Synthesis and Catalytic Activities of Manganese Oxides Prepared by Precipitation Method: Effects of Mixing Modes of Reactants and Calcination Process

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Abstract. The two phases of manganese oxides are prepared by two different mixing modes using the same precipitation method from the solutions of KMnO₄ dan maltose, resulting in marked different phase structures and catalytic activities. The oxides synthesized by adding dropwise of the maltose solution into KMnO₄ solution (method A) resulted in the formation of layer manganese oxide birnessite, which turns into tunnel structured manganese oxide cryptomelane following the calcination at 600°C for 4 hours. The simultaneous addition of KMnO₄ solution and maltose solution (method B) also produced birnessite before calcination, but remain unchanged as birnessite phase after calcination with cryptomelane as minor product. The samples without calcination obtained from method A posseses higher surface area and poor crystallinity compared to that with calcination. The catalytic test using Fenton-like Reaction for methylene blue (MB) degradation indicated the tremendous difference in their catalytic activities for both samples without and with calcination. The birnessite catalysts (without calcination) prepared using method A show the highest activity and are able to degrade 93% methylene blue within 10 minute, much higher than other samples.

1. Introduction
Manganese oxides exist in nature with different phases and combine with other minerals such as iron oxides. Manganese oxide are known to have tunnel and layer structure, which is formed by edge-sharing of MnO₆ octahedra, producing single, double or triple chains. These chains are linked together through corner-sharing to form tunnel such as 1x1 tunnel (pyrolusite), 2x2 tunnel (cryptomelane) and 3x3 tunnel (todorokite). Manganese oxide also has a layer structure such as birnessite and busserite. The existence of tunnel and layered structures make this oxides very attractive to chemical researchers. Its features include ion exchange properties, large surface area such rechargeable batteries, a catalyst and an absorbent [1].

Manganese oxides have been reported to be active as heterogeneous Fenton catalysts to degrade wastewater containing the residues of synthetic dyes. The Fenton process-based advanced oxidation processes is based on the generation of highly reactive radicals such as OH with high oxidation potential (3.8 V), which are able to attack and degrade non-selectively most organic pollutions including synthetic dyes into water, carbon dioxide and other oxidised products. In the Fenton-like reaction, manganese oxide react with H₂O₂ to produce various types of active radicals as intermediaries for dye degradation [2]. Formation •OH, O₂•‾, and HO₂• to degrade methylene blue by β-MnO₂ (pyrolusite)/H₂O₂ has reported by Cui et al [3] and Cheng et al. [4].
Manganese oxide can be synthesized with various synthetic methods, such as sol-gel [5,6,7,8], hydrothermal [2], reflux [9], solvent-free method [10], and precipitation methods [11,12,13,14]. Among other methods, the precipitation method was very simple method, requires short time synthesis, easy control of particle size and composition. In general, the different synthesis methods, precursors, reaction conditions often lead to different structure, morphologies, and surface properties of manganese oxides [11].

In this study, the manganese oxides with tunnel and layer structures were prepared by two different mixing strategies of reactants, denoted to as method A and method B. The use of maltose as reducing agent to synthesize manganese oxides by precipitation method has never been reported previously. Their catalytic activities are then evaluated for the degradation of methylene blue using H$_2$O$_2$ as an oxidant.

2. Methodology

2.1. Synthesis

The manganese oxides were prepared via precipitation method with two variations of reactant mixing [9]. The two different methods (A and B) were adopted for the synthesis of manganese oxides by the order of mixing the reactants of same concentrations.

2.1.1. Method A. 250 mL of 0.08 M maltose solution was added to 250 mL of 0.24 M KMnO$_4$ solution dropwise through a burette at a flow rate of 1 mL / min while stirring using a magnetic stirrer at a speed of 300 rpm. After 250 ml of KMnO$_4$ has been added, the mixture is stirred using a magnetic stirrer at 300 rpm for 30 minutes at 60°C and dried in an oven at 120°C for 6 hours until a catalyst without calcination is obtained. Then the catalyst was calcined at 600°C for 4 hours and a calcination catalyst was obtained. The as-synthesized catalysts were denoted as MA-UC birnessite for maltose-prepared un-calcined method A, MA-C for maltose-prepared calcined method A.

