Research Article

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Morphology evolution and quantitative analysis of β-MoO₃ and α-MoO₃

1 Introduction

Transition metal oxides, such as V₂O₅, CrO₃, WO₃, and MoO₃, show several types of complex structures, formed mainly by two- or three-dimensional frameworks of octahedral or tetrahedrals [1–3]. Among these materials, MoO₃ has been recognized as a promising material for a rapidly increasing number of applications such as chemical synthesis, petroleum refining, gas sensor devices, photoluminescence, photochromism, electrochromism, smart windows, catalysis, and display devices [4]. MoO₃ has different structures that can be divided into four polymorphs [5–9]: (1) thermally stable orthorhombic phase, α-MoO₃; (2) metastable monoclinic phase, β-MoO₃; (3) metastable phase at high-pressure conditions, β’-MoO₃; and (4) hexagonal phase, h-MoO₃. In all these MoO₃ structures, the MoO₆ octahedron is the primary unit, and its arrangement results in differences in the structures. The two most commonly studied polymorphs are α-MoO₃ and β-MoO₃; however, β-MoO₃ is believed to possess more novel and enhanced properties in catalysis and electrochemical applications when compared with α-MoO₃ [10]. It is regrettable that the synthesis of pure β-MoO₃ is usually difficult at ambient conditions [11,12], whereas mixtures of α-MoO₃ and β-MoO₃ are much easier to produce [13–16]. To make full use of the mixtures of α-MoO₃ and β-MoO₃ that are usually produced, it is necessary to quantitatively analyze the mixtures and evaluate the amount of β-MoO₃, which may be an evaluation index, and to better understand the properties of the mixtures.

X-ray diffraction (XRD) is widely used for the quantitative analysis of geological samples [17,18]. Hillier [19] conducted the accurate quantitative analysis of clay and other minerals in sandstones by XRD using the relative intensity ratio (RIR), which gave accuracy within ±3 mass % at the 95% confidence level. Vaverka and Sakurai [20] investigated the composition of steelmaking slag, and the amount of free lime was determined by the X-ray powder diffraction and the standard addition method. Recently, Shu et al. [21] adopted the quantitative XRD analysis to calculate the ratio of mass percentages of reactant...
(CaWO<sub>4</sub>) and product (W) from the intensities of the strongest peaks, from which fractional conversion was calculated, thus enabling the kinetics of reduction of CaWO<sub>4</sub> by Si to be successfully described.

Although many methods have been used for quantitative determination of different sample mixtures, XRD is nondestructive, and the samples can be used for other chemical analyses. However, there are no specific reports on the quantitative relationship between α-MoO<sub>3</sub> and β-MoO<sub>3</sub>. In the present study, the quantitative XRD analysis was used to determine the quantitative relationship between α-MoO<sub>3</sub> and β-MoO<sub>3</sub> and to evaluate the amount of β-MoO<sub>3</sub> in mixtures. The morphology evolution from β-MoO<sub>3</sub> (spherical) to α-MoO<sub>3</sub> and the possible decomposition mechanism of β-MoO<sub>3</sub> were also elucidated.

2 Materials and experimental procedures

2.1 Raw materials (β-MoO<sub>3</sub>)

Pure ultra-fine β-MoO<sub>3</sub> (green), prepared by the method of sublimation [22,23], was used. The X-ray diffraction pattern of the sample is shown in Figure 1. The intensity of the strongest peak for this sample was located at 2θ = 23.04° with a reflection of (011). Field-emission scanning electron microscopy (FE-SEM) images of samples at different magnifications are shown in Figure 2. All powders appeared to have a spherical shape and fine crystalline size although their size was nonuniform.

2.2 Preparation of α-MoO<sub>3</sub>

The transformation temperature from β-MoO<sub>3</sub> to α-MoO<sub>3</sub> obtained from the previous literature [9,10,15] is around at 673–723 K. Therefore, in the present study, α-MoO<sub>3</sub> was prepared by roasting β-MoO<sub>3</sub> at 773 K in the air; the higher roasting temperature was used to complete the transformation within a short time and to control the MoO<sub>3</sub> vapor. After confirming that the prepared products were all pure α-MoO<sub>3</sub>, samples were prepared for morphology observation and used to synthesize mixed MoO<sub>3</sub> specimens.

