Sol-gel synthesis and photocatalytic activity of biomimetic calcium manganese oxide catalysts

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Abstract. The water contaminations by dye residues are increasingly becoming serious concerns worldwide due to dye toxicity and persistent characteristics. Manganese oxide-based catalysts having similar structures with manganese compounds found in nature (biomimetic) have been considered as a very promising and effective photocatalyst for the degradation of organic pollutions in wastewater. This paper focuses on the synthesis of calcium manganese oxide catalysts from the octahedral layered birnessite-type manganese oxide and calcium carbonate via sol-gel method with citric acid as the complexing agent. The as-synthesized oxide was then tested as a photocatalyst for the degradation of methylene blue (MB) dye. The calcium manganese oxides prepared by the two different mole ratios of CaCO3/MnO2 resulted in the similar crystallinity and crystal phases but difference in the crystal sizes. The photocatalytic activities of the prepared calcium manganese oxides for the degradation of methylene blue are compared to that of the calcium manganese oxide prepared from tunnel cryptomelane-type manganese oxide. Both the calcium manganese oxides prepared from the different manganese oxide phases show the remarkable performance for the photocatalytic degradation of methylene blue after 10 minutes of reaction times. The birnessite-prepared calcium manganese oxide displays slightly higher photocatalytic performance than cryptomelane-prepared calcium manganese oxide.

1. Introduction
Water pollution due to organic contaminants has become a serious concern all over the world. The organic pollutants containing residual dyes have an inverse effect to environments and human health because they are toxic, mutagenic, and carcinogenic. They are also highly visible, persistent, and non-biodegradable since they have a polymeric structure. The different strategies have been applied to degrade this refractory material such as biological, physical, and chemical methods. The biological methods have been considered to be the most widely applied and economical to remove the contaminants but suffers from the length of time used for the process. In addition, the method cannot be applied if the pollutants are toxic to the microbes used in the process. Although the physical method such as adsorption is also widely used to treat organic wastewater containing dyes and is simple and effective, this method creates additional problems due to the transfer of the pollutant to the adsorbent.
The advanced oxidation processes (AOPs) are perceived as highly promising pathways to treat the recalcitrant materials such as dyes by using the strong powerful hydroxyl radical -OH as the main oxidant. The hydroxyl radical, whose standard redox potential is 2.8 V, immediately attack and non-selectively degrade most organic contaminants. Hydroxyl radicals react via hydrogen abstraction, electrophilic addition to double bond, and electron transfer reactions.

The wide ranges of technique are applied to generate hydroxyl radical in the AOP method such as Fenton and related process, electrochemical oxidation, wet air oxidation, photocatalytic reaction, and so forth. Photocatalytic reactions are widely used for the treatment of dyes and use photocatalysts, which usually semiconductor materials using light of energy greater than the semiconductor band-gap to promote an electron from valence band to the conduction band. This leaves an electron vacancy or hole in the valence band. The hole is highly oxidative and immediately reacts with organic molecules such as dyes adsorbed in the photocatalyst surface. The hole also reacts with adsorbed water molecules, generating hydroxyl radicals that in turn degrade organic molecules.

Manganese oxides-based catalysts have been reported as an active photocatalyst for the abatement of organic wastewater. Among a wide range of manganese oxides photocatalysts, calcium manganese oxides have been regarded as biomimetic redox catalysts because they are ubiquitous in the earth and have structural similarities to the µ-oxo-Mn₄Ca cluster in the Photosystem-II protein used for the water splitting in natural photosynthesis. The calcium manganese oxide-based perovskite structures are reported as an excellent candidate for photocatalysts [1]. Several studies have succeeded in synthesizing CaMnO₃ using the solid reaction method with CaCO₃ and MnCO₃ as starting material [2]. The previous synthesis of perovskite based-manganese oxides has been conducted by sol-gel and ceramic methods with different starting materials. The cryptomelane-type manganese oxide has been used to synthesize calcium manganese oxide with distinctive properties. It is believed that the different crystal structures of manganese oxides may have the profound effect on the resulting calcium manganese oxides. The manganese oxides with different crystal structures and properties have been successfully synthesized by sol-gel method [3–6], ceramic method [7], and precipitation method [8–10].

In the present study, calcium manganese oxide catalysts were synthesized by sol-gel method via the reaction between birnessite-type manganese oxide with calcium carbonate. The manganese oxide was first synthesized by ceramic method using potassium permanganate and citric acid, which is then reacted with calcium carbonate with two different mole ratios. The use of the birnessite-type manganese oxide as the starting material for the synthesis of calcium manganese oxide-based perovskite has never been reported previously and would play a crucial role in the production of calcium manganese oxides with distinctive structure and properties. The as-synthesized calcium manganese oxide materials are applied as a photocatalyst for the degradation of methylene blue dye.