2.1.2. Method B. The KMnO$_4$ solution and maltose were mixed in a glass beaker together and then stirred using a magnetic stirrer at a speed of 300 rpm for 30 minutes. The mixture is stirred again for 30 minutes at 60°C. The precipitate obtained was dried in an oven at 120°C for 6 hours to obtain a catalyst without calcination. Then the catalyst was calcined at 600°C for 4 hours and a calcination catalyst was obtained. The as-synthesized catalysts were denoted as MB-UC birnessite for maltose-prepared un-calcined method B, MB-C for maltose-prepared calcined method B.

2.2. Characterization

X-ray powder diffraction (XRD) was performed on a Shimadzu 700 Maxima X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54060$ Å), operating at 40 kV, and a current of 30 mA. The data were collected with scan speed 2º per minute in 2θ from 10º-80º. The Brunauer-Emmett-Teller (BET) surface area measurements and Barrett-Joyner-Halenda (BJH) adsorption were carried out using Quantachrome Nova instruments.

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). About 10 mg of manganese oxide catalyst was placed into the glass beaker, added 10 mL of H$_2$SO$_4$ 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:

$$\text{K/Mn ratio} = \frac{\text{Conc. K/39.10}}{\text{Conc. Mn/54.94}}$$
2.4. Catalytic activities
The catalytic reaction was carried out in a 250 mL batch reactor, which contained 25 mL of 50 ppm methylene blue, 70 mL of DDW, and 50 mg of catalyst. The mixture was stirred using a magnetic stirrer at 400 rpm for 30 minutes and added 5 mL hydrogen peroxide 30%. The optical absorbance measurements were taken by pipetting 5 mL aliquots of the reaction mixture at various time intervals during the reaction. The solution was immediately centrifuged for 15 min at 3000 rpm to remove any solid particulates. 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:

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\% \text{ decrease MB} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]

Where Co was initial concentration and Ct was final concentration in the reaction mixture at a given time respectively.

3. Result and Discussion
Manganese oxides have been successfully synthesized by precipitation method with the two different mixing strategies of the reactants. The reactants used in this study were potassium permanganate as an oxidizing agent and maltose as reducing agent. During the course of reaction in method A, the color of KMnO₄ solution initially turned into purple and then into a blackish brown suspension at the addition of ± 30 mL maltose at pH ± 7.8. In the method B, the suspension containing manganese oxides was formed suspension after 15 minute-reaction time at pH ± 7.5. The formed suspension is again stirred using a magnetic stirrer for 30 minutes at 60°C to maximize the formation of manganese oxide deposits. The generation of suspension indicates that the reaction is complete and the solution pH turns to alkaline. Subramanian et al. [9] reported the similar generation of suspension following the addition of oxalic acid into KMnO₄. The resulting precipitate is heated at 120°C to remove water molecules until a solid manganese oxide catalyst is obtained.

X-ray diffraction was used to characterize the phase and crystallinity of the as-synthesized manganese oxide samples. Figure 1 showed the XRD patterns of the resulting manganese oxide products synthesized under mole ratio 3:1 of KMnO₄ and maltose with two mixing strategies. The oxides produced by two different strategies without calcination processes are denoted to as MA-UC and MB-UC, respectively. The oxides displayed low intensities and broad peaks, indicating the low crystalline nature, more defects, and smaller crystal sizes. The diffraction peaks of these manganese oxides (MA-UC and MB-UC) match well with the standard pattern of moniclinic phase of birnessite (JCPDS card no. 80-1098). The diffraction peaks at 2θ values of 12.56°; 24.90°; 37.30°; and 66.28° can be ascribed to the reflections of (001), (002), (-111), and (021) planes of the birnessite (figure 1a). The data from XRD results indicated that the simultaneous addition of solutions of KMnO₄ and maltose (method B) resulted in the similar XRD patterns to that in method A with 2θ values of 12.40°; 25.64°; 38.34°; and 66.78° for samples without calcination.
Figure 1. The XRD patterns of as-synthesized manganese oxide catalysts using two different mixing modes, method A and method B. MA-UC (black line), MA-C (red line), MB-UC (blue line), and MB-C (purple line). *(B) for birnessite-type, and (C) cryptomelane-type.