2.3 Preparation of mixtures of β-MoO<sub>3</sub> and α-MoO<sub>3</sub>

To identify the quantitative relationship between β-MoO<sub>3</sub> and α-MoO<sub>3</sub>, standard mixtures with a mass ratio (W) of β-MoO<sub>3</sub> to the total mass of β-MoO<sub>3</sub> and α-MoO<sub>3</sub> that varied from 0 to 1 were prepared, i.e.:

\[
W = \frac{m_{\text{β-MoO}_3}}{m_{\text{β-MoO}_3} + m_{\text{α-MoO}_3}},
\]

where W was in the range of 0–1.

After carefully weighing and mixing β-MoO<sub>3</sub> and α-MoO<sub>3</sub> based on the specified mass ratio, the mixtures were homogenized for 30 min by milling in an agate mortar and then subjected to the quantitative XRD analysis.

The total mass of mixtures of β-MoO<sub>3</sub> and α-MoO<sub>3</sub> was fixed at 500 mg. The morphologies of β-MoO<sub>3</sub> and α-MoO<sub>3</sub> were observed by FE-SEM (ZEISS SUPRA 55, Oberkochen, Germany). Phase compositions were analyzed by the XRD (Model TTR III, Rigaku Corporation, Japan) using Cu Kα-filtered radiation with a scanning speed of 6°/min and scanning step of 0.02°.

3 Results and discussion

3.1 Crystalline modification and morphology evolution

Figure 3 shows the XRD pattern of the roasted products. It can be seen that pure α-MoO<sub>3</sub> can be prepared by roasting β-MoO<sub>3</sub> at 773 K in air. In addition, the color was converted from green to white, which demonstrated that the transformation from β-MoO<sub>3</sub> to α-MoO<sub>3</sub> is
photochromic. The intensity of the strongest peak of $\alpha$-MoO$_3$ was located at $2\theta = 27.36^\circ$ with a reflection of (021). FE-SEM micrographs of the as-prepared $\alpha$-MoO$_3$ at different magnifications are shown in Figure 4. The morphologies of the as-prepared $\alpha$-MoO$_3$ no longer maintained the perfect spherical shape of $\beta$-MoO$_3$ as shown in Figure 2. Numerous spiral fringes formed around the oval $\alpha$-MoO$_3$ particles, which led to the formation of a layer structure.

The changes of the morphology and the color on conversion from $\beta$-MoO$_3$ to $\alpha$-MoO$_3$ indicated that the structures of the two phases were different. The crystal structure of $\beta$-MoO$_3$ shown in Figure 5 indicated that $\beta$-MoO$_3$ has a ReO$_3$-type structure in which the MoO$_6$ octahedrons only share corners with each other; each oxygen atom is shared by two octahedrons. In contrast, the crystal structure of $\alpha$-MoO$_3$ ($\alpha$-MoO$_{11}$O$_2$O$_3$) has a unique two-dimensional layer structure in which each layer is built up of MoO$_6$ octahedrons connected along $ac$-planes by common edges and corners to form zigzag rows and along $ab$-planes by common corners only, as shown in Figure 6. The interlayer interaction is weak and bounded in the $a$-axis direction by van der Waals forces. The transformation from $\beta$-MoO$_3$ to $\alpha$-MoO$_3$ is explained by the metal off-center displacement toward O$_1$ (and a little less toward O$_2$) centers, which is stabilized by an increase in covalence between the Mo and O atoms [24]. When heating $\beta$-MoO$_3$ at $T = 773$ K in air, the crystals mainly grow by coalescence with neighboring crystallites, driven by the heat treatment process, and the crystal has a tendency to form a layer structure, so the morphology of $\alpha$-MoO$_3$ has many spiral fringes.

### 3.2 Determination of quantitative relationship curves

Quantitative curves were determined by using the quantitative X-ray analysis based on RIR values [18]. The ratios of the mass of $\beta$-MoO$_3$ to the total mass of $\beta$-MoO$_3$ and $\alpha$-MoO$_3$ were calculated by the intensities of the strongest peaks for $\beta$-MoO$_3$ (peak (011)) and $\alpha$-MoO$_3$ (peak (021)). The XRD patterns of mixtures of $\beta$-MoO$_3$ and $\alpha$-MoO$_3$ at different mass ratios are displayed in Figure 7. The intensity of the strongest peak of $\beta$-MoO$_3$ gradually increased and that of $\alpha$-MoO$_3$ gradually decreased with the increase of mass ratio ($W$). The intensity changes are listed in Table 1. The values of $I_B/(I_B + I_a)$ had a strong linear relationship with $W$, as shown by the results presented in Figure 8. According to these results, it is easy to obtain the mass percent of $\beta$-MoO$_3$ in mixtures of $\beta$-MoO$_3$ and $\alpha$-MoO$_3$.

It is worth noting that another RIR method that measures the integrated peak intensity may have advantages and higher accuracy, but it is hard to accurately measure
Figure 4: Field-emission scanning electron micrographs of the as-prepared α-MoO₃ with different magnifications: (a) 15000 times; (b) 50000 times.

Figure 5: Crystal structure of β-MoO₃.

Figure 6: Crystal structure of α-MoO₃.

Figure 7: X-ray diffraction patterns of mixtures of β-MoO₃ and α-MoO₃. (a) Changes of intensity of strongest peaks of β-MoO₃ and (b) changes of intensity of strongest peaks of α-MoO₃ (W represents the ratio of the mass of β-MoO₃ to the total mass of β-MoO₃ and α-MoO₃).
In the present study, it was obvious that the integrated intensity and deal with interferences from other phases. In the present study, it was obvious that the strongest peak of $\beta$-MoO$_3$ had some overlap with the small peak of $\alpha$-MoO$_3$, as shown in Figure 7(a), so it would be difficult to accurately measure the integrated intensity. If we adopted the multiple-peak separation method, it would waste a lot of time and have no practical application. Moreover, although the application of the Riveted quantitative analysis has demonstrated its excellent potential for complex samples, the time required for data processing is very long and does little to popularize its application. In contrast, the RIR method proposed in this study (measurement of the intensity of the strongest peaks of different phases) exhibits its own advantages: it is easy, quick, time-saving, and has high accuracy. Therefore, this method can be widely applied for the rough quantitative analysis of mixtures of $\beta$-MoO$_3$ and $\alpha$-MoO$_3$. In the present study, both $\beta$-MoO$_3$ and $\alpha$-MoO$_3$ had a small particle size (spherical or oval shaped, respectively), and so preferred orientation was eliminated. If the preferred orientation existed, for example, if peaks with a reflection of (0k0) for $\alpha$-MoO$_3$ were stronger, this method could not be applied.

### Table 1: Changes of intensity of strongest peaks of $\beta$-MoO$_3$ and $\alpha$-MoO$_3$ for different mixture ratios.

| $W$ | 0   | 0.2 | 0.4 | 0.6 | 0.8 | 1   |
|-----|-----|-----|-----|-----|-----|-----|
| $I_\beta$ (a.u.) | 0   | 3,215 | 6,090 | 8,095 | 10,435 | 14,970 |
| $I_\alpha$ (a.u.) | 0 | 11,860 | 10,310 | 7,805 | 5,210 | 2,830 |
| $I_\beta / (I_\beta + I_\alpha)$ | 0 | 0.2377 | 0.4383 | 0.6084 | 0.7867 | 1 |

![Figure 8](image)

**Figure 8:** Plot of $I_\beta / (I_\beta + I_\alpha)$ as a function of $W$, the ratio of $\beta$-MoO$_3$ to the sum of $\beta$-MoO$_3$ and $\alpha$-MoO$_3$.

3.3 Decomposition of $\beta$-MoO$_3$

Before successfully preparing $\alpha$-MoO$_3$ by roasting $\beta$-MoO$_3$ at 773 K in air, another method was attempted, that is, roasting $\beta$-MoO$_3$ at 773 K in a highly pure Ar atmosphere (<5 ppm O$_2$); however, pure $\alpha$-MoO$_3$ could not be obtained. The corresponding XRD pattern is shown in Figure 9. The roasted products were very complicated and included not only $\alpha$-MoO$_3$ but also MoO$_2$ and Mo$_4$O$_{11}$. Here, Mo$_4$O$_{11}$ included two crystalline structures: orthorhombic Mo$_4$O$_{11}$ ($\alpha$-Mo$_4$O$_{11}$) and monoclinic Mo$_4$O$_{11}$ ($m$-Mo$_4$O$_{11}$). In addition, the color of the roasted products was dark or gray, rather than white, which is shown in Figure 10.

It has been reported that raw green $\beta$-MoO$_3$ may contain a number of oxygen vacancies [25–27]. When roasting $\beta$-MoO$_3$ in air, the samples have enough opportunity to interact with O$_2$. Maximum interaction between air and $\beta$-MoO$_3$ is important to ensure that the following chemical equilibrium is shifted to the left [28]:

$$2\text{MoO}_3 \xrightarrow{\text{Ar}} \text{2MoO}_3.x + x\text{O}_2$$

(2)

Oxygen exchange between the lattice and air has been investigated using isotope ($^{18}$O$_2$) labeling and Raman spectroscopy, which showed that gaseous O$_2$ is able to incorporate into the oxygen-deficient $\beta$-MoO$_3$ [29]. Therefore, perfect $\alpha$-MoO$_3$ can be prepared under air; however, when roasting $\beta$-MoO$_3$ in the argon atmosphere, no O$_2$ was provided to counter the oxygen-deficient $\beta$-MoO$_3$, which led to shifting of the chemical equilibrium (2) to the right and the production of low-valent molybdenum oxides, such as MoO$_2$ and Mo$_4$O$_{11}$. Once the oxygen defects were exhausted,

![Figure 9](image)

**Figure 9:** X-ray diffraction pattern of products obtained by roasting $\beta$-MoO$_3$ at 773 K in highly pure argon atmosphere.
the remaining components formed perfect α-MoO₃. Therefore, different molybdenum–oxygen compounds can coexist in the roasted products created under argon atmosphere conditions. The residue of α-MoO₃ also indicated that α-MoO₃ cannot be decomposed under the current experiment conditions, which was further supported by the data given in Figure 11. Figure 11 shows that whether using air or argon atmosphere, pure α-MoO₃ was the only phase present in the final roasted products, that is, pure α-MoO₃ cannot be decomposed, but β-MoO₃ can be easily decomposed into MoO₂ and Mo₄O₁₁. The corresponding decomposition correlations are summarized in Figure 12.

4 Conclusions

In the present study, the morphology evolution and the quantitative analysis of β-MoO₃ and α-MoO₃ were clarified. It was found that the morphology and color displayed obvious changes when β-MoO₃ was transformed into α-MoO₃. Spherical-shaped β-MoO₃ had the tendency to form oval-shaped α-MoO₃ when the heating temperature was around 773 K. XRD was used to quantitatively analyze the amount of β-MoO₃ in mixtures of β-MoO₃ and α-MoO₃. It was found that the mass of β-MoO₃ in the mixtures had a strong linear relationship with the intensities of the strongest peaks of β-MoO₃ and α-MoO₃. This provides an easy and convenient way to determine the amount of β-MoO₃ in MoO₃ mixtures. This approach may provide guidance for evaluation of the catalytic efficiency of MoO₃ mixtures. In addition, the decomposition of β-MoO₃ under argon gas atmosphere may result from the existing oxygen defects, which may contribute to the formation of MoO₂ and Mo₄O₁₁.

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