Research Article

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

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Abstract: The morphology evolution from monoclinic molybdenum trioxide (β -MoO₃) to orthorhombic molybdenum trioxide (α -MoO₃) and quantitative analyses of their mixtures were examined. It was found that the morphology (from spherical to elliptical shape) and color (from green to white) displayed obvious changes when β -MoO₃ converted to α -MoO₃ in ambient air at 773 K. The transformation from β -MoO₃ to α -MoO₃ resulted from a change of the internal crystalline structure. The mass percent of β -MoO₃ in MoO₃ mixtures showed an excellent linear relationship with the relative intensity ratio of the strongest peaks in X-ray diffraction patterns. This approach provides a simple and time-saving method to evaluate the amount of β -MoO₃, which is a promising material in catalyst and electrochemical applications, in such mixtures. This finding may provide guidance for the analysis of catalytic performance of MoO₃ mixtures. In addition, it was found that β -MoO₃ can be easily decomposed into suboxides such as MoO₂ and Mo₄O₁₁ in pure argon gas atmosphere. The possible decomposition mechanism of β -MoO₃ is discussed.

Keywords: morphology, molybdenum trioxide, quantitative analysis, decomposition

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

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(CaWO₄) and product (W) from the intensities of the strongest peaks, from which fractional conversion was calculated, thus enabling the kinetics of reduction of CaWO₄ 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 -MoO₃ and β -MoO₃. In the present study, the quantitative XRD analysis was used to determine the quantitative relationship between α -MoO₃ and β -MoO₃ and to evaluate the amount of β -MoO₃ in mixtures. The morphology evolution from β -MoO₃ (spherical) to α -MoO₃ and the possible decomposition mechanism of β -MoO₃ were also elucidated.

2 Materials and experimental procedures

2.1 Raw materials (β -MoO₃)

Pure ultra-fine β -MoO₃ (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 $2\theta = 23.04^\circ$ 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.

Figure 1: X-ray diffraction pattern of the studied β -MoO₃ sample.

2.2 Preparation of α -MoO₃

The transformation temperature from β -MoO₃ to α -MoO₃ obtained from the previous literature [9,10,15] is around at 673–723 K. Therefore, in the present study, α -MoO₃ was prepared by roasting β -MoO₃ at 773 K in the air; the higher roasting temperature was used to complete the transformation within a short time and to control the MoO₃ vapor. After confirming that the prepared products were all pure α -MoO₃, samples were prepared for morphology observation and used to synthesize mixed MoO₃ specimens.

2.3 Preparation of mixtures of β -MoO₃ and α -MoO₃

To identify the quantitative relationship between β -MoO₃ and α -MoO₃, standard mixtures with a mass ratio (W) of β -MoO₃ to the total mass of β -MoO₃ and α -MoO₃ that varied from 0 to 1 were prepared, i.e.:

$$W = \frac{m_{\beta\text{-MoO}_3}}{m_{\beta\text{-MoO}_3} + m_{\alpha\text{-MoO}_3}}, \quad (1)$$

where W was in the range of 0–1.

After carefully weighing and mixing β -MoO₃ and α -MoO₃ 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 -MoO₃ and α -MoO₃ was fixed at 500 mg. The morphologies of β -MoO₃ and α -MoO₃ 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 K α -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 -MoO₃ can be prepared by roasting β -MoO₃ at 773 K in air. In addition, the color was converted from green to white, which demonstrated that the transformation from β -MoO₃ to α -MoO₃ is

Figure 2: Filed-emission scanning electron micrographs of the studied β - MoO_3 sample with different magnifications: (a) 20000 times; (b) 50000 times.

photochromic. The intensity of the strongest peak of α - MoO_3 was located at $2\theta = 27.36^\circ$ with a reflection of (021). FE-SEM micrographs of the as-prepared α - MoO_3 at different magnifications are shown in Figure 4. The morphologies of the as-prepared α - MoO_3 no longer maintained the perfect spherical shape of β - MoO_3 as shown in Figure 2. Numerous spiral fringes formed around the oval α - MoO_3 particles, which led to the formation of a layer structure.

