The Tremendous Influence of Calcination Process on the Phase Structure and Catalytic Activity of Precipitation-Processed MnO₂

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Abstract. The layer and tunnel manganese oxides are versatile materials and have been proposed for various applications. These materials are prepared by a wide range of methods such as sol-gel, solid-state, precipitation and etc. Here, both manganese oxides of birnessite (layer) and cryptomelane (tunnel) have been successfully synthesized using the precipitation method by the reaction between KMnO₄ and glucose with a mole ratio of 3:1. XRD results indicated that the birnessite-type manganese oxide was obtained when the brownish-black precipitate was heated up to 120°C, whereas cryptomelane-type manganese oxide was generated when the as-synthesized sample was further calcined up to 600°C. The birnessite sample displays poor crystalline material with low intensity and broad peak. The heat-treated birnessite up to 600°C leads to the formation much more crystalline tunnel cryptomelane–type manganese oxide. The catalytic activities of the as-synthesized catalysts were tested for the degradation of methylene blue (MB) dye with H₂O₂ as an oxidant. The birnessite catalyst shows much higher catalytic activity for the degradation of methylene blue compared to the cryptomelane catalyst. The tremendous improved catalytic activity of birnessite catalyst are correlated with its poor crystallinity and higher surface area of as indicated by the BET surface area and the XRD results.

1. Introduction
Dye effluents discharged from textile and dyeing industries are a major environmental issue. These effluents are difficult to biodegrade and are stable to heat, light and oxidizing agents. Dyes are a color substance that attaches strongly to a substrate and are harmful to human and aquatic life. It is known that about 10-25% of the dyes are lost during dyeing process and 2-20 % are released into waterways as wastewater. One of commonly used synthetic dyes for cotton, leather, and fiber is MB, which is cationic thiazine dye. The adverse effect of this dye includes headache, vomiting, skin irritation, respiratory tract, danger of liver cancer, etc. Therefore, the wastewater containing MB dye pose a severe environmental problem and must be treated before being released into the environment.

The dye waste can be overcome by several methods such as the adsorption method and the Advanced Oxidation Processes (AOP) method. Although the adsorption method is considered simple and cost-effective, but suffers from a large production of sludge containing Fe species, thus creating secondary pollutants. The AOP is promising and known to be the most effective method for treatment of wastewater. In AOP, highly reactive radicals, which is mainly OH•radicals, are produced and able
to attack and degrade non-selectively most organic contaminants. The radicals are the second-most powerful oxidant after fluorine.

The manganese oxides are known to have various different structures such as tunnel and layer materials. Different tunnel manganese oxides exist in nature and could be synthesized in a laboratory. The basic structural units of Mn (III/IV) oxides are MnO$_6$ octahedra, which are arranged to form tunnel structures and layer structures, by sharing edges and/or corner. The tunnel structures of manganese oxides, also known as octahedral molecular sieves, are formed by sharing edges to generate single, double and triple chain and the chains are then connected together by sharing corners. The layer structures of manganese oxides are created by stacking sheets of edge-sharing MnO$_6$ octahedra. The edge and/or corner-sharing of MnO$_6$ octahedra results in different tunnel sizes such as 3x3 tunnel structure (todorokite), 2x2 tunnel structure (cryptomelane), 1x1 tunnel structure (pyrolusite), and etc. The layer structures of edge-sharing MnO$_6$ octahedra occur in nature, such as birnessite. The application of both birnessite and cryptomelane-type manganese oxides as heterogeneous Fenton-like catalysts for degradation of organic contaminants such as dyes have been intensively studied.

The heterogeneous Fenton process-based advanced oxidation processes (AOP) is one of the AOP methods, which use a solid catalyst and H$_2$O$_2$ as an oxidant. In this system, the catalyst interacts with H$_2$O$_2$ generating highly reactive radicals, mainly OH radicals. These radicals are then reacted with organic pollutants, resulting water and carbon dioxide if complete oxidation occurs. Several metal oxides have been reported to be very active for the complete oxidation of organic contaminants [1].

Manganese oxides with various structures have been studied extensively for the degradation of many recalcitrant organic pollutants, such as synthetic dyes, pharmaceuticals and etc. and are considered as a promising catalyst for that purposes. Manganese oxide can be synthesized with various synthetic methods, such as sol-gel [2, 3, 4, 5], hydrothermal [6], reflux [7], solvent-free method [8] and precipitation methods [9, 10, 11, 12] Among these methods, the precipitation method is a relatively easy to prepare and produces materials with unique properties, controllable particle size and composition. The technique is also able to modify particle surface properties and overall homogeneity. The previous preparation method were conducted via the reaction between KMnO$_4$ oxidant and organic acids such as citric acid [9, 10] and oxalic acid [11].

