Structure and Thermal Decomposition of $\text{K}_x\text{MnO}_2 \cdot \gamma \text{H}_2\text{O}$ Prepared by Sol-Gel Method

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The birnessite-type $\text{K}_{0.28}\text{MnO}_2 \cdot \gamma \text{H}_2\text{O}$ hydrates with the average crystalline size of about 10-20 nm have been prepared by a sol-gel method using KMnO$_4$ and glucose aqueous solutions. Their crystal structure and thermal stability have been investigated by XRD, TG-DTA, and TEM-EDX. The dehydration reaction occurs at around 180°C. The samples heated in between 600 and 800°C transform into a cryptomelane-type phase with 2×2 tunnel type structure. Not so much change in the crystalline size due to the above phase transformation was observed. The heating at above 900°C causes the decomposition reaction into the tetragonal spinel-phase Mn$_3$O$_4$ and the layered K-rich birnessite, $\text{K}_{0.31}\text{MnO}_2$, accompanied with the release of oxygen and the 4 times increase in the crystalline size.

Key words: birnessite, cryptomelane, layered structure, tunnel-type structure, phase transformation

1. INTRODUCTION

Birnessite-type $\text{A}_x\text{MnO}_2 \cdot \gamma \text{H}_2\text{O}$ ($\text{A}$:alkaline metals) has a layered-type structure in which $\text{A}^+$ ions and $\text{H}_2\text{O}$ molecules occupy the interlayer sites between CdI$_2$-type MnO$_2$ layers. They are used as selective ion-exchanger and heterogeneous catalysis, and so on. To synthesize birnessite-type $\text{K}_x\text{MnO}_2 \cdot \gamma \text{H}_2\text{O}$, several methods, the precipitation from the aqueous solution [1, 2], solid-state reaction [3, 4], hydro-thermal method [5], and sol-gel methods [6, 7], have been employed. In the sol-gel methods, xerogels are obtained by adding a reducing agent such as glucose [6] or fumaric acid [7] into the KMnO$_4$ aqueous solution and drying the gel at 110°C. Birnessite-type fine particles are obtained by heating the xerogel at 400°C. The sample prepared by the sol-gel methods has small particle sizes of several tens nano-meter, suitable for the practical use. However the details of the crystalline quality have not been investigated by using TEM.

It is also to be noted that the heat treatment of the xerogel at 600°C causes the formation of cryptomelane with 2×2 tunnel structure [8]. However, the relation of water and K compositions to the structural transformation, and also the mechanism of structural transformation are still uncertain, although a TEM study has been reported for the sample prepared by the precipitation from the aqueous solutions [9]. In this study, high-quality samples have been prepared by using above mentioned sol-gel method. Samples obtained by the heat treatments in the range from 400 to 1000°C were studied by XRD, TG-DTA, and TEM.

2. EXPERIMENTAL

2.1 Sample preparation

Birnessite-type $\text{K}_x\text{MnO}_2 \cdot \gamma \text{H}_2\text{O}$ was prepared according to the procedure reported by Ching et al. [6]. The initial aqueous gel was prepared by mixing 0.38M KMnO$_4$ and 1.4 M glucose aqueous solutions in a volume ratio of 5 to 2, at room temperature. The gel was dried at 110°C to obtain xerogel and the xerogel was heat treated at 400°C. The obtained product was thoroughly washed five times with deionized water. It was dried at 110°C overnight and then kept under the water vapor pressure of 13.7 mmHg equilibrated with the saturated NH$_4$Cl aqueous solution.

2.2 Characterization

The phase identification and the analyses of particle shape and size were performed by powder XRD and transmission electron microscopy(TEM), using a RIGAKU RINT2200 powder x-ray diffractometer and a JEOL JEM2010F transmission electron microscope (TEM). For the examination of the phase stability and the phase change on heating, TG-DTA curves were measured by using a MacScience TG-DTA2000S apparatus. According to the TG-DTA results, samples heated up to 400, 500, 600, 800, and 1000°C in the TG-DTA apparatus and in air were also examined by XRD and TEM. The heating rate of 10°C/min and the cooling rate of 20°C/min were employed. The atomic ratio of K and Mn atoms were evaluated by the energy dispersive x-ray analysis in the TEM.

3. RESULTS AND DISCUSSION

3.1 As-prepared sample

Figure 1 shows the powder x-ray diffraction pattern of as-prepared birnessite-type sample. It shows intense two peaks due to the layer spacing of about 7.11Å. However, peaks are rather broad and the other peaks in the higher angle range are overlapped. The profile fitting programs were written to estimate lattice parameters, peak intensities and the half width at maximum (FWHM) of diffraction peaks, assuming the
monoclinic and hexagonal unit cells. A good agreement with the observed profile was obtained for the monoclinic system with the lattice parameters of $a = 5.13 \text{ Å}$, $b = 2.84 \text{ Å}$, $c = 7.25 \text{ Å}$, and $\beta = 101.4^\circ$ ($V_{\text{Unit}} = 103.5 \text{ Å}^3$). A confidence plot of the fitting is shown in Fig. 1 as a line drawing. The FWHM's of peaks in the $2\theta$ angle range in Fig. 1 were fitted to be equal to 0.49°. The average size of crystallites calculated from the FWHM using Scherrer formula is 120 Å. A small peak is seen in Fig. 1 at around $2\theta = 32.2^\circ$, which is assigned to 103 peak of the impurity phase, tetragonal MnO$_2$.

