Study on oxidation mechanism and kinetics of MoO₂ to MoO₃ in air atmosphere

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Abstract

The oxidation mechanism and kinetics of MoO₂ to MoO₃ in air atmosphere from 750 K to 902 K have been investigated in the present work. These results show that temperature has significant effects on the oxidation process. It is found that the produced MoO₃ has a tendency to form big platelet-shaped particle and the surface appears to be smooth at the high reaction temperature (902 K); while at the low reaction temperature (750 K), the micrographs of final products MoO₃ become rough and irregular. The intermediate product Mo₄O₁₁ will be formed only when the temperature is above 810 K. It is found that the oxidation reaction was controlled by the interface chemical reaction at the reaction interface (from MoO₂ to Mo₄O₁₁) and diffusion (from Mo₄O₁₁ to MoO₃), respectively, by using the dual-interface reaction model in the temperature range of 810 K to 902 K. While in the temperature range of 750 K to 779 K, the oxidation reaction (one-step reaction, from MoO₂ to MoO₃ directly) was controlled by the diffusion model.

Keywords: Mechanism; Kinetic; Morphology; Oxidation reaction

1. Introduction

Transition metal oxides such as CrO₃, V₂O₅, WO₃ and MoO₃ have been subjected to numerous investigations owing to their considerable industrial importances [1, 2]. Among these, MoO₃ is one of the most interesting intercalation materials for ambient temperature solid-state lithium batteries [3]. Moreover, MoO₃ is usually used as the basic starting material for the preparation of most of the industrially molybdenum products such as molybdenum metal, ferromolybdenum alloy and other pure chemical molybdenum compounds. The production of industrial grade MoO₃ at present is by the oxidation roasting of molybdenite concentrate in conventional multiple hearth roasters. Various studies [4-7] on the oxidation kinetics of molybdenite concentrate have been reported and most of them shown that the oxidation process proceeds through the intermediate product MoO₂, and the corresponding oxidation processes can be described as follows,

The kinetics of oxidation roasting of molybdenite concentrate is of technical interest for the design and use of equipment and in the choice of conditions for the roasting process. The purpose of the present study is to explore the further oxidation process of MoO₂ during the roasting process of molybdenite concentrate, which can contribute to a better understanding on the roasting

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mechanism of molybdenite concentrate.

What is more, several phases with different stoichiometric ratio of Mo : O are existed, such as MoO_3 , MoO_2 , Mo_4O_{11} , Mo_5O_{14} , Mo_8O_{23} , $\text{Mo}_{17}\text{O}_{47}$, $\text{Mo}_{18}\text{O}_{52}$ and etc [8, 9]. Among these, MoO_3 and MoO_2 are the most thermodynamically stable phases. Consequently, the mechanism and kinetics of hydrogen reduction of MoO_3 to MoO_2 have been widely studied by many investigators [10-19] in the past decades. However, only several studies [20-25] have been carried out with respect to the oxidation of MoO_2 to MoO_3 .

Ressler et al. [20] investigated the oxidation of MoO_2 in oxygen by in situ X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) technologies, the minority intermediate phase $\text{Mo}_{18}\text{O}_{52}$ was detected and reported that the reaction kinetics was governed by the diffusion model. Ramadoral et al. [21] carried out the studies on the oxidation of powdered MoO_2 to MoO_3 under a variety of temperatures and reported that the parabolic kinetics were to be followed when the temperatures are below 733 K; while when the temperatures are above 733 K, the surface products are non-protective and the linear oxidation kinetics are observed. Also, it is reported that only MoO_3 was found as the oxidation product without the formation of any intermediate products. Kahruman et al. [22] conducted the investigations on the kinetics of oxidation of MoO_2 to MoO_3 by oxygen atmosphere in the temperature range of 674 K to 791 K, and reported that the reaction belongs to one-step reaction and 0.6 th-order with respect to oxygen concentration, the activation energy was found to be 148 kJ/mol. Aleman-Vazquea et al. [25] studied the non-isothermal kinetics of the oxidation of MoO_2 to MoO_3 , it was found that the isoconversional analysis shows a complex activation energy (E_a) _{α} dependence on reaction extent (α) and a 2D (two-dimensional diffusion) mechanism with a variable activation energy value in the range of 110-200 kJ/mol were obtained.

