mn oxidation state (Shen *et al.*, 1996). Although the detail of the transformation is still not well understood, the breaking of the bridges is important for the conversion. The experimental results show that the temperature and time of reaction significantly influenced the formation of todorokite in hydrothermal conditions (Liu *et al.*, 2002; Feng *et al.*, 2005). The conversion time would need to be prolonged from 2 to 6 h with the temperature decreased from 200 to 120ºC, and the formation of todorokite would take more than 8 h when highly crystalline Na-birnessite was used as the precursor in a refluxing process at atmospheric pressure (Feng *et al.*, 2004b, 2005). With the time extended from 2 to 18 h, the temperature required would decrease from 100 to 90ºC; the transformation would need more than 24 h with the temperature at 80ºC; the Mg-buserite would not convert completely to todorokite at lower temperatures (*e.g.* 40ºC in our experiment). These results suggest that the transformation should be an endothermic process. Moreover, the bond dissociation essentially also involves an endothermic process, and we cannot rule out the possibility that the transformation involves the bond dissociation steps.

Todorokite could be synthesized at pH 5$-$9, but the rate of formation of todorokite in an acidic medium is slower than that in a neutral or alkali medium. According to the chemical analysis of the acid-treated sample, 95% of the interlayer Mg^{2+} ions of Mg-buserite were extracted by the acid treatment (Liu *et al.*, 2005). When Mg-buserite was treated in a slightly acidic medium, the interlayer Mg^{2+} of the Mg-buserite could be extracted by H^{+} in the solution. Moreover, some of the remaining Mn$^{3+}_{\text{layer}}$ cations could migrate from the layer into the interlayer and disproportionate to form Mn$^{4+}_{\text{layer}}$, vacancies, and Mn$^{2+}_{\text{aq}}$. The Mn$^{2+}_{\text{aq}}$ could re-adsorb above or below vacant sites at pH 5 (Silvester *et al.*, 1997; Lanson *et al.*, 2000). These may be the reasons that some Mg-buserite could not be converted into todorokite. On the other hand, todorokite can form in a weak alkali medium or in a slightly acidic medium in our experiment, but no todorokite has been found in acid soils so far. There is a lack of base ions such as Ca^{2+} and Mg^{2+} in acid soils because of strong eluviation (Tan *et al.*, 2000). Transmission electron microscopy bright-field images of the intermediates shows that the fibers of various lengths appeared first and extended outwards from a platy matrix under refluxing conditions; the matrices were actually fibrous crystals trilling together at an angle of 120º (Feng *et al.* 2004b; Cui *et al.*, 2005). The fibrous todorokite crystals were easily broken when poorly crystalline Na-birnessite was used as the precursor, and it could be converted completely to todorokite in a shorter time than that when highly crystalline Na-birnessite was used. Although the conversion rate of the todorokite was reduced with a decrease of the interlayer Mg^{2+}, todorokite was still obtained when the reflux time was prolonged. Therefore, we cannot rule out the possibility that a little Mg^{2+} may have been exchanged into natural birnessite which was then transformed to todorokite. Moreover, the poorly crystalline birnessite may be more easily converted to todorokite. Natural todorokites typically occurring as poorly crystalline nm-sized particles or present as coatings coexist with many minerals such as Fe oxides and clay minerals. When Na-buserite was synthesized in the presence of montmorillonite or goethite, some Na-buserite would be present as a coating on the surface of montmorillonite or the goethite. More Na-buserite would coat the surface of the montmorillonite or goethite with an increase in those minerals. These Na-buserites associated with the clay minerals would be converted to todorokite more slowly than pure Na-buserite. When the montmorillonite associated with the Na-buserite and Mg-buserite, the former can adsorb the latter, and the interface between the latter and the reaction solution would be reduced, leading to the reaction activity of the latter being decreased. On the other hand, competition for adsorption of Mg^{2+} between the buserites and the montmorillonite may occur. These may be the reasons that the conversion rate of todorokite was decreased when buserites co-existed with montmorillonite. Goethite has positive surface charge and can adsorb the Mn oxides with negative surface change though electrostatic interaction. The reaction activity of the Mn oxides would be reduced, and the reaction time would also be prolonged. However, the details of the montmorillonite and goethite slowing down the formation reaction of todorokite in the reflux process are still not clear.

CONCLUSIONS

The formation of todorokite was affected by several reaction conditions at atmospheric pressure. The conversion rate and crystallinity of todorokite decreased with falling temperature, and Mg-buserite could not be completely transformed to todorokite at a relatively lower temperature (40ºC). The poorly crystalline Na-buserite could be converted into todorokite more easily than that of highly crystalline Na-buserite. Todorokite can be prepared within pH 5–9, but the rate of conversion and crystallinity of todorokite was related to the following sequence: neutral ≈ alkali > acidic. The conversion rate of todorokite decreased with decrease in the amount of interlayer Mg^{2+} in Mg-buserite. When Mg-buserite was associated with montmorillonite or goethite, the conversion rate to todorokite decreased, and the reaction time prolonged with an increase in the amounts of montmorillonite and goethite.

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