The observed lattice parameters of the as-prepared sample well agree with those reported in the literatures. Post et al. [1] reported that the lattice parameters for K$_{0.23}$MnO$_2$ prepared from the aqueous solutions, are $a = 5.149 \text{ Å}$, $b = 2.843 \text{ Å}$, $c = 7.176 \text{ Å}$, $\beta = 100.7^\circ$. $V_{\text{Unit}} = 103.0 \text{ Å}^3$. Gaillot et al. [4] reported that those for K$_{0.312}$Mn$_{0.976}$O$_{2.37}$H$_2$O, prepared by the thermal decomposition reaction of KMnO$_4$, are $a = 5.130 \text{ Å}$, $b = 2.850 \text{ Å}$, $c = 7.131 \text{ Å}$, $\beta = 100.8^\circ$, $V_{\text{Unit}} = 102.4 \text{ Å}^3$. The small differences in the lattice parameters are attributed to the difference in the K and water compositions.

Figure 2(a) shows a TEM image of a typical particle, in which fine crystallites with the average size in the range from 10 to 20 nm are aggregated. The electron diffraction (ED) pattern of a fairly large crystallite marked in Fig. 2(a) is shown in Fig. 2(b). It shows a twin pattern in which two [100] zone ED patterns of monoclinic phase are overlapped. The diffuse nature of diffraction spots also indicates the poor crystallinity, particular for the layer stacking. The atomic ratio of K to Mn was estimated from the energy dispersive x-ray spectra taken for the several crystallites in Fig. 2(a). They give an average atomic ratio $x$ in K$_{0.28}$MnO$_2$ of 0.28±0.02. This value well agrees with the composition, K$_{0.28}$MnO$_{2.49}$H$_{0.19}$O, reported by Ching et al. [6], although no detailed analysis of lattice parameters has not been reported by Ching et al.

Figure 3 show TG-DTA curves of as-prepared sample. The heating rate of 10°C/min and the cooling rate of 20°C/min were employed. The DTA curve shows two endothermic peaks at around 180 and 900°C, accompanied with the weight decrease about −5.7 and −4.7%, relative to the as-prepared state, respectively. It also shows a small exothermic peak at around 520°C, accompanied with +0.8% weight increase. The first endothermic DTA peak is well attributed to the dehydration of interlayer water. From the weight decrease up to 200°C, the water composition is evaluated to be $y = 0.40$ in K$_{0.28}$MnO$_{2.49}$H$_{0.19}$O. Similar TG-DTA curves have been reported by O. Prieto et al. [8]. To investigate the details of structural change on heating, we have heat-treated the samples at several temperatures and have characterized them.

3.2 Samples heat-treated at high temperatures

Figure 4 shows powder XRD patterns of samples heated up to 400, 500, 600, 800, and 1000°C in air and then cooled down to room temperature. The pattern (b) for the samples heated up at 400°C can be indexed as layered birnessite-type ones. The intense two peaks at $2\theta = 12.48$ and 25.04°, corresponding to the layer spacing, show no change in the peak positions from those of as-prepared sample. When the samples are
heated up to 500 (c), 600 (d), and 800°C (e), the intense two peaks in (a) are greatly reduced their intensity and the peak positions are slightly increased up to 2θ = 12.68 and 25.64°, whereas intense peaks appear at 2θ = 18.02, 28.72 and 37.44°. The whole patterns can be indexed as those for 2×2 tunnel-type structure of cryptomelane. No apparent difference in the peak positions was observed among the diffraction patterns (c), (d), and (e).

When the sample was heated up to 1000°C, the pattern is thoroughly changed and intense peaks appear at 2θ = 12.62 and 25.32° similarly to the diffraction patterns (a), (b) for layered-type ones. Also the narrowing of peak widths is observed. The whole pattern can be indexed as that of the mixture of layered biminesite type K₅MnO₄ and tetragonal spinel-type Mn₃O₄. Above results indicate that a structural transformation from layered biminesite type to tunnel-type one occurs above 500°C and the decomposition of tunnel type one into the layered type one and Mn₃O₄ occurs above 900°C.

Figures 5(a) and (b) show the results of profile analysis for the powder XRD patterns of samples heated up to 600 and 1000°C, respectively. All the peaks in Fig. 5(a) can be indexed as a tetragonal tunnel-type structure with the lattice dimension of a = 9.847 Å and c = 2.864 Å. The observed lattice parameters agree with those for K₁.₃MnO₄ (x = 0.166 in KₓMnO₄, a = 9.866 Å c = 2.872 Å) reported by J. Vicat et al. [10]. The slight differences in the lattice parameters may be attributed for the difference in the K composition. The evaluated average FWHM by J. Vicat et al. [10] are in the range 0.125≤x≤0.133.

The observed value of K composition is larger than these reported values. It is suggested that the excess K is released during the phase transformation from layered-type to tunnel-type structure and it remains in the sample as an oxide or hydroxide. The observed increase in weight at around 500°C from the TG measurement may be ascribed to the oxidation of released K atoms in air during the phase transformation, because no weight increase was observed when TG curve was measured.

![Fig. 4 XRD patterns of the samples heat-treated in the range from 400°C to 1000°C and as-prepared.](image)

![Fig. 5 Results of profile analysis of XRD patterns for samples heat-treated in the range from 400°C to 1000°C and as-prepared.](image)
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4. CONCLUSION

The high-quality K-birnessites fine particles with the average crystalline size of 10-20 nm were prepared by sol-gel method. The annealing of the xerogel at 400°C and the washing by water gives the hydrated birnessite type sample, with the composition of $K_{0.28}MnO_2 \cdot 0.4H_2O$. It dehydrates at around 180°C. At around 520°C, the birnessite type anhydrates to tunnel-type $K_{0.20}MnO_2$ (crypromelane). The weight decrease is caused by the release of oxygen. Under this assumption, the weight decrease due to the oxygen release is calculated to be 3.75 wt.%, whereas the observed weight decrease is 5.0 wt. %.

5. REFERENCES