As mentioned above, the studies on the mechanism and kinetics behaviors of oxidation of MoO_2 to MoO_3 are limited and unresolved. Meantime, most of them are carried out in oxygen atmosphere but not air, whereas, in the multiple hearth roasters, air is used. In addition, the phase transitions and morphology evolutions during the oxidation processes are also lacked. In order to make up for this gap, the present studies are initiated.

2. Materials and experimental procedures

2.1. Materials

Commerically available MoO_2 powders from Jinduicheng Molybdenum Co., Ltd. were used for the experimental purposes. Fig. 1 shows the X-ray diffraction patterns of the studied MoO_2 powders. As can be seen from it, the raw material has a very high purity. The images of the raw MoO_2 are presented in Fig. 2, from which it can be known that the powders are composed of many platelet-shaped MoO_2 grains and are fairly loose.

2.2. Experimental procedures

In order to monitor the weigh change continuously during the oxidation process, a thermal analysis system (HTC-2, Beijing Hengjiu Instrument Ltd. China), which includes a thermo-gravimetry (TG) microbalance with a precision of $\pm 1 \mu\text{g}$, was used, and the corresponding schematic diagram is displayed in Fig. 3. In each experimental run, MoO_2 samples of about 100 mg were used and filled into the alumina crucible “3”, which has a dimension of 7

mm in inner diameter and 7 mm in height. A “dead-burnt” identical alumina crucible “2” was used as the standard reference material. After the crucible “3” with samples were positioned on the supported holder “4”, Ar gas was introduced into the system to drive the air out and then the furnace was heated from room temperature to desired oxidation temperatures with the heating rate of 10 K/min. When the temperature was in stable state and the air was driven out completely, Ar gas was switched to the oxidizing gas Air to start the oxidation reaction. After the experiment was finished, Air was switched to Ar again and the samples were cooled down to the room temperature. The isothermal kinetic experiments were conducted at 750 K, 760 K, 779 K, 810 K, 840 K, 870 K and 902 K, respectively.

In all the experimental runs, a constant gas flow rate of 60 ml/min of Air was kept during the oxidation process, this level was found to be sufficient for diminishing the diffusion resistance in the gas-boundary layer around the particle. The gas flow rate was controlled by gas flow controllers “1” (Allicant, Model MC-500SCCM-D). XRD technology (Model TTRIII, Japan) was used to identify the phase compositions. FE-SEM (ZEISS SUPRA 55) was used to observe the evolution processes of morphologies.

3. Results

3.1. Isothermal oxidation kinetics

The reaction extent (α) of MoO₂ powders by air was calculated as the ratio of weight gain W_t to the theoretical maximum weight gain W_{max} as shown in equation (3),

$$\alpha = \frac{W_t}{W_{max}} \times 100\% \quad (3)$$

The corresponding kinetic curves were shown in Fig. 4. It can be seen that the reaction extent depended strongly on the reaction temperature. The higher the reaction temperature is, the faster the reaction rate will be. When the temperature is above 810 K, the oxidation processes are very fast and can be completed within 100 min. In addition, it can be easily seen that the initial oxidation rates are rapid when the temperature is above 810 K. However, when the temperature is below 779 K, the reaction rates were very slow and took several or tens hours to oxidize completely, as shown in Fig. 4 (b).