2. Experimental

2.1. Materials
KMnO₄, glucose, HCl, CaCO₃, citric acid, and HNO₃ were all purchased from Merck (Germany), without any further purification.

2.2. Synthesis of MnO₂
The octahedral layered manganese oxide was prepared via a solvent-free method [6]. The mole ratios of KMnO₄ and glucose are set to 3:1 and grounded into a fine powder. The resulting fine-powder of KMnO₄ and glucose were then mixed and ground in one mortar. The mixture was calcined at 700°C for 7 hours. The final product was cooled up to room temperature, washed using HCl 0.1 M and distilled water. The black product was dried at 110°C. As compared, the octahedral tunnel cryptomelane was synthesized using the method reported in the literature [3].
2.3 Synthesis of calcium manganese oxide

The oxide was prepared via sol-gel method. The appropriate amount of CaCO₃ and MnO₂ are shown in Table 1. The fine-powder was dissolved in 200 mL HNO₃ and stirred for ± 3 minutes. The mixture was added 25.2168 g citric acid and stirred until 7 hours. The solution is heated at 100°C to gel, dried at 110°C until 12 h and calcined at 270°C (2h). The product was calcined at 700°C.

| Mole ratio | Amount (g) |
|------------|------------|
| CaCO₃      | 3:4        | 1.50       |
| MnO₂       | 3:4        | 1.74       |
| CaCO₃      | 1:1        | 2.50       |
| MnO₂       | 1:1        | 2.17       |

2.4 Characterization

X-ray powder diffraction (XRD) was performed on a Shimadzu 700 Maximax X-ray diffractometer operating at 40 kV and a current of 30 mA with Cu Kα radiation (X = 1.54060 Å⁻¹). The data were collected with scan speed 2° per minute in 2θ, from 2θ = 10° to 90°.

2.5 Photocatalytic activities

The photocatalytic activities of the sample were evaluated via the photocatalytic oxidation of 30 ppm MB under UV light irradiation. A 250 watt (Philips) UV lamp (350-400 nm) was used as a light source. Prior to illumination, 50 mg catalyst was added to the MB solution (100 mL, pH 2). The degradation efficiency of MB was analyzed using a UV-Vis spectrometer. Peaks were observed to be present at 660 nm and were assigned as the absorption, which was indicative of the degradation of MB.

3. Result and discussion

The synthesis of calcium manganese oxide in this study used nitric acid as the solvent and citric acid as the chelating agent. X-ray diffraction was used to characterize the phase, purity, crystallinity, and the size crystal of the as-synthesized manganese oxide and the corresponding calcium manganese oxides. Figure 1 (a) shows the XRD patterns of the as-synthesized manganese oxide, which indicates the presence of peaks at 2θ: 12.53; 25.2; 35.2 ; 37.3; 39.88; 42.4; 40; 65.5 corresponding of diffraction planes of (001), (002), (201), (111), (201), (112), (113) and (321), respectively. The oxide belongs to layered manganese oxide, birnessite (JCPDS 80-1098). The products of the reaction between calcium carbonate and birnessite with the two different mole ratios (3:4 and 1:1) are the calcium manganese oxides (JCPDS 076-1133). The XRD patterns of the calcium manganese oxides are shown in figure 1 (b) with a strong peak at 2θ of 30° due to the presence of un-reacted CaCO₃. The XRD results suggested that the calcination temperature at 700°C was not high enough to decompose and convert fully CaCO₃ into CaMnO₃, which is typical stoichiometric calcium manganese oxide perovskite. The different mole ratios (3:4 and 1:1) used in this experiment merely resulted in the difference in peak intensity due to CaCO₃ indicating the difference in calcium content in the as-synthesized calcium manganese oxides. Kim et al. (2014) synthesized CaMnO₃ and oxygen-deficient perovskite Ca₂Mn₂O₅ from CaCO₃ and manganese nitrate using citric acid as the complexing agent via sol-gel method [11]. The product CaMnO₃ was then calcined at 900°C to generate crystalline CaMnO₃, which was further reductive annealing to generate Ca₂Mn₂O₅. The Ca₂Mn₂O₅ perovskite displayed higher oxygen evolution reaction than that CaMnO₃ perovskite due to the presence of oxygen vacancies. Zhang et al. (2016) also indicated that the presence of an oxygen vacancy in the Ca₂Mn₂O₅ induced enhancement of photochemical water oxidation compared to CaMnO₃ [12]. In this study, the
perovskite CaMnO$_3$ was first synthesized by using the birnessite-type manganese oxide prepared from sol-gel method. Farag et al. (2017) prepared CaMnO$_3$ with distinctive properties from the reaction of CaCl$_2$ and MnCl$_2$ using sol-gel method with the increased electrical conductivity in higher temperatures [2]. Gagrani et al. (2020) studied the different calcium manganese oxide nanoparticles (Ca$_3$Mn$_3$O$_8$, CaMn$_2$O$_4$, and CaMnO$_3$) used as photocatalysts for the degradation of the dye [1]. The photocatalytic activities of as-prepared calcium manganese oxides increase in the order Ca$_3$Mn$_3$O$_8$ $<$ CaMnO$_3$ $<$ CaMn$_2$O$_4$. It is believed that the presence of oxygen vacancy in certain perovskite is responsible for the enhancement of their catalytic activity.

