The enhanced catalytic activities of octahedral layer birnessite-type manganese oxide synthesized via precipitation method for the degradation of methylene blue

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Abstract. The catalytic activities of the octahedral layer birnessite-type manganese oxides for the degradation of methylene blue (MB) dye have been studied. The oxide catalysts were prepared via a facile precipitation method using the reaction between KMnO4 (oxidant) and citric acid or oxalic acid (reductant), where the acid is added dropwise into KMnO4 until certain volume achieved to generate a brownish black precipitate. The solid product was treated with either calcination or without calcination process, respectively. The samples without calcination display poor crystallinity with low intensity and broad peak and are identified as birnessite-type manganese oxides. The calcination, however, led to the formation of the highly crystalline birnessite materials. The birnessite catalysts synthesized by the different reductants displayed different crystallinity, morphology, average oxidation state (AOS) of manganese, zero-point charge pH (pHzpc) and particle size that affect their catalytic activities. The results indicated that the activities of birnessite-type manganese oxide catalysts for MB degradation correlated with the nature of catalysts. The citric acid-prepared manganese oxide catalyst (CAC) showed slight higher crystalline phase compared with the oxalic acid-prepared manganese oxide catalyst (OAC). The data from AOS of manganese suggested that the CAC catalysts have a lower value of AOS of manganese than OAC catalysts, indicating more defects due to the presence of more oxygen vacancy or more Mn3+ content. The smaller particle size and AOS of manganese for CAC catalysts are also considered to be responsible for their higher catalytic activities for MB degradation. The birnessite-type manganese oxide catalysts prepared without calcinations also showed much enhanced catalytic activities for MB degradation.

Keywords: birnessite; manganese oxide; precipitation method; methylene blue

1. Introduction

The manganese oxide materials used as a heterogeneous catalyst in Fenton process-based advanced oxidation process have gained a wide range of attention over few decades due to their unique structures, low cost, environmentally benign material, mixed-valent Mn and high catalytic activity. The basic structural unit of the oxide is MnO6 octahedra, which combine to generate numerous polymorphs such as alpha-MnO2 (cryptomelane), beta-MnO2 (pyrolusite), and delta-MnO2 (birnessite). The different synthetic methods have been developed to prepare these materials, including sol-gel [1], hydrothermal [2], reflux [3], precipitation [4], and solid-state [5]. In addition, a wide range of stating materials have been used to generate this versatile material. Most of the reactions for the preparation of manganese
oxides are based on the reduction of Mn precursor such K MnO₄ or oxidation of Mn precursor such as MnCl₂.

The ultimate goal of various synthetic methods used for the preparation of birnessite-type manganese oxides is to find the most appropriate preparation method for synthetic birnessite with a unique property for a given application. For example, Hou et al. [6] prepared birnessite with the morphologies of nanoflower, nanowire, and nanosheets with excellent catalytic activity for benzene oxidation. Qin et al. [7] reported the three-dimensional microflower morphology of birnessite with high purity for catalytic degradation of rhodamine B. Cui et al. [8] also reported the synthesis of birnessite for decolourization of rhodamine B.

The degradation of synthetic dyes using manganese oxides as a heterogeneous catalyst is considered as one of the hottest topics. The various manganese oxides with different crystal structures and morphologies with different synthetic approaches have been used to degrade this synthetic dyes. For example, Awaluddin et al. [9] used the sol-gel method to synthesize the cryptomelane-type manganese oxide octahedral molecular sieve (OMS-2) for the degradation of MB and reported the 88.6% of MB degradation. Recently, Siregar and Awaluddin [5] reported the synthesis of birnessite-type manganese oxide using the solid-state method (solvent-free method) for the catalytic degradation of MB and the maximum degradation of MB was 50% with 90 minutes of reaction time.

Most of the synthetic manganese oxides reported previous studies had some disadvantages such as the use of a high energy input for solid-state for complete reaction to occur, high reducing volume of gel occurred during reaction for the sol-gel method and high temperature and pressure needed for the hydrothermal method. It is advantageous to find a way to prepare controllable properties birnessite but using moderate condition. Among the available synthetic strategies for birnessite preparation, the precipitation method is considered to be as the simplest method for the preparation of the birnessite and cryptomelane-type manganese oxides. In this work, birnessite-type octahedral layer manganese oxide catalysts have been synthesized using precipitation method with two types of reducing agents, citric or oxalic acid. The different catalytic activities of the as-synthesized birnessite for degradation of MB have been correlated with the different properties of as-synthesized birnessite such crystallinity, morphology, AOS of Mn, and K/Mn due to different Mn³⁺ content or oxygen vacancy defect and particle sizes.