3.2. X-ray diffraction analyses

3.2.1. 810 to 902 K

The XRD patterns of oxidation products at 902 K for different reaction extents are presented in Fig. 5. It can be easily seen that raw materials MoO₂ and final products MoO₃ are decreased and increased, respectively. However, the peaks for Mo₄O₁₁ are also detected, which can be more obviously seen from Fig. 5 (b). It is indicated that Mo₄O₁₁ as an intermediate product is formed during the oxidation process. Meantime, the amount of Mo₄O₁₁ increases at first and then goes down gradually until disappearance. In addition, it is found that the final products MoO₃ show predominantly (0k0) orientation, and lines at (020), (040) and (060) are clearly observed, which indicated that the anisotropic growth of the final MoO₃.

The XRD patterns of oxidation products at 810 K for different reaction extents are shown in Fig. 6. From which it can be observed that the peaks for Mo₄O₁₁ are also detected, which suggests that

the intermediate products Mo_4O_{11} are also formed during the oxidation process even though the amount are a little fewer compared to that at 902 K.

3.2.2. 750 to 779 K

The XRD patterns of oxidation products of MoO_2 powders at 779 K and 750 K for different reaction extents are presented in Fig. 7 and Fig. 8, respectively. It can be obviously seen that MoO_2 are oxidized to MoO_3 directly both at 779 K and 750 K without any intermediate products formed. Combined with the results obtained at 810 K and 902 K, it suggests that the mechanism of oxidation process from MoO_2 to MoO_3 is different at different reaction temperatures. The absence of Mo_4O_{11} at low reaction temperatures (from 750 K to 779 K) may be resulted from the instability of Mo_4O_{11} at low temperatures, or due to that the oxidation rate of Mo_4O_{11} to MoO_3 is much faster than that of MoO_2 to Mo_4O_{11} , hence, the intermediate products Mo_4O_{11} can't be accumulated which makes the oxidation reactions seem to be one-step process. Exact reasons need to be further explored in future.

3.3. FE-SEM for morphologies analyses

3.3.1. 810 to 902 K

The typical images of oxidation products obtained at the high reaction temperature (902 K) are displayed in Fig. 9. It can be seen that the micrographs have obvious changes even if the reaction extent is only 0.3381, as shown in Fig. 9 (a) and Fig. 9 (A). The agglomerated particles are fairly compact and bigger compared to the raw materials shown in Fig. 2. When the oxidation reaction continues, the particles became more compact and bigger. The surfaces of particles are smooth and the contact interfaces between different grains are obvious. Several platelet-shaped and flake-like products also can be observed. When the reaction extent is achieved at 0.7849, the amount of platelet-shaped products are increased and the agglomerated structures are decreased gradually, whereas, the surface of each particles are still very smooth, as shown in Figs. 9 (c) and (C). As the oxidation reaction proceeds forward, as seen in Figs 9 (d) and (D), most of the products appear to be platelet-shaped. After MoO_2 are oxidized completely, the final products MoO_3 almost reveal platelet-shaped, and the particles size have been growth up and bigger than the raw MoO_2 particles.

3.3.2. 750 to 779 K

The typical images of oxidation products obtained at the low reaction temperature (750 K) can be seen in Fig. 10. From Fig. 10 it can be known that the morphologies also have great changes compared to the raw materials shown in Fig. 2. When the reaction extent is 0.2801, as shown in Fig. 10 (a), there are a great number of small particles deposited on the big particles, which lead to the formation of rough surface. As the reaction proceeds forwards, the images of oxidation products are also composed of large amounts of small particles and the surface are still rough and coarse. The characteristic of the rough and irregularity surface are conserved when the oxidation reaction continues until completely, as shown in Figs. 10 (c) and (d), which are obviously different from the smooth surface obtained at 902 K. In addition, it can be easily seen that the volume of each platelet-shaped particles have expanded and size became bigger compared to the raw MoO_2 , as shown in Figs. 10 (e) and (f).

4. Discussion

4.1. Oxidation mechanism

As the results sections mentioned above (XRD analyses and FE-SEM observes), it may be induced that the mechanisms of oxidation of MoO₂ to MoO₃ by air are different at different reaction temperatures. In order to further understand the oxidation mechanism, the density and molar volumes of the various Mo-O species [6, 26, 27] involved are summarized in Table 1.