The changes of the morphology and the color on conversion from β - MoO_3 to α - MoO_3 indicated that the structures of the two phases were different. The crystal structure of β - MoO_3 shown in Figure 5 indicated that β - 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 α - MoO_3 (α - $\text{MoO}_{11}\text{O}_{22}\text{O}_{33}$) 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 β - MoO_3 to α - 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 β - 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 α - 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 β - MoO_3 to the total mass of β - MoO_3 and α - MoO_3 were calculated by the intensities of the strongest peaks for β - MoO_3 (peak (011)) and α - MoO_3 (peak (021)). The XRD patterns of mixtures of β - MoO_3 and α - MoO_3 at different mass ratios are displayed in Figure 7. The intensity of the strongest peak of β - MoO_3 gradually increased and that of α - MoO_3 gradually decreased with the increase of mass ratio (W). The intensity changes are listed in Table 1. The values of $I_\beta/(I_\beta + I_\alpha)$ 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 β - MoO_3 in mixtures of β - MoO_3 and α - 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 3: X-ray diffraction pattern of the as-prepared α - MoO_3 .

Figure 4: Field-emission scanning electron micrographs of the as-prepared α - MoO_3 with different magnifications: (a) 15000 times; (b) 50000 times.

Figure 5: Crystal structure of β - MoO_3 .

Figure 6: Crystal structure of α - MoO_3 .

Figure 7: X-ray diffraction patterns of mixtures of β - MoO_3 and α - MoO_3 . (a) Changes of intensity of strongest peaks of β - MoO_3 and (b) changes of intensity of strongest peaks of α - MoO_3 (w represents the ratio of the mass of β - MoO_3 to the total mass of β - MoO_3 and α - MoO_3).

Table 1: Changes of intensity of strongest peaks of β -MoO₃ and α -MoO₃ for different mixture ratios.

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

Figure 8: Plot of $I_{\beta}/(I_{\beta} + I_{\alpha})$ as a function of W , the ratio of β -MoO₃ to the sum of β -MoO₃ and α -MoO₃.

the integrated intensity and deal with interferences from other phases. In the present study, it was obvious that the strongest peak of β -MoO₃ had some overlap with the small peak of α -MoO₃, 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 β -MoO₃ and α -MoO₃. In the present study, both β -MoO₃ and α -MoO₃ 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 α -MoO₃ were stronger, this method could not be applied.

3.3 Decomposition of β -MoO₃

Before successfully preparing α -MoO₃ by roasting β -MoO₃ at 773 K in air, another method was attempted, that is, roasting β -MoO₃ at 773 K in a highly pure Ar atmosphere (<5 ppm O₂); however, pure α -MoO₃ could not be obtained. The corresponding XRD pattern is shown in Figure 9. The roasted products were very complicated and included not only α -MoO₃ but also MoO₂ and Mo₄O₁₁. Here, Mo₄O₁₁ included two crystalline structures: orthorhombic Mo₄O₁₁ (o-Mo₄O₁₁) and monoclinic Mo₄O₁₁ (m-Mo₄O₁₁). 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 β -MoO₃ may contain a number of oxygen vacancies [25–27]. When roasting β -MoO₃ in air, the samples have enough opportunity to interact with O₂. Maximum interaction between air and β -MoO₃ is important to ensure that the following chemical equilibrium is shifted to the left [28]:

Oxygen exchange between the lattice and air has been investigated using isotope (¹⁸O₂) labeling and Raman spectroscopy, which showed that gaseous O₂ is able to incorporate into the oxygen-deficient β -MoO₃ [29]. Therefore, perfect α -MoO₃ can be prepared under air; however, when roasting β -MoO₃ in the argon atmosphere, no O₂ was provided to counter the oxygen-deficient β -MoO₃, which led to shifting of the chemical equilibrium (2) to the right and the production of low-valent molybdenum oxides, such as MoO₂ and Mo₄O₁₁. Once the oxygen defects were exhausted,

Figure 9: X-ray diffraction pattern of products obtained by roasting β -MoO₃ at 773 K in highly pure argon atmosphere.

Figure 10: Color changes of roasted products obtained at 773 K: (a) raw β -MoO₃; roasted under (b) air and (c) pure argon atmospheres.

Figure 11: X-ray diffraction patterns of products obtained by roasting highly pure α -MoO₃ in different atmospheres.

the remaining components formed perfect α -MoO₃. Therefore, different molybdenum–oxygen compounds can co-exist 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.

Figure 12: Schematic of the transformation of β -MoO₃ under different conditions.

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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References

- [1] Stephens, J., and D. Cruickshank. The crystal structure of CrO₃. *Acta Crystallographica Section B: Structural Science*, Vol. 26, 1970, pp. 222–226.
- [2] Liu, D., W. Lei, J. Hao, D. Liu, B. Liu, X. Wang, et al. High-pressure Raman scattering and X-ray diffraction of phase transitions in MoO₃. *Journal of Applied Physics*, Vol. 105, 2009, id. 023513.
- [3] Enjalbert, R., and J. Galy. A refinement of the structure of V₂O₅. *Acta Crystallographica Section C*, Vol. 42, 1986, pp. 1467–1469.

- [4] Zhao, J., P. Ma, and J. Wang. Synthesis and structural characterization of a novel three-dimensional molybdenum-oxygen framework constructed from Mo_3O_9 units. *Chemistry Letters*, Vol. 38, 2009, pp. 694–695.
- [5] Farneth, W., E. McCarron, A. Sleight, and R. Staley. A comparison of the surface chemistry of two polymorphic forms of molybdenum trioxide. *Langmuir*, Vol. 3, 1987, pp. 217–223.
- [6] Bando, Y., Y. Kato, and T. Takada. Crystal Growth of Molybdenum Oxides by Chemical Transport. Bulletin of the Institute for Chemical Research, Kyoto University, Vol. 54, 1976, pp. 330–334.
- [7] Navas, I., R. Vinodkumar, K. Lethy, A. Detty, V. Ganesan, V. Sathe, et al. Growth and characterization of molybdenum oxide nanorods by RF magnetron sputtering and subsequent annealing. *Journal of Physics D: Applied Physics*, Vol. 42, 2009, id. 175305.
- [8] Phuc, N. H. H., H. Ohkita, T. Mizushima, and N. Kakuta. Simple method to prepare new structure of metastable molybdenum(VI) oxide. *Materials Letters*, Vol. 76, 2012, pp. 173–176.
- [9] McCarron, E. β - MoO_3 : a metastable analogue of WO_3 . *Journal of the Chemical Society, Chemical Communications*, Vol. 4, 1986, pp. 336–338.
- [10] Mizushima, T., Y. Moriya, N. H. H. Phuc, H. Ohkita, and N. Kakuta. Soft chemical transformation of α - MoO_3 to β - MoO_3 as a catalyst for vapor-phase oxidation of methanol. *Catalysis Communications*, Vol. 13, 2011, pp. 10–13.
- [11] Mizushima, T., K. Fukushima, T. M. Huong, H. Ohkita, and N. Kakuta. Synthesis of β - MoO_3 by simple evaporation of molybdic acid solution containing nitric acid. *Chemical Letters*, Vol. 34, 2005, pp. 986–987.
- [12] Parise, J., E. McCarron, R. Von Dreele, and J. Goldstone. β - MoO_3 produced from a novel freeze drying route. *Journal of Solid State Chemistry*, Vol. 93, 1991, pp. 193–201.
- [13] Mcevoy, T. M., K. J. Stevenson, J. T. Hupp, and X. Dang. Electrochemical preparation of molybdenum trioxide thin films: effect of sintering on electrochromic and electroinsertion properties. *Langmuir*, Vol. 19, 2003, pp. 4316–4326.