The calcination temperatures at 600°C have a sizably impact in the structure and crystallinity of the as-synthesized manganese oxides. The XRD results from calcined catalysts, denoted to as MA-C for method A, produce cryptomelane-type manganese oxide. The diffraction peaks of the cryptomelane prepared from maltose match well with the cryptomelane phase of MnO₂ (JCPDS cryptomelane), with the diffraction peaks at 2θ values of 12.66°; 17.98°; 28.72°; 37.52°; 49.92°; 60.06° for method A (red line in Figure 1). The diffraction peaks in the method B following calcination of sample produce mixed phases of manganese oxides, but birnessite remains the main product, with minor phases of cryptomelane shown in Figure 1 (purple line). The diffraction peaks at 2θ values of 12.46°; 17.98°; 25.12°; 28.64°; 37.40° can be ascribed to the reflections of (001) plane of birnessite, (200) plane of cryptomelane, (002) plane of birnessite, (310) and (211) planes of the cryptomelane. All the calcination samples displayed sharp peaks with high intensities, indicating the crystalline nature of the samples following calcination process. The same observation were also reported by previous studies [11,13,14], in which the samples with calcination displayed much higher crystallinity that that without calcination. It is believed that the calcination temperature at 600 °C provides enough energy for the samples to rearrange their structures to attain the final products with a smaller defect. Table 1 shows the elemental analysis, BET surface areas, pore volume, and radius of the selected as-synthesized samples. The contents of K⁺ ions and Mn ions of samples from method A before calcination are higher than that following calcinations, which support data from XRD results. Higher K⁺ ions content for the samples prior to calcinations suggested that the presence of more defects due to oxygen vacancies and/or more Mn³⁺ ions in the framework of the sample as reported by previous studies. The BET surface areas shown in table 1 showed the much higher surface areas of the samples without calcinations compared with the samples with calcinations. These results are also in line with the XRD results and the elemental analysis results. The samples with low crystallinity, more defects, and higher K⁺ ion concentrations often possesses higher BET surface areas.
Figure 2. Percentage degradation of MB. The maltose-prepared un-calcined method A birnessite (blue line), maltose-prepared calcined method A cryptomelane (green line), maltose-prepared un-calcined method B birnessite (red line), and maltose-prepared calcined method B cryptomelane (purple line).

Figure 2 displayed the percentage degradation of MB by the as-synthesized catalysts, birnessite and cryptomelane-type manganese oxides. It is evident from the figure 2 that the samples without calcination for method A have the highest catalytic activities than other samples. The higher catalytic activities are related with low crystalline nature and more defects for the MA-UC sample shown by XRD results. The MA-UC sample is also have higher BET surface areas and higher K⁺ ion concentrations as displayed in table 1. The MA-UC sample are able to degrade more than 93% MB within 10 minutes of degradation times. The samples with calcinations by method B (MB-C) show the opposite trend and have higher catalytic activities compared to the MA-C sample. The MB degradation for MB-UC is relatively low, reaching only 31% after 10 minutes of reaction times. Following calcination, MB-C catalytic activities improved to 52% of MB degradation. The reason for the difference in catalytic activities between the samples from method A and B is believed to be related with the difference in crystal phases, surface area and the presence of defects. The different mixing modes affect the rate of crystal growth. With method B, the crystal growth of MnOₓ crystallite runs faster since the reactants are mixed simultaneously. The slow addition of maltose solution into KMnO₄ results in much slower growth of MnOₓ crystallite in method A. The MB degradation by the oxides was also characterized by changes in sample color after degradation. The colorless of MB following degradation process by MA-UC indicates high degradation ability.

Table 1. K-Mn ratio, textural properties of birnessite and cryptomelane samples.

| Sample  | Atomic Absorption Spectroscopy (AAS) | BET surface area (m² g⁻¹) | Pore volume (cm³ g⁻¹) | Pore radius (Å) (BJH) |
|---------|------------------------------------|---------------------------|------------------------|------------------------|
|         | Conc. K (ppm)                      | Conc. Mn (ppm)            | K/Mn                   |                        |
| MA-UC   | 3.903 ± 0.143                      | 7.116 ± 0.014             | 0.770                  | 67.466                 | 0.172                   | 15.898                   |
| MA-C    | 3.231 ± 0.249                      | 5.294 ± 0.013             | 0.860                  | 38.334                 | 0.174                   | 16.166                   |
| MB-UC   | -                                  | -                         | -                      | -                      | -                       | -                        |
| MB-C    | -                                  | -                         | -                      | 6.971                  | 0.025                   | 16.077                   |
4. Conclusion

In summary, the manganese oxides with tunnel structure of cryptomelane and layer structure of birnessite have been successfully synthesized via precipitation method using two different strategies of mixing solutions of KMnO$_4$ and maltose. The samples without calcination produce birnessite-type manganese oxide, whereas with calcination process generate cryptomelane type manganese oxide (method A), whereas a mixture of birnessite and cryptomelane-type manganese oxides are produced for method B. The birnessite obtained without calcination process showed the highest catalytic activity for MB degradation.

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