4.1.1. 810 to 902 K

In the authors' previous studies [9, 17, 19], the reduction of MoO₃ to MoO₂ by hydrogen has confirmed to obey the consecutive reaction mechanism with the formation of intermediate product Mo₄O₁₁, i.e. MoO₃ is firstly reduced to Mo₄O₁₁, and then Mo₄O₁₁ is further reduced to MoO₂, which are shown as Eqs. 4 and 5.

In the present study, as clearly shown in Figs. 5 and 6, it can be known that Mo₄O₁₁ as an intermediate product is also formed during the oxidation process of MoO₂ to MoO₃ in the temperature range of 810 K to 902 K. In view of the inverse process and the similarity, it is reasonable to assume that the consecutive reaction mechanism can be applied to the oxidation process, which will be further certified by the following kinetics analyses. So the corresponding oxidation equations can be described as Eqs. 6 and 7.

In addition, an interesting aspect of MoO₂ oxidation process is that the formation of Mo₄O₁₁ leads to a suboxide with a much larger molar volume than MoO₂ as shown in Table 1, which gives rise to the expansion of particles volume, thus the products will contact with each other tightly and exhibited a compact surface layer. Meantime, the formation of MoO₃ also leads to a larger volume increase as compared to MoO₂. Meantime, MoO₃ has a tendency to grow up to be a layer structure with the preferentially growing direction of (001) orientation [28] at the high temperature because of its inherent two-dimension layer crystalline structure in which each layer is built up of MoO₆ octahedron, as shown in Fig. 11. It can also be seen from Fig. 9 that the surface of particles are very smooth, since at the high temperature, diffusion abilities of atoms/molecules at the surface are higher, it is easy for them to diffuse to lead to a low energy state of system. Meanwhile, due to the increasing vapor pressure of MoO₃ as increasing the temperature [29], so the vapor pressure of MoO₃ at 902 K is high and the vapor will transport into a far position and then condensate, which are also contributed to the formation of platelet-shaped and long MoO₃ crystal. What is more, a more interesting phenomenon has been found that many small agglomerate molybdenum oxides particles were embedded in the big platelet-shaped MoO₃ matrix, as shown in Fig. 12. As the reaction goes on, the MoO₃ moleculars in the small MoO₃ particles will diffuse toward the large platelet-shaped MoO₃ particles until the small particles disappear and to be a part of the large platelet-shaped particles (as shown the final product MoO₃ shown in Fig. 9 (e) and (E)), which can be described by the classical Ostwald Ripening mechanism [30].

4.1.2. 750 to 779 K

It can be obtained that from Figs. 7 and 8 in the low temperature range of 750 K to 779 K, the oxidation process of MoO₂ to MoO₃ was proceeding via one-step oxidation mechanism without any intermediate product formed.

Moreover, due to the molar volume of MoO₃ is larger than that of MoO₂, when 1 mol MoO₂ is oxidized into 1 mol MoO₃ completely, the volume will be increased by 55.18 %, as shown in Table 1. Therefore, the compact MoO₃ shell will be formed around the raw MoO₂ particle, which will hinder the diffusion of O₂ from the bulk to the reaction interface seriously. On the other hand, due to the low reaction temperature (750 K to 779 K), even if the stable crystalline polymorphs phase of MoO₃ is orthorhombic molybdenum trioxide (α -MoO₃) and it also has the tendency to form the platelet-shaped or layer-shaped structure oxides, the atoms/molecules on the product surface don't have enough diffusion ability to achieve the low energy state positions, so the surface of products seem to maintain the rough or random structure, as shown in Fig. 10. Meantime, the vapor pressure of MoO₃ at the low temperatures are also very low, which are also disadvantage for the formation of platelet-shaped MoO₃.