Figure 1. XRD patterns of birnessite MnO$_2$ (black-line), calcium manganese oxides CaMnO$_3$ 3:4 (blue-line), and calcium manganese oxides CaMnO$_3$ 1:1 (green-line).

The crystal sizes of the birnessite-type manganese oxide and the corresponding calcium manganese oxides with the different mole ratios are shown in table 2. The birnessite displayed much lower crystal size compared to the calcium manganese oxides. The two calcium manganese oxide synthesized with the different mole ratios indicated the marked difference in the crystal sizes. The one synthesized with the 3:4 mole ratio resulted in the perovskite with the much higher crystal size than that of 1:1 mole ratio calculated by Scherrer equation shown in table 2. Thus, the difference in mole ratios of starting
materials play a crucial role in the production of the difference crystal sizes of calcium manganese oxide.

Figure 2 displayed the catalytic activities of the calcium manganese oxide as a photocatalyst for the degradation of MB at the different pH ranges. The results indicated that the working pH plays a crucial role in the degradation of MB using the calcium manganese oxide as the photocatalyst. The moderate acidic condition (pH 5) and basic pH (pH 8) displayed less than 60% of MB degradation after 120 minutes of degradation reaction. On the other hand, the highly acidic condition (pH 2) resulted in considerable degradation of MB even after 10 minutes of degradation reaction.

Figure 3 displayed the MB degradation using three different photocatalysts, the birnessite-type manganese oxide, the calcium manganese oxide prepared from birnessite with the ratio of 3:4 (CaCO$_3$/birnessite) and the calcium manganese oxide prepared from cryptomelane-type manganese oxide with the ratio of 3:4 (CaCO$_3$/cryptomelane). It is obvious (inset in figure 3) that the as-synthesized calcium manganese oxides prepared from two different crystal structures of manganese oxides show the much higher catalytic activities than that of the MnO$_2$ (birnessite) at the same experimental condition. The calcium manganese oxide catalysts prepared from different crystal structures also resulted in the difference in catalytic performance. The calcium manganese oxide prepared from layered birnessite-type manganese oxide shows slightly higher catalytic activity than that prepared from tunnel cryptomelane-type manganese oxide.

**Table 2.** Average crystal sizes of birnessite and calcium manganese oxide.

| Samples                      | Average crystal sizes (nm) |
|------------------------------|----------------------------|
| Birnessite                   | 30.273                     |
| Calcium manganese oxides 3:4 | 149.035 x 10$^3$           |
| Calcium manganese oxides 1:1 | 100.422                    |

![Figure 2](image-url)  
**Figure 2.** Degradation of methylene blue (MB) by the calcium manganese oxide at pH 2 (red line), pH 5 (blue line), and pH 8 (green line).
Figure 3. Degradation of MB by MnO$_2$ (blue line), calcium manganese oxide prepared via 3:4 mole ratio of CaCO$_3$/birnessite (red line), and calcium manganese oxide prepared via 3:4 mole ratio of CaCO$_3$/cryptomelane (green line). The inset shows the difference in the percentage of degradation (magnification).

4. Conclusion
The calcium manganese oxides with perovskite structure have been successfully synthesized from calcium carbonate and birnessite-type manganese oxide with two different mole ratios. The oxides have a similar crystal structure and crystallinity but difference in the crystal size. The as-synthesized calcium manganese oxide displayed much higher catalytic activity as photocatalysts compared to birnessite-type manganese oxide for the degradation of methylene blue. The working pH wastewater seems to play a key role for the degradation of MB dye.

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