In this study, birnessite and cryptomelane-type manganese oxides were synthesized through the precipitation method using glucose as a reducing agent. The use of glucose for manganese oxide synthesis by the precipitation method has never been reported by previous studies. Glucose is cheap, available in large quantities and is easy to obtain. It is also a reducing sugar because it has an aldehyde group in its structure. For this reason, the use of glucose is believed to produce manganese oxide with a unique surface properties and different catalytic activity than that reported by previous studies. One of the goal of this current researches is study the effect of calcinations process on the phase structures and catalytic activities of manganese oxides.

2. Methodology

2.1. The preparation of the catalyst

The catalysts of manganese oxides were prepared using precipitation method by the reaction between KMnO$_4$ (oxidant) and glucose (reductant) [9, 12]. Briefly, 250 mL of 0.08 M glucose solution was added into the 250 mL of 0.24 M KMnO$_4$ with the rate of 1 mL min$^{-1}$ under constant stirring (300 rpm) at room temperature. The resulting product was a black-brown turbid suspension, which was digested at 60°C for 30 min and dried at 120°C for 6 h. The dried powder product was brittle and denoted to as un-calcined catalyst. The uncalcined catalyst was then calcined at 600°C for 4 h and denoted to as calcined catalyst. The catalysts were then cooled and put into the bottle and stored in the desiccators prior to further use. The obtained manganese oxide catalysts were then characterized and applied for methylene blue degradation studies.
2.2. Characterization
The XRD was used to characterize crystal structure, phase purity and crystallinity. Patterns of all manganese oxide samples were recorded using Shimadzu XRD 7000 maxima using Cu Kα radiation (λ=1.5406 Å) as the X-ray source. The surface area is determined based on the principles of Brunauer, Emmett and Teller (BET).

2.3. Atomic Absorption Spectroscopy (AAS)
The total amount of potassium (K) and manganese (Mn) of the samples were determined by Atomic Absorption Spectroscopy (Shimadzu AA7000) [10, 11, 12]. About 10 mg of manganese oxide catalyst was placed into the glass beaker, added 10 mL of H₂SO₄ and diluted with DDW up to 100 mL. The mixture was then analyzed using an Atomic Absorption Spectrophotometer (AAS) to determine potassium (K) and manganese (Mn) content. The K and Mn ratios are calculated using the following equation:

\[
\frac{K}{Mn} = \left(\frac{\text{Conc. K}}{39.10}\right) : \left(\frac{\text{Conc. Mn}}{54.94}\right)
\]

2.4. Catalytic activity
Approximately 25 mL of 50 ppm methylene blue (MB) was placed into a 250 mL of a glass container and added with 70 mL of DDW and 50 mg of catalyst for the catalytic reaction [10,11,12]. The resulting slurry was stirred by a magnetic stirrer and added with 5 mL of hydrogen peroxide at the speed of 400 rpm for 30 minutes. The absorbance of the MB following the catalytic reaction was monitored by pipetting 5 mL aliquots of the reaction mixture at various time intervals during the reaction. The absorbance of the solution was analyzed using Optima SP-300 Spectrophotometer at a wavelength of 660 nm. The results were determined using the equation:

\[
\% \text{ decrease MB} = \frac{C_o - C_t}{C_o} \times 100
\]

Where Co and Ct are the initial and final concentration of MB, respectively.

3. Result and Discussion
Manganese oxide with a layer structure of birnessite and tunnel structure of cryptomelane have been successfully synthesized by precipitation method. The formation of both manganese oxides was obtained by a redox reaction between the solutions of KMnO₄ oxidant and glucose reductant with a mole ratio of 3:1. The reaction between the KMnO₄ solution and glucose is an exothermic reaction resulting in an increase in temperature during the reaction process and produces small bubbles, indicating that this reaction produces CO₂.

During the course of a reaction, the color of KMnO₄ solution changes from purple to light brown and finally turns to blackish brown when the suspension is formed. This suspension indicates that the reaction is completed and the pH of the mixture has increased to alkaline condition. The suspension is achieved with the addition of ± 47 mL glucose at pH ± 7.6. The resulting suspension is again stirred using a magnetic stirrer for 30 minutes at 60°C to maximize the formation of manganese oxide deposits. The similar results are also reported by Subramanian et al. [9], but oxalic acid is used as a reducing agent instead of glucose. The resulting precipitate is heated at 120°C to remove water molecules until a solid manganese oxide catalyst is obtained and denoted to as uncalcined catalyst.

The some catalysts were further calcined at 600°C for 4 hours to study the effect of the calcination process on phase structure and their catalytic activities. The calcination at a temperature of 600°C is chosen based on the previous studies using a similar method but difference in reducing agent [9]. The temperature is considered appropriate to provide high kinetic energy for the atoms in the solid MnOx for structuring their structure, resulting in a high degree of crystallinity. The four-hour calcination processes of the MnOx solid used in this study prove to produce high crystalline manganese oxide, as shown by XRD results in figure 1. The similar calcination time is also reported by previous studies [9] using the same method for the formation of cryptomelane-type manganese oxide.
Figure 1. Diffractogram of manganese oxide synthesized with potassium permanganate and glucose. The oxide without calcination is shown in red line and with calcination green line.

The as-synthesized manganese oxide is characterized by X-ray diffraction producing peaks, as shown in Figure 1. It is obvious from the diffractogram that the calcined manganese oxides have much higher crystallinity compared to un-calcined ones, which is related to certain energies required to attain more ordered structures [9, 13]. A similar result was reported by previous researchers, in which birnessite-type manganese oxide experienced an increase in crystallinity after calcination [10, 11, 12]. In addition, the calcination process can also provide different forms of manganese oxide. Subramanian et al. [9] reported that birnessite-type manganese oxide undergoes deformation after calcination.

In contrast to previous report that the calcination process reduced the K⁺ levels to obtain cryptomelane-type manganese oxide [14], in present study, the opposite is true. The K⁺ ion concentrations increase upon calcination process. K⁺ ion concentrations are reported to correlate with the presence of defects in the manganese oxides, that is, higher K⁺ concentrations produce more defects. In current studies, the birnessite-type layer manganese oxide transforms into tunnel structure of cryptomelane after calcinations. The same observations are also reported by Subramaniam, to which the layer birnessite was transformed into tunnel cryptomelane upon calcination using oxalic acid instead of glucose as a reducing agent. In contrast, other studies reported that the crystal phase of birnessite remain unchanged after calcinations [10, 11].

Table 1. Crystal size, surface area, pore volume, pore radius and element analysis of birnessite and cryptomelane samples.

| Catalysts   | Crystal size (nm) *Scherrer | BET surface area (m² g⁻¹) | Pore volume (cm³ g⁻¹) | Pore radius (Å) (BJH) | Atomic Absorption Spectroscopy (AAS) | K/Mn |
|-------------|----------------------------|---------------------------|-----------------------|-----------------------|-------------------------------------|------|
|             |                            |                           |                       |                       | Concent. K (ppm) | Concent. Mn (ppm) |      |
| Birnessite  | 1.76                       | 80.51                     | 0.07                  | 48.62                 | 2.96±0.1884        | 7.06±0.0084        | 0.58 |
| Cryptomelane| 8.87                       | 19.59                     | 0.20                  | 15.88                 | 3.36±0.4184        | 6.84±0.0002        | 0.69 |

X-ray diffraction can also be used to determine the crystallite size using the Scherrer equation (Table 1). Table 1 displays that birnessite-type catalysts have smaller crystalline sizes compared to cryptomelane-type catalysts. This is in line with previous research which explains that birnessite without calcination has a very small crystal size because it is difficult to distinguish peak intensities on
the diffractogram [10, 11, 12]. Cheney et al. [15] reported that differences in the size of the crystal are influenced by the width of the diffraction peak, the wider the diffraction peak, the size of the crystal will decrease and tend to produce nanocrystalline. This, in turn, could have a different effect on its interaction with dye or hydrogen peroxide.

**Figure 2.** Percentage degradation of MB

Figure 2 illustrates the catalytic activities of as-synthesized catalysts against MB degradation using hydrogen peroxide as an oxidant. The birnessite-type catalysts displayed much higher catalytic activities for the degradation of MB than that of the cryptomelane-type catalysts using the same condition. Using the cryptomelane-type catalysts, the catalytic degradation of MB achieved only about 40±0.002% after 10 minutes of reaction time, whereas almost 91±0.010% degradation of MB was obtained using birnessite-type catalysts after 10 minutes of reaction times. Much higher catalytic activities of the birnessite catalysts compared to cryptomelane catalysts are believed to correlate with the catalyst surface area and the crystalline nature of uncalcined sample. The surface area of birnessite-type catalysts is much greater than that of cryptomelane-type catalysts (Table 1). The calcination process is likely provide enough energy for the birnessite sample to rearrange its structure to attain the most stable structure and higher crystallinity. This process has a sizable impact on the surface area and crystal size of the resulting cryptomelane. Surface area is one of the main parameters considered in the selection of heterogeneous catalysts because higher surface area of a material means that the material has higher active site. In line with this research, that birnessite-type catalysts has a higher percent degradation of methylene blue because it has a greater surface area than cryptomelane catalysts.

4. Conclusion

In current study, the birnessite-type manganese oxide and the cryptomelane-type manganese oxide have been successfully synthesized using the reaction between potassium permanganate and glucose by the precipitation method. The calcination process facilitates the transformation of the layer birnessite-type manganese oxide into tunnel cryptomelane-type manganese oxide. The cryptomelane-type catalyst has lower catalytic activity than binessite-type for catalytic degradation of methylene blue. The differences in catalytic activities are attributed to the differences in surface area, crystal phase and crystallinity.

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