4.2. Oxidation kinetics

4.2.1. 810 to 902 K

According to the dual interface reaction model [17, 19], the oxidation of MoO₂ to Mo₄O₁₁ and Mo₄O₁₁ to MoO₃ are occurred simultaneously, the overall reaction extent can be expressed as a linear relationship with α_1 and α_2 with the corresponding weighting factors (α_1 and α_2 represent the reaction extents of Eqs. 6 and 7, respectively). So, the overall reaction extent can be expressed as

$$\alpha = \varepsilon_1 \alpha_1 + \varepsilon_2 \alpha_2 \quad (8)$$

where ε_1 and ε_2 are the constants depending on the complete insertion of oxygen of Eqs. 6 and 7. So, it is easy to obtain that ε_1 and ε_2 are equal to 0.75 and 0.25, respectively.

Table 2 lists the algebraic expressions of integral functions $g(\alpha)$ and the explicit forms α [17, 19, 31, 32]. These expressions are widely applied for the kinetic analysis of gas-solid reactions and encompass most common mechanisms. In Table 2, k is the rate constant as a function of temperature, and the temperature dependence of the rate constant is described as the Arrhenius equation,

$$k = A \exp\left(-\frac{\Delta E}{RT}\right) \quad (9)$$

where A (min⁻¹) is the pre-exponential factor (frequency factor), ΔE (J/mol) is the activation energy, R (8.314 J/mol/K) is the gas constant and T (K) is the absolute temperature.

Substituting Eq. (9) and different models in Table 2 into Eq. (8), and the corresponding reaction kinetics models can be obtained.

As mentioned above, the oxidation kinetics curves obtained from 810 K to 902 K, as shown in Fig. 4 (a), have an obvious linear relationship at the initial stage. After that the oxidation rate was decreased gradually, which indicated that the oxidation mechanism may be different at different reaction extent. Moreover, according to the best fitting of the experimental data, it is found that Model 4 and Model 8 can best describe the oxidation processes of MoO₂ to Mo₄O₁₁ and Mo₄O₁₁ to

MoO₃, respectively. Thus the total reaction extent α can be written as

$$\alpha = \varepsilon_1 \left\{ 1 - \exp \left[- \left(A_1 \exp \left(- \frac{\Delta E_1}{RT} \right) t \right) \right] \right\} + \varepsilon_2 \left\{ 1 - \left[1 - \left(A_2 \exp \left(- \frac{\Delta E_2}{RT} \right) t \right)^{\frac{1}{2}} \right]^2 \right\} \quad (10)$$

where numbers 1 and 2 represent Eqs. 6 and 7, respectively.

Fig. 13 shows the comparisons of the results of measured and calculated reaction extent with Eq. (10), it can be easily seen that the model calculated results agree well with the experimental data. So it can be concluded that the oxidation reaction of MoO₂ to Mo₄O₁₁ and Mo₄O₁₁ to MoO₃ are controlled by first-order interface chemical reaction and diffusion model, respectively. The extracted activation energies are 77.691 kJ/mol and 158.664 kJ/mol, respectively.

In the “oxidation mechanism” section, it has been speculated that the oxidation process from MoO₂ to MoO₃ is a consecutive reaction mechanism with the formation of intermediate product Mo₄O₁₁ in the temperature range of 810 K to 902 K. The present results further confirmed that the rationality of the hypothesis. Therefore, the corresponding kinetics equation can be given as shown in Eq. (11).

$$\begin{aligned} \alpha &= 0.75 \times \left\{ 1 - \exp \left[- \left(1.3127 \times 10^4 \exp \left(- \frac{77691}{RT} \right) t \right) \right] \right\} + 0.25 \times \left\{ 1 - \left[1 - \left(1.211 \times 10^8 \exp \left(- \frac{158664}{RT} \right) t \right)^{\frac{1}{2}} \right]^2 \right\} \\ &= 1 - 0.75 \times \exp \left\{ - \left[1.3127 \times 10^4 \exp \left(- \frac{77691}{RT} \right) t \right] \right\} - 0.25 \times \left\{ 1 - \left[1.211 \times 10^8 \exp \left(- \frac{158664}{RT} \right) t \right]^{\frac{1}{2}} \right\}^2 \end{aligned} \quad (11)$$

