Catalytic Activity of Biomorphic α -MoO₃ in the Degradation of Methyl Violet Dye

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Abstract

A network of fibers comprising orthorhombic molybdenum trioxide (α -MoO₃) crystals were synthesized using paper as template via a biomorphic approach. The template was completely removed by annealing the sample at 600°C for 5 min. Monoclinic MoO₃ was formed and consequently converted into orthorhombic α -MoO₃ after prolonged annealing. Three milligrams of the biomorphic α -MoO₃ could degrade up to 90% of a methyl violet aqueous solution with a concentration of 20 mg/L under normal visible light. The size of the α -MoO₃ grains and the porosity of the biomorphic sample affected catalytic performance.

Key words: biomorphic; calcinations; chemical properties; functional applications; microstructure-final

Introduction

ORTHORHOMBIC MOLYBDENUM TRIOXIDE (α -MoO₃) was reported to have photocatalytic enhancement in oxidative dehydrogenation of alcohol (Ono *et al.*, 1986) and oxidation of hydrocarbons (Marcinkowska *et al.*, 1984). It is known that the increase in surface area of the catalyst would further enhance the catalytic activities. Thus, porous α -MoO₃ in the forms of fibers (Niederberger *et al.*, 2001) and mesostructured toroids (Antonelli and Trudeau, 1999) had been studied. Recently, MoO₃ nanorod was found to have superior catalytic ability in decomposing toluidine blue O dye under visible light (Shakir *et al.*, 2010). In this work, a self-support porous α -MoO₃ structure has been developed by using a biomorphic method. In the sample, the original microstructure of the template is retained. Various biotemplates such as paper (Fukahori *et al.*, 2007; Koga *et al.*, 2009; Li *et al.*, 2008), silk (Li *et al.*, 2010), sea wool sponge (Tang *et al.*, 2007), and egg shell membrane (Li *et al.*, 2009) had been used to synthesize biomorphic materials. The products are self-support and usually possess high porosity with hierarchical microstructures. They are lightweight and have high permeability, which can be used in various industrial applications (Fan *et al.*, 2009; Wang *et al.*, 2007).

Methyl violet (MV) is a water-soluble cationic triphenyl-methane dye. It is stable in most of the common oxidizing agents. It is reported that its degradation can be achieved by using MoO₃ and TiO₂ mixture under ultraviolet (UV) light (Tchatchueng *et al.*, 2009). Upon receiving UV radiation, MoO₃ enhances the production of hydroxyl radical $\cdot$ OH from the water. They would participate in a fast nonselective re-

action with the organic pollutant to give dehydrogenated or hydroxylated intermediates, and that would in turn undergo mineralization. Thus, MV would be transformed into CO₂, water, and inorganic ions. Previously, we reported the fabrication of porous α -MoO₃ by using paper template (Li *et al.*, 2008). In this work, α -MoO₃ biomorphic products fabricated under different synthetic conditions have been characterized. Their photocatalytic ability to degrade MV under UV and visible light is being evaluated and compared.

Experimental Procedures

In a typical preparation (Li *et al.*, 2008), the precursor ammonium molybdate tetrahydrate [(NH₄)₆·MoO₃·4H₂O; Ajax Finechem] was dissolved into distilled water to make a 0.2 M solution. The 1 cm × 1 cm paper templates (prepared from an M-fold paper towel; Sunlight) were soaked in the precursor solution for 24 h before drying at 60°C in air for 2 h. The dried infiltrated samples were annealed in air at 600°C for different durations from 10 s to 1 h.

The crystalline structures of products were identified by using X-ray diffractometry (XRD) with a diffractometer (Huber) and an X-ray generator (RU-300; Rigaku). To determine the components in the final product, Fourier transform infrared (FTIR) spectra of the samples were obtained by the standard KBr pellet approach in using an FTIR spectrometer (Nicolet 670; Thomas Nicolet). The morphology of the product was studied by scanning electron microscopy (SEM, 1450VP; LEO). The thermal properties of the raw paper, the precursor, and the infiltrated template were studied by differential thermal analysis (DTA; Perkin-Elmer) and thermogravimetric analysis (TGA; Perkin-Elmer).

The evaluation of the photocatalytic performance of the biomorphic product was conducted according to its effects on the degradation of a 20 mg/L MV solution under UV (15W,

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Philips, UVC: 100–280 nm) and visible light (3W, 6500K: peak wavelength at about 450 nm) irradiation. During the evaluation, 3 mg of the biomorphic product was put into 50 mL of the dye solution. The solution was placed at a distance of 20 cm under the irradiation lamp and being stirred continuously by a digital magnetic stirrer (RSH-1D, Rexim) at a speed of 300 rpm. The light source was turned on when the stirring started. About 1 mL of treated solution was then collected at some regular time intervals. The residue in the sample solution was separated by a centrifuge (Mikro 120, Hettich) rotating at 10,000 rpm for 20 min. The absorption spectra of the sample solutions were recorded by a UV-Visible spectrophotometer (U3501; Hitachi). Based on the Beer's Law (Beer, 1852), we expected that the absorbance of light in the range of 10^{-4} to 2 was linearly dependent on the concentrations of MV. Since the degradation of MV is related to the decrease in MV concentration, it can be expressed by the absorbance of the light directly; that is, $\frac{A_0 - A_t}{A_0} \times 100$, where A_0 and A_t are the light absorbance by the solution under a light at 580 nm at initial and after time t , respectively. This evaluation was also performed with a commercial MoO₃ powder (99.5% International Laboratory), P25 powder (99.5% Sigma Aldrich), and ZnO powder (99.8% Merck) for comparison.

Results

Thermal properties

Figure 1a shows the result of the TGA analysis of the (NH₄)₆·MoO₃·4H₂O precursor. The TGA curve indicated that there were four stages in the change of mass in different thermal ranges of 120°C–140°C, 230°C–250°C, 320°C–340°C, and 790°C–800°C. This result was consistent with the DTA results shown in Fig. 1b. In the DTA curve of the precursor, four endothermic peaks at 138°C, 237°C, 341°C, and 793°C were observed. Based on the TGA and DTA results, we proposed that the first three stages corresponded to the following reactions (Shaheen and Selim, 2000):

FIG. 1. (a) Thermogravimetric analysis and (b) DTA curves of the precursor (NH₄)₆·Mo₇O₂₄·4H₂O, and DTA curves of (c) the raw and (d) the infiltrated paper template. DTA, differential thermal analysis.

The above reactions depicted that the decomposition of the (NH₄)₆·MoO₃·4H₂O precursor involved the removal of H₂O and NH₃ before it was finally decomposed to MoO₃. The final DTA endothermic peak at about 790°C corresponded to the melting point of MoO₃ (Aylward and Findlay, 1974). Beyond this point, a sharp decrease in mass was observed. It was probably due to the vaporization of the MoO₃ as its vapor pressure increased rapidly with temperature (Lange, 2005). The amounts of mass change of the samples related to these chemical reactions are listed in Table 1. Meanwhile, they were calculated according to Reactions (1)–(3) with the mass before reaction as denominator. We found that the mass loss in the reactions from the TGA measurements is in good agreement with the theoretical estimation.

Figure 1c and 1d shows the DTA curves of the raw paper template and the chemical-infiltrated template. The paper template completed its decomposition at 600°C. During 300°C–500°C, its constituents were broken down into carbon, oxidized, and released in gaseous form, as confirmed by the exothermic peaks shown in Fig. 1c. In Fig. 1d, the three endothermic peaks with the dips at 138°C, 233°C, and 316°C corresponded to the decomposition of the (NH₄)₆·MoO₃·4H₂O precursor.

Phases and compositions

Figure 2 shows the FTIR curves of the MoO₃ products sintered at 600°C for different durations. All of the curves contained an absorption peak that was centered at around 993 cm⁻¹. It became sharper as the annealing duration increased. This peak corresponded to the Mo=O unresolved stretching vibrations of α-MoO₃ (Seguin *et al.*, 1995). Thus, it confirmed the existence of α-MoO₃, even in sample after a very short sintering. The FTIR curves also contained two absorption peaks of which their peak positions shifted from 644 to 600 cm⁻¹, and from 864 to 876 cm⁻¹ with the annealing duration. This shift could be explained by the overlapping of the absorption bands of α-MoO₃ and monoclinic MoO₃ (β-MoO₃). The α-MoO₃ had two wide absorption bands with maxima 876 cm⁻¹ and 600 cm⁻¹ while the β-MoO₃ also had similar bands centered at 843 and 640 cm⁻¹ (Seguin *et al.*, 1995). When these two phases coexisted, the two absorption

TABLE 1. PERCENTAGE OF MASS LOSSES OF THE PRECURSOR IN INCREASING TEMPERATURE

Thermal step	Temperature range °C	Calculated mass loss%	Theoretical mass loss%	Proposed formulae
1	120–140	6.78	6.67	1/5(NH ₄) ₄ ·Mo ₅ O ₁₇
2	230–250	4.46	4.42	1/4(NH ₄) ₂ ·Mo ₄ O ₁₃
3	320–340	7.00	7.37	MoO ₃
4	790–800	Unknown	Unknown	MoO ₃

FIG. 2. Fourier transform infrared spectra of the products after sintering at 600°C in air for 10 s, 20 s, 1 min, 5 min, 15 min, and 60 min, and the commercial MoO₃ powder without any treatment.

bands could be centered in the range of 843–876 cm⁻¹ and 600–640 cm⁻¹, respectively. In addition, the monoclinic phase would be converted into orthorhombic phase that was more thermodynamically stable at high temperature or in prolonged heating. As a result, the peaks would move toward to those of the orthorhombic phase after 15-min sintering, indicating the complete conversion of the monoclinic phase to the orthorhombic phase. Simultaneously, the intensities of both peaks increased as the sintering process lasted. This corresponded to the anisotropic growth of the crystalline structure. It is worth noting that the spectra of the sample prepared at 600°C for 1 h were similar to that of the sample prepared at 500°C for 1 h.

On the other hand, the broad absorption band from 1030 to 1650 cm⁻¹ was observed in the spectra of the sample annealed for <5 min. It was due to the superposition of several contributions from the bonds between carbon, hydrogen, and nitrogen (Lazar *et al.*, 2005; Yang *et al.*, 2007). They were originated from the decomposition of cellulose and the precursor in the samples. After 5 min of heating, this absorption band disappeared, which indicated that the residues from the cellulose structure had been completely removed. These results were consistent with the XRD results (not shown).

Surface morphology

The morphology of sample was retained after annealing, only that it was slightly shrunk. Figure 3 shows a series of SEM images of the products prepared at 600°C in air for different annealing durations. While most of the products retained their own fiber structure with rough surface, some grain structures started to appear on the fibers after 10 s of annealing (Fig. 3a). The distinguishable grains were found on the surface after being annealed for 60 s (Fig. 3b). These grains were about 2–3 μm in length, and most of them were plate-like structure owing to the anisotropic growth of the α-MoO₃ crystals. Fig. 3c and 3d showed the morphologies of the grains on the fiber in the samples annealed for 5 and 60 min, respectively. The size of the grains increased in prolonged annealing. They reached to a size of 5 μm after 1 h of heat treatment. Simultaneously, their shapes evolved toward the inherent lamellar structure.

The surface morphology of the sample prepared at 500°C for 1 h was similar to that of the 600°C-prepared sample.

However, its grain size was about 0.5–2 μm (Fig. 3e), which was much smaller than that of the 600°C-prepared sample. The pores on the fiber were also smaller. On the other hand, the size of the grains ranged from 1 to 10 μm in the commercial MoO₃ powder (Fig. 3f).

Degradation of MV under visible light irradiation

The as-prepared biomorphic MoO₃ was used to degrade the 20 mg/L MV dye aqueous solution. To study the effects of sample annealing on the catalytic performance, we had selected and used the samples that were prepared at 500°C and 600°C. In these samples, the paper template had been completely removed after 1 h of annealing.

Figure 4 shows the degree of degradation (in%) of the MV solution under different durations of visible light in the presence of the sample prepared at 500°C (top curve), and at 600°C (second from top). It was observed that the curve corresponding to the 500°C products was always above that of the 600°C product. This suggested that the 500°C product had better catalytic ability, especially at the initial stage of the catalysis. After 1 h, about 50% of MV was degraded by the 500°C sample, while the value for 600°C sample only dropped by 31%. Note that, the initial degradation rate also included the adsorption of MV on the surface of catalysts. It was reported that cationic dyes could be adsorbed much more than anionic dyes on the surface of catalysts before decomposition (Baran *et al.*, 2008b). The adsorption process consisted of three steps (Dogan and Alkan, 2003). Before the dye was adsorbed and anchored at the sites of the catalytic product on the surface of the cellulose fibers, it had to diffuse across a boundary layer. The 600°C product experienced a further rapid grain growth thus the number of grains was less. As a result, the anisotropic grown larger α-MoO₃ grains in the sample had less total surface area hence weakened the catalytic ability. In contrary, the 500°C sample had smaller grains. It remained quite porous and resembled to that of the paper template, and keeping the unique catalytic ability with the fibrous structure. Its grains were dispersed on the fiber, and enhancing the adsorption ability than that of the commercial powder. After 7 h of irradiation, the degree of degradation by the 500°C product reached 92% and that by the 600°C products was only 74%. As reported, the surface adsorption by the catalyst would play an important role in photocatalysis even as a prerequisite condition in some cases (Machado *et al.*, 2003; Minero *et al.*, 1992). The superior catalytic ability of our products resulted in the efficient degradation of MV in the aqueous solution.

Figure 4 also shows the degradation curves of MV solution in the presence of commercial MoO₃ powder, P25 powder, ZnO powder, pure MV, and pure MV covered by Al foil under different durations of visible light irradiation. The degree of degradation of these samples remained below 15% throughout the irradiation process. It implied that the catalytic ability of the commercial MoO₃ product, P25, and ZnO was rather low. The MV itself could not be directly decomposed under visible light irradiation. When comparing the results obtained from the biomorphic samples under visible and UV (not shown) light irradiation, the trend of catalytic performance was similar, but the catalytic ability of the biomorphic samples would be more effective under visible light irradiation. It is worth noting that MV could be directly decomposed under UV irradiation. About 66% of MV was

FIG. 3. Scanning electron microscopy images of (a), (b), (c), and (d) the products after being annealed at 600°C in air for 10 s, 1 min, 5 min, and 1 h, respectively; (e) the products annealed at 500°C for 1 h; and (f) the commercial MoO_3 powder without any treatment.

FIG. 4. Degree of degradation of the MV dye under different duration of visible light irradiation: degradation of MV dye mixed with a 500°C annealed MoO_3 (◆), 600°C annealed MoO_3 (■), commercial MoO_3 (△), P25 (○), and ZnO (+); degradation of pure MV (×) and that covered with Al foil (*). MV, methyl violet.

decomposed after 7 h of UV irradiation. However, when the biomorphic samples were added in MV and under visible irradiation, the efficiency was much higher, which would be more useful in practical applications.

There are several important operational parameters affecting the degradation process. The factors are pH value, amount of catalyst, initial concentration of pollutant (MV dye, in our case), additives, and operation temperatures (Rauf and Ashraf, 2009). In this work, the performance of our biomorphic MoO_3 product was compared with commercial MoO_3 powder under the similar settings. Figure 3 shows that the biomorphic MoO_3 possessed an interweave structure with porous fibers after annealing. This porous structure was responsible for the enhancement of the catalytic ability. This not only provided more contact surface area for the MV, but also for the irradiation light (Ibhadon *et al.*, 2008). Thus more MV could be involved in the reaction when using biomorphic MoO_3 under irradiation than that using the commercial MoO_3 powder. On the other hand, the turbidity of the solution might induce the screening effect (Baran *et al.*, 2008a), which would limit the effectiveness of the catalyst. Even under the same weight of biomorphic MoO_3 and commercial MoO_3 , their solution turbidity was not the same because of the shapes of particles. During the catalysis process, the biomorphic MoO_3 might maintain their fiber structures while the commercial MoO_3 powder dispersed in the dye solution and formed colloid. The formation of colloid would significantly increase the turbidity of the solution, resulting in a decrease in light penetration and the photoactivated volume (Ibhadon *et al.*, 2008). This would have a weakening effect while using powder form in photocatalytic activity under irradiation.

Conclusions

The orthorhombic α - MoO_3 with the porous interweave paper structure had been further evaluated under different synthetic conditions. It was found that the template could be completely removed after annealing at 600°C for 5 min. Monoclinic MoO_3 was found in the samples with short annealing duration. Prolonged annealing could convert them into orthorhombic-phase α - MoO_3 . Moreover, the grain size of α - MoO_3 increased from 2 to 5 μm during 1 h of annealing. The biomorphic product degraded more than 90% of the MV in water within 7 h under UV and visible light irradiation. In addition, the biomorphic products showed better catalytic properties under visible light irradiation, and those samples prepared at 500°C for 1 h were better than that prepared at 600°C.

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Author Disclosure Statement

No competing financial interests exist.

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