- [14] Ding, Q., H. Huang, J. Duan, J. Gong, S. Yang, X. Zhao, et al. Molybdenum trioxide nanostructures prepared by thermal oxidation of molybdenum. *Journal of Crystal Growth*, Vol. 294, 2006, pp. 304–380.
- [15] Wang, L., G. H. Zhang, K. C. Chou. Mechanism and kinetic study of hydrogen reduction of ultra-fine spherical MoO_3 to MoO_2 . *International Journal of Refractory Metals and Hard Materials*, Vol. 54, 2016, pp. 342–350.
- [16] Yang, W. Q., Z. R. Wei, M. Gao, Y. Chen, J. Xu, C. L. Chen, et al. Fabrication and field emission properties of needle-shaped MoO_3 nanobelts. *Journal of Alloys and Compounds*, Vol. 576, 2013, pp. 332–335.
- [17] Pawloski, G. A. Quantitative determination of mineral content of geological samples by X-ray diffraction. *American Mineralogist*, Vol. 70, 1985, pp. 663–667.
- [18] Chung, F. H. Quantitative interpretation of X-ray diffraction patterns of mixtures. I. Matrix-flushing method for quantitative multicomponent analysis. *Journal of Applied Crystallography*, Vol. 7, 1974, pp. 519–525.
- [19] Hillier, S. Accurate quantitative analysis of clay and other minerals in sandstones by XRD: comparison of a Rietveld and a reference intensity ratio (RIR) method and the importance of sample preparation. *Clay Minerals*, Vol. 35, 2000, pp. 291–302.
- [20] Vaverka, J., and K. Sakurai. Quantitative determination of free lime amount in steelmaking slag by X-ray diffraction. *ISIJ International*, Vol. 54, 2014, pp. 1334–1337.
- [21] Shu, Q. F., J. Wu, and K. C. Chou. Kinetics study on reduction of CaWO_4 by Si from 1423 K to 1523 K. *High Temperature Materials and Processes*, Vol. 34, 2015, pp. 805–811.
- [22] Wang, L., G. H. Zhang, Y. J. Sun, X. W. Zhou, and K. C. Chou. Preparation of ultrafine β - MoO_3 from industrial grade MoO_3 powder by the method of sublimation. *Journal of Physical Chemistry C*, Vol. 120, 2016, pp. 19821–19829.
- [23] Wang, L., G. H. Zhang, Z. L. Xue, and C. M. Song. Shape-controlled preparation of Mo powder by temperature-programmed reduction of MoO_3 by NH_3 . *Chemistry Letters*, Vol. 48, 2019, pp. 475–478.
- [24] Sayede, A., T. Amriou, M. Pernisek, B. Khelifa, and C. Mathieu. An ab initio LAPW study of the α and β phases of bulk molybdenum trioxide, MoO_3 . *Chemical Physics*, Vol. 316, 2005, pp. 72–82.
- [25] Julien, C., A. Khelifa, O. Hussain, and G. Nazri. Synthesis and characterization of flash-evaporated MoO_3 thin films. *Journal of Crystal Growth*, Vol. 156, 1995, pp. 235–244.
- [26] Simmons, J., and G. Nadkarni. Alternating current electrical properties of evaporated molybdenum oxide films. *Journal of Vacuum Science and Technology*, Vol. 6, 1969, pp. 12–17.
- [27] Varlec, A., D. Arčon, S. D. Škapin, M. Remškar. Oxygen deficiency in MoO_3 polycrystalline nanowires and nanotubes. *Materials Chemistry and Physics*, Vol. 170, 2016, pp. 154–161.
- [28] Zeng, H., C. Sheu, and H. Hia. Kinetic study of vapor-phase preparation of orthorhombic molybdenum trioxide. *Chemistry of Materials*, Vol. 10, 1998, pp. 974–979.
- [29] Mestl, G., P. Ruiz, B. Delmon, and H. Knozinger. Oxygen-exchange properties of MoO_3 : an in situ Raman spectroscopy study. *The Journal of Physical Chemistry*, Vol. 98, 1994, pp. 11269–11275.