4.2.2. 750 to 779 K

Similarity, as analyzed above, the oxidation of MoO₂ to MoO₃ by air in the temperature range of 750 K to 779 K is one-step reaction process without the formation of intermediates. What is more, according to the analyses of the micrographs, it is found that the product surface is surrounded by the compact MoO₃ protective layer which will hinder the penetration of O₂ from the bulk to the reaction interface seriously, so the diffusion of O₂ in the product layer might be the rate-controlling step. Furthermore, according to the best fitting of the experimental data, it is found that diffusion model 8 can describe the oxidation process best. Combining Eq. (9) with model 8, the oxidation extent can be written as

$$\alpha = 1 - \left\{ 1 - \left[A_3 \exp \left(- \frac{\Delta E_3}{RT} \right) t \right]^{\frac{1}{2}} \right\}^2 \quad (12)$$

Fig. 14 shows the comparisons of the results of measured and calculated reaction extent with Eq. (12), from which it can be seen that model 8 can fit the experimental data fairly well. The extracted activation energy is 170.067 kJ/mol, which is in well agreement with the values obtained by previous studies [20, 21, 25]. So, the corresponding kinetic formula can be given as Eq. (13).

$$\alpha = 1 - \left\{ 1 - \left[1.38 \times 10^9 \exp \left(- \frac{170067}{RT} \right) t \right]^{\frac{1}{2}} \right\}^2 \quad (13)$$

5. Conclusions

In the present study, the oxidation mechanism and kinetic of MoO_2 to MoO_3 by air in the temperature range of 750 K to 902 K was investigated by using thermo-gravimetric analysis. The following conclusions can be drawn, which will give a better understanding of the oxidation roasting process of molybdenite concentrate in the multiple hearth furnaces.

- ◆ The intermediate product Mo_4O_{11} will form when the oxidation temperature is above 810 K; whereas when the oxidation temperature is below 779 K, Mo_4O_{11} will not be observed.
- ◆ The final product of MoO_3 has a tendency to form platelet-shaped and smooth particle at high oxidation temperature due to the high atoms/molecules mobility ability and the high vapor pressure of MoO_3 ; While that at the low oxidation temperature, the formed MoO_3 became bigger and rough agglomerate particles.
- ◆ The two-interface reaction kinetic model is applied to describe the oxidation kinetic of MoO_2 to MoO_3 in the temperature range of 810 K to 902 K. It is found that the oxidation processes of MoO_2 to Mo_4O_{11} and Mo_4O_{11} to MoO_3 is controlled by the first-order interface chemical reaction and two-dimension diffusion, respectively. The corresponding activation energies are 77.691 kJ/mol and 158.664 kJ/mol, respectively.
- ◆ When the oxidation temperature is in the range of 750 K to 779 K, MoO_2 is oxidized to MoO_3 directly without the formation of intermediate product Mo_4O_{11} . The oxidation rate is controlled by the two-dimension diffusion model with the extracted activation energy of 170.067 kJ/mol.

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List of Figure Captions

Fig. 1. XRD patterns of studied MoO_2 powders.

Fig. 2. FE-SEM micrographs of studied MoO_2 powders.

Fig. 3. Schematic diagram of the experimental apparatus for the TG analysis. 1. Gas flow meter; 2. Calibrated alumina crucible; 3. Experimental alumina crucible; 4. Sample holder and thermo-couple; 5. HTC-2 TG analyzer; 6. Data collector; 7. Beaker flask A; 8. Beaker flask B; 9. Exhaust gases.

Fig. 4. Isothermal oