Shape Modification of Manganese Oxide Prepared by Solvothermal: Effect of Precipitation Agent

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Abstract. Nano-sized manganese oxide was synthesized by the solvothermal method. Manganese sulfate was used as a precursor, which is obtained from the Sumbawa manganese ore. Two kinds of the precipitating agent, ammonium persulfate and sodium hydroxide, were used in this study and the effect on the solvothermal product were examined thoroughly. The solvothermal temperature and time were 120°C for 18 hours, respectively, for both precipitating agents. The results showed that the phase of manganese oxide was influenced by the precipitating agent, as indicated by X-ray diffraction analysis. Phase α-MnO₂ was obtained from the reaction between MnSO₄ and ammonium persulfate, while Mn₃O₄ for the sodium hydroxide. The formation of α-MnO₂ was influenced by the excess of NH₄⁺ which came from the manganese ore leaching into MnSO₄. One notable finding in this study is that the morphology of manganese oxide was also affected by the precipitating agent. For instance, the shape of MnO₂ and Mn₃O₄ was needle and sphere, respectively. Moreover, the strict long thinner needle of α-MnO₂ was formed and the aspect ratio increased at a higher temperature. While the particle size of Mn₃O₄ decreased with the increased temperature. These results imply that variation of a precipitating agent is imperative to obtain the specific manganese oxide product, including the shape.

Keywords: α-MnO₂, Mn₃O₄, solvothermal, needle, sphere

1. Introduction

Manganese has wide application in human life and industry, indicated by the extensive study to the synthesis of manganese oxide and its application. Moreover, manganese is one of element which interesting and unique properties because of its various oxidation state, which influenced the different structure. The most common oxidation numbers of manganese are +2, +3, +4, +6 and +7.
Nanomaterial of manganese oxide is one of important functional metal oxide as a catalyst [1,2], supercapacitor [3], waste treatment [4,5] and pharmaceutical/medical [6] owing to excellent physical and chemical properties. Two of manganese oxides are extensive use, i.e., manganese dioxide (MnO₂) and tri manganese tetroxide (Mn₃O₄) [7]. MnO₂ is a polymorph, which has α, β, γ, δ and ε structure [8]. In order to control the structure of MnO₂, stabilize the tunnel structure is important. Several factors that influence the tunnel structure are pH, counteraction, temperature and concentration and the existing of the inorganic cation. Moreover, the size of MnO₂ is the results of a different tunnel [9]. The tunnel structure of α-MnO₂, β- MnO₂, γ- MnO₂ are 2×2, 1×1 and 1×2 Mn octahedral tunnels (1D), respectively, while δ-MnO₂ is a 2D layered structure [10,11]. Tri manganese tetroxide (Mn₃O₄) that found in stable temperature form is tetragonal hausmannite and a metal oxide which has two cations, Mn²⁺ and Mn³⁺ that occupied the tetrahedral and octahedral position, respectively. This counterpart is important to encourage its pseudo-capacitance supercapacitors [12,13].

From the above perspective, in order to obtain a desirable manganese oxide, attention needs to pay in the controlling reaction system. The soft chemical route is a solution process with easy controllable reaction condition and provides many alternative sources of reactant, also more suitable for large-scale production of nanomaterial with specific morphology [14]. Solvothermal is the simple method which most favorable to synthesis manganese oxide. This method also provides the nanostructure and phase convenient to control.

The objectives of this study are synthesis manganese oxide with different precipitating agents using a solvothermal method. Moreover, we use manganese ore instead of commercial one to synthesis manganese sulfate as a precursor to synthesis manganese oxide. The precipitating agents used in this study are sodium hydroxide and ammonium persulfate. The effect of solvothermal temperature on the phase and shape of manganese oxide was examined thoroughly.

2. Experimental method
This research used manganese ore from Sumbawa, West of Nusa Tenggara, Indonesia as starting material. All chemical reagents which used in this research are analytically pure grade. The sulfuric acid 95% (H₂SO₄), hydrogen peroxide 30% (H₂O₂) and ammonium sulfate 25% ((NH₄)₂SO₄) from Merck were used in synthesis manganese hydroxide from its ore. The 510 mmol of H₂SO₄ solution was heated at 70 °C using a hot plate that equipped with a magnetic stirrer. Ten grams of manganese ore was added slowly to the solution. Subsequently, 147 mmol of H₂O₂ was added carefully drop by drop to ignore the bumping solution. The leaching process was continued for 90 minutes. After the leaching solution cooling down, the slurry and filtrate were separated used Buchner funnel that connected with a vacuum pump. The red wine solution was added by 25% of NH₄OH till brown precipitate formed and the pH of the solution was 8. The clear manganese sulfate (MnSO₄) solution was ready to be used as a precursor.

The precipitating agents used in this study were sodium hydroxide (NaOH, Merck) and ammonium persulfate NH₄OH, XiLong Scientific). Manganese oxide was synthesis by solvothermal method. The process was started by pouring 45 mL of manganese sulfate into beaker glass and added the 180 mmol of NaOH or four mmol of ammonium persulfate. The total volume was adapted with the volume Teflon jar in the solvothermal reactor. The solution then was mixed for 15 minutes at room temperature. Then, the solution was poured into Teflon jar-lined stainless-steel autoclave. The solvothermal reaction was done for 18 hours in a variety of temperature; 90, 120 and 150 °C. The final product from NaOH and ammonium persulfate precipitating agent was dark brown and black, respectively. Then, the powder was washed till pH 7 using demineralization water and ethyl alcohol.

The phase of the final product was characterized by room temperature X-ray diffraction (XRD: Shimadzu 7000 Maxima-X tube, Japan) using CuKα line. The morphology of the manganese oxide powder was observed by field emission scanning electron microscope (Fe-SEM: JIB-4610F Multi Beam System, JEOL, Japan). The average particle size and aspect ratio were determined using SEM image by calculate 100 particles and analyzed statistically.
3. Results and discussion

Figure 1 displays the XRD patterns of manganese oxide from the solvothermal using different precipitating agents. Although our previous study shows that many types of manganese oxide products might be formed due to the reaction of MnSO₄ and NaOH [15], the spontaneous reaction only occurred for the reaction that the product was Mn₃O₄ based on the Gibbs free energy calculation. This calculation was verified by the experimental. Fortunately, our theoretical calculation matches the experimental results, as shown in Figure 1 (a). However, α-MnO₂ was obtained after a solvothermal reaction between MnSO₄ with (NH₄)₂S₂O₈. The difference of manganese oxide product phase that obtained after the solvothermal reaction is interesting, hence, it seems the formation of manganese cation plays an important role to determine the manganese product.

![Figure 1. X-ray Diffraction of manganese oxide in different precipitating agent.

The formation of Mn₃O₄ from the reaction between MnSO₄ and NaOH can be seen in Equation (1). However, several steps occurred in the formation of Mn₃O₄. By nature, manganese sulfate dissolves in the water to form Mn²⁺, while NaOH imparts OH⁻ ion in the system. The OH⁻ oxidized the Mn²⁺ to form MnO, as shown in Equation (2). Simultaneously, the formation of Mn₂O₃ is also appeared, as shown in Equation (3). Hence, the presence of MnO and Mn₂O₃ is essential for the formation of Mn₃O₄ (Equation (4)), which is having a role to oxidizing Mn²⁺ from manganese sulfate. Hydroxide ion oxidized Mn²⁺ into Mn³⁺ and together with Mn²⁺ formed Mn₃O₄. However, there is a possible direct reaction to form Mn₃O₄, as shown in Equation (5). Regardless of the direct or indirect reaction, Mn₃O₄ is the product of the reaction between MnSO₄ and NaOH.