2. Experimental

2.1. The preparation of the catalyst
The catalysts of birnessite-type manganese oxides were prepared using precipitation method by the reaction between of KMnO₄ (oxidant) and citric acid or oxalic acid (reductant) [4]. Briefly, 250 mL of 0.04 M citric acid solution was added to the 250 mL of 0.2 M KMnO₄ 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 solid product obtained (un-calcined catalyst) was then calcined at 600°C for 4 h (calcined catalyst). The similar procedure was used for the preparation of the oxalic-prepared birnessite except oxalic acid was used as a reductant. The products obtained from citric acid was called CA-UC birnessite for un-calcined sample and CA-C birnessite for calcined sample, whereas the products obtained from oxalic acid was called OA-UC birnessite for un-calcined samples and OA-C birnessite for calcined sample.

2.2. Characterization
The XRD was used to characterize crystal structure, phase purity, and crystallinity, whereas SEM and AAS were used to reveal the morphology and bulk chemical composition of the as-synthesized manganese oxide. 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. For sample morphology, SEM JEOL JSM-6330F was used with acceleration potential of 15-20 kV. The total amount of potassium (K) and manganese (Mn) of the samples were determined by atomic absorption spectroscopy (Shimadzu XRD 7000 maxima). About 10 mg of manganese oxide catalyst was placed into a glass beaker and added 10
mL of H$_2$SO$_4$ and diluted with DDW up to 100 mL. The mixture was then analysed using an Atomic Absorption Spectrophotometer (SSA) to determine potassium (K) and Manganese (Mn) content. The conventional potential voltammetric titration method was used to determine the average oxidation states (AOS) of manganese in the samples [10] and prolonged salt titration (PST) method was used to determine the Zero Point Charge (pH$_{zpc}$) [11].

2.3. 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 birnessite catalyst for the catalytic reaction. 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 analysed using Optima SP-300 Spectrophotometer at a wavelength of 660 nm. The results were determined using the equation:

$$\% \text{ decrease MB} = \frac{C_o - C_t}{C_o} \times 100$$ (1)

Where $C_o$ and $C_t$ are initial and final concentration of MB, respectively.

3. Result and Discussion

![Figure 1](image-url)

**Figure 1.** The XRD patterns of as-synthesized manganese oxide catalysts using two different reducing agents, oxalic acid (OAC) and citric acid (CAC).

The crystal structure and phase purity of the as-synthesized manganese oxide catalysts were examined using XRD and shown in Fig. 1. The oxides were prepared from redox reaction between KMnO$_4$ and an organic acid as the reducing agent, either oxalic acid or citric acid, using a facile precipitation approach. The oxides produced without calcination process (OAC-UN 2:3 and CAC-UN 5:1) displayed low intensities and broad peaks, indicating the low crystalline materials, the presence of more defects, and smaller crystal sizes of the materials. Following the calcination treatment of the samples, the peak intensity significantly improved for both citric and oxalic-prepared samples, and the samples prepared from oxalic acid displayed, in general, lower peak intensity compared from those prepared from citric acid. Thus, the different reducing agent led to the different crystallinity of the as-synthesized samples. The peak angles of the as-synthesized samples indicated the typical birnessite-type octahedral layer
manganese oxide (JCPDS 80-1098). The poor crystallinity of uncalcined samples also suggested that the energy provided during the reaction is not enough for the reactants to react to form more crystalline material. The synthetic approach applied in this study was the same as reported by Subramanian et al. [4] using KMnO₄ and oxalic acid (reductant), except this study, citric acid is also used as reducing agent to study the effect of different reducing agents on the properties of the resulting oxide materials. Subramanian et al. [4] observed the transformation of birnessite into cryptomelane, octahedral molecular sieve manganese oxide (OMS-2), upon calcination processes at 400°C. In contradiction to Subramanian et al. report, the as-synthesized birnessite in this work remained unchanged upon calcination, either using oxalic or citric acid precursor. The different results obtained from this study compared to the previous report are probably originated from the different K⁺ content in the samples. Ching et al. [12] conducted various treatment of the manganese oxide gels and reported that the samples with proper treatment resulting low K⁺ content generated cryptomelane-type manganese oxide, whereas the samples without treatment (high K⁺ content) resulted in birnessite. Ching et al. [12] explained that too much concentration of K⁺ led to layered manganese oxide birnessite, whereas the moderate concentration of K⁺ produced cryptomelane-type manganese oxide octahedral molecular sieve (OMS-2). Siregar and Awaluddin [5] also reported the formation of birnessite by reacting between KMnO₄ with glucose using the solvent-free method without further treatment. Thus, the concentration of K⁺ ions remained high in the reaction mixture, thus producing birnessite-type manganese oxides. Ziller et al. [13] reported the sol-gel approach for the preparation of birnessite-type manganese oxides without post-treatment. The results are similar with the previous reports that the samples without further treatments resulted in the birnessite phase of manganese oxide.