\[
\begin{align*}
\text{MnSO}_4 + \text{NaOH} & \rightarrow \text{Mn}_3\text{O}_4 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \\
\text{Mn}^{2+} + \text{OH}^- & \rightarrow \text{MnO} + \text{H}^+ \\
2\text{Mn}^{2+} + 3\text{OH}^- & \rightarrow \text{Mn}_2\text{O}_3 + \text{H}^+ \\
\text{MnO} + \text{Mn}_2\text{O}_3 & \rightarrow \text{Mn}_3\text{O}_4 \\
3\text{Mn}^{2+} + 4\text{OH}^- & \rightarrow \text{Mn}_3\text{O}_4 + 2\text{H}^+ 
\end{align*}
\]
Figure 2. SEM images of the $\alpha$-MnO$_2$ after solvothermal at (a) 90°C, (c) 120°C and (e) 150°C, Mn$_3$O$_4$ after solvothermal at (b) 90°C, (d) 120°C and (f) 150°C.
On the other hand, the oxidation of Mn\(^{2+}\) into higher oxidation number, i.e., Mn\(^{4+}\), happens when (NH\(_4\))\(_2\)S\(_2\)O\(_8\) uses as an oxidizing agent, resulting in the formation of \(\alpha\)-MnO\(_2\) (Equation (6) and (7)). Other study showed the formation of \(\alpha\)-MnO\(_2\) along with \(\beta\)-MnO\(_2\) using analytical-high purity grade MnSO\(_4\) and (NH\(_4\))\(_2\)S\(_2\)O\(_8\) [16]. Moreover, the excess of (NH\(_4\))\(_2\)SO\(_4\) in our system occurs due to reaction of NH\(_3\)OH with excess SO\(_4^{2-}\) from leaching agent during iron removal procedure, it seems responsible for the formation of \(\alpha\)-MnO\(_2\) without \(\beta\)-MnO\(_2\). The existing of NH\(_4^+\) ion gives effect to stabilize 2 × 2 tunnels forming significantly, thus enhance the formation of SO\(_4^{2-}\), which decreases the formation of Mn\(^{4+}\) [16].

\[
\text{MnSO}_4 + (\text{NH}_4)_2\text{S}_2\text{O}_8 \rightarrow \text{MnO}_2 + (\text{NH}_4)_2\text{SO}_4 \quad (6)
\]

\[
\text{Mn}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Mn}^{4+} + 2\text{SO}_4^{2-} \quad (7)
\]

Figure 2 presents the SEM images of the manganese oxide product after the solvothermal reaction at various temperature. It should be noted that the shape of manganese oxide depends on the phase of manganese oxide. For instance, the needle shape was obtained when the phase was \(\alpha\)-MnO\(_2\) (Figure 2 (a)), while spherical shape for the Mn\(_3\)O\(_4\) (Figure 2 (b)). The needle shape of \(\alpha\)-MnO\(_2\) is more likely due to an excess of SO\(_4^{2-}\) in the system, which suppresses the formation of \(\beta\)-MnO\(_2\) [16]. \(\alpha\)-MnO\(_2\) has a double chain of Mn\(_6\) octahedral structure and lead to the needle shape formation. In contrast, as a transition metal oxide with the normal spinel structure, Mn\(_3\)O\(_4\) was found in tetragonal, which Mn\(^{3+}\) and Mn\(^{2+}\) ions fill in the octahedral and tetrahedral position of the spinel structure [17].

Interestingly, in our study, we found that increase in the temperature lead to the decrease of particle size, in particular for the Mn\(_3\)O\(_4\), as shown in Figures 2 (b), (d) and (f). The average particle size of Mn\(_3\)O\(_4\) at 90, 120 and 150°C was 63.14, 66.74 and 42.04 nm, respectively. The shape of Mn\(_3\)O\(_4\) improves with the increasing temperature, while the perfect sphere was observed in the solvothermal temperature of 150°C (Figure 2 (f)). Generally, the particle size increase with the increasing temperature, however, in our study, we found opposing results. This is more likely due to the nucleation rate is the function of the temperature. In our system, the nucleation rate is faster than crystallization growth, therefore, the crystallite size decrease with increasing temperature. This phenomenon can be understood due to the increasing temperature, i.e., 150 °C, increase the thermal energy, which is related to the faster Brownian motion [18]. Moreover, the rate of oxidation of Mn\(^{2+}\) appeared sooner in this system. By considering that the cation formation initiated the nucleation, it can be confirmed that at a higher temperature the systems prefer to form the nuclei rather than the growth of particle. The crystallite size of Mn\(_3\)O\(_4\) at 90 and 150°C was 39.3 and 27.2 nm, respectively, showing that the crystallinity of Mn\(_3\)O\(_4\) decrease with increasing temperature. In order to have a better understanding, we performed an investigation to elucidate the effect of crystallization. Solvothermal at 150°C for 24 h were done and the results showed that the average particle size of Mn\(_3\)O\(_4\) at 150°C was 59.3 nm, indicating that the particle size increase with prolongs the time of solvothermal. This can be explained that after the nucleation phase finished, the Ostwald ripening phenomenon occurs and result the large particle.

In the case of the \(\alpha\)-MnO\(_2\), longer and thinner needle shape enhance with the increasing temperature. This result similar to the other study, which defined that aspect ratio of \(\alpha\)-MnO\(_2\) and \(\beta\)-MnO\(_2\) is influenced the product morphology. From their study, high temperature affected the growth anisotropic of crystal and gave a higher aspect ratio product [10]. The aspect ratio of \(\alpha\)-MnO\(_2\) at 90, 120 and 150°C was 12.41, 18.33 and 32.88, respectively, indicating that at 150°C the diameter of the needle thinner compared to 90°C.

4. Conclusion
Manganese oxide with different phase and shape were successfully synthesized using different precipitating agents and solvothermal method. In the first step, the precursor, i.e., manganese sulfate, for the synthesis of the manganese oxide was prepared from the local manganese ore. Then, \(\alpha\)-MnO\(_2\) and Mn\(_3\)O\(_4\) was obtained from the reaction of manganese sulfate with sodium hydroxide or ammonium...
persulfate, respectively, for 18 h of solvothermal. Indeed, the formation of Mn$_3$O$_4$ by the reaction of manganese sulfate with sodium hydroxide can be understood due to its lowest Gibbs free energy, therefore the reaction is spontaneous. Moreover, the presence of OH$^-$ is imperative to oxidize the Mn$^{2+}$ into Mn$^{3+}$ while there is still Mn$^{2+}$ and led to the formation of Mn$_3$O$_4$. Meanwhile, the formation of α-MnO$_2$ due to the existence of ammonium persulfate as a precipitating agent that forms Mn$^{4+}$. The phase also affects the morphology of the particle. For instance, two types of shape were obtained after the solvothermal method for 18 h; needle and sphere which belonged to α-MnO$_2$ and Mn$_3$O$_4$, respectively. One notable finding in this study is the crystallinity of the Mn$_3$O$_4$ decreased with increasing the solvothermal temperature, as indicated by decreasing the crystallite size from 39.3 nm at 90°C of solvothermal to 27.2 nm at 150°C of solvothermal. Moreover, the average particle size also decreased with increasing temperature, which is 63.14, 66.74 and 42.04 nm were obtained after solvothermal reaction at 90, 120 and 150°C, respectively. This phenomenon is more likely due to the competition of the nucleation rate and crystallization rate, where the nucleation rate is dominant in our case. The needle shape of α-MnO$_2$ was thinner and longer at 150°C of solvothermal reaction compared to 90°C. The aspect ratio of α-MnO$_2$ was 12.41, 18.33 and 32.88 after solvothermal reaction at 90, 120 and 150°C, respectively.

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