**Figure 2.** The morphology of as-synthesized birnessites prepared using two different reducing agents (a) citric-prepared birnessite without calcination (b) citric-prepared birnessite following calcination, (c) oxalic-prepared birnessite without calcination, (d) oxalic-prepared birnessite following calcination.
The morphologies of the as-synthesized manganese oxides are revealed using SEM and shown in Fig. 2. In general, the morphologies of birnessite-type manganese oxides are dependent upon different factors such as synthetic method, precursors used, synthetic condition, post-treatment, etc. The morphology of citric-prepared birnessite prior to calcination displayed a well-defined particle with smooth faces, but upon calcination, the crystal-face particles of citric-prepared birnessite turned to fibre-like appearance. On the other hand, oxalic-prepared birnessite displayed bulk particles appearances, which changed to aggregates of separate particles upon calcination. Since both citric-prepared birnessite and oxalic-prepared birnessite samples were prepared using the same methods and have the same birnessite structure, the changes of morphologies when oxalic acid was used as a reductant suggested a different particle growth behaviour compared to when used citric acid as a reductant. Using similar synthetic approach, Subramanian et al. [4] prepared the birnessite by the reactant between KMnO$_4$ and oxalic acid and reported the changed morphology upon the calcination of samples due to the phase transformation from birnessite to cryptomelane. In this work, however, the phase crystal of birnessite remained unchanged upon calcination except for the morphology. The previous study by Awaluddin et al. [9], also reported the different morphology between glucose-prepared cryptomelane and oxalic-prepared cryptomelane synthesized using sol-gel method. The oxalic-prepared cryptomelane displayed disk-like morphology, whereas glucose-prepared cryptomelane showed cotton-like appearance.

Table 1. Elemental analysis, AOS, crystal size and pH$_{zpc}$.

| Catalyst | K/Mn | AOS | Crystal size (nm) *scherrer | pH$_{zpc}$ |
|----------|------|-----|-----------------------------|-----------|
| CAC      | 0.48 | 3.75| 13.41                       | 3.80      |
| CAC-UN   | 2.06 | 3.25| 0.54                        | 4.00      |
| OAC      | 0.6  | 4.00| 9.63                        | 3.21      |
| OAC-UN   | -    | 3.75| 1.56                        | -         |

Table 1 depicted the crystal sizes, AOS Mn, pH$_{zpc}$, Ratio K/Mn of as-synthesized birnessite catalysts. The crystal sizes of the as-synthesized birnessite were calculated according to the Scherrer equation and indicated that samples without calcination have much smaller crystal sizes compared to those with calcination. Compared to oxalic-prepared birnessite without calcination, citric-prepared birnessite also showed smaller particle size. The samples without calcination also have lower the AOS of Mn compared to those upon calcination, suggesting the presence of more defect due to Mn$^{3+}$ or oxygen vacancy according to the reaction [6]:

\[
\text{Mn}^{4+}\text{O}_2^2^- + x\text{K}^+ \rightarrow K_x\text{Mn}^{4+}_{1-x}\text{Mn}^{3+}_y\text{O}_2^2^- \quad (2)
\]

\[
-\text{Mn}^{4+}\cdot\text{O}^2^- = \text{Mn}^{4+} \rightarrow -\text{Mn}^{3+} - \square = \text{Mn}^{3+} - + \frac{1}{2}\text{O}_2 \quad (3)
\]

The overall reaction can be written as follows:

\[
\text{Mn}^{4+}\text{O}_2^2^- + x\text{K}^+ \rightarrow K_x\text{Mn}^{4+}_y\text{Mn}^{3+}_{1-y}\text{O}_2^2^- + \frac{1}{2}\text{O}_2 \quad (4)
\]

Where $y=1-x-2z$, and $\square$ is the oxygen vacancy created due to the presence of Mn$^{3+}$.

Similarly, citric-prepared birnessite also displayed lower AOS of Mn than oxalic-prepared birnessite, indicating more Mn$^{3+}$ or oxygen vacancy defect in the citric-prepared birnessite. The K/Mn for uncalcined birnessite prepared from citric acid precursor also showed much higher value (2.06) than calcined birnessite (0.48), indicating much more K$^+$ content occupied in the interlayer of the birnessite. The high K$^+$ content has a direct correlation with high Mn$^{3+}$ content, suggesting un-calcined birnessite samples contain much higher oxygen vacancy defect. Table 1 also displayed the zero point charge pH for the as-synthesized birnessite. It is obvious from the table that the citric-prepared birnessite has the higher value of pH$_{zpc}$ than oxalic-prepared birnessite, indicating that it requires higher pH for citric-
prepared birnessite to have zero net electrical charge on its surface. This, in turn, could have the different effect for its interaction with dye or hydrogen peroxide.

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**Figure 3.** Percentage of MB degradation over different birnessite-type manganese oxides, CAC=calcined citric-prepared birnessite, CAC-UN=uncalcined-citric prepared birnessite, OAC=calcined oxalic-prepared birnessite, OAC-UN=uncalcined oxalic-prepared birnessite.

Fig. 3 depicted the catalytic activities of the as-synthesized birnessite for the degradation of MB using hydrogen peroxide as an oxidant. It is obvious from Fig. 3 that the uncalcined samples displayed much higher catalytic activities for the degradation of MB compared to calcined samples. It is also indicated in Fig. 3 that citric-prepared birnessite displayed slightly higher catalytic degradation of MB compared to oxalic-prepared birnessite. Using the calcined samples, the catalytic degradation of MB achieved about 80% after 10 minutes of reaction time, whereas almost 95% degradation of MB was obtained after 10 minutes of reaction times.

The much higher catalytic activities of the uncalcined samples compared to calcined samples are possibly correlated with higher Mn$^{3+}$ content or oxygen vacancy defect, smaller particle size, and higher K⁺ content. It is known that electron in Mn$^{3+}$ birnessite has d⁴ high spin-configuration, where one electron is occupied in antibonding e_g¹, which is highly reactive. Thus, it is possible that this highly reactive electron in Mn$^{3+}$ would interact readily with H$_2$O$_2$ to generate more OH radicals for the uncalcined samples, which degrade more MB. The higher Mn$^{3+}$ content or oxygen vacancy defect has been reported by previous studies to be responsible for the catalytic activities of manganese oxide catalysts. Hou et al. [6] reported the tremendous catalytic activities of the birnessite with nanoflowers compared to nanowires and nanosheets for benzene oxidation due to their higher concentration of oxygen vacancy defect or Mn$^{3+}$. The uncalcined birnessite also contain more the K⁺ ions compared to calcined birnessite, which may affect their catalytic activities. K⁺ ions are occupied in the interlayer spacing of birnessite to balance the negative charge of MnO$_6$ framework due to the presence of Mn$^{3+}$. The ions are also responsible for the stability of birnessite. Recently, it has been reported that K⁺ ions in birnessite or cryptomelane also play a significant role in the catalytic oxidation of organic materials. The much higher concentration of K⁺ ions in the uncalcined birnessite compared to calcined birnessite, in this work, may contribute to higher its catalytic activity for degradation of MB. Table 1 also displayed the particle sizes of the as-synthesized birnessite. The uncalcined samples also displayed much smaller particle sizes compared calcined samples, with citric-prepared birnessite being slightly smaller particle size than oxalic-prepared birnessite. The smaller particle sizes for citric-prepared birnessite may also have a significant effect on its catalytic activity. The smaller particle size for a given volume of materials means the more surface area that the particle has, which lead to provide the more possible interaction with MB and H$_2$O$_2$. Thus, the more interaction between MB or H$_2$O$_2$ with citric-prepared birnessite compared to oxalic-prepared birnessite occurred, leading to the higher catalytic degradation of MB.
4. Conclusion
The birnessite-type octahedral layer manganese oxide catalysts have been successfully synthesized using the precipitation methods by redox reaction between KMnO₄ and citric acid or oxalic acid as reductants. The different reducing agents used in this study resulted in the different morphologies as revealed by SEM. The samples without calcination for both oxalic or citric-prepared birnessite displayed poor crystalline phase but showed much enhanced catalytic activity for MB degradation compared to calcined samples. The citric-prepared birnessite exhibited slightly higher catalytic activity than oxalic-prepared birnessite. The higher catalytic activities for un-calcined samples has been correlated with higher Mn³⁺ content or oxygen defect vacancy, high K⁺ content and smaller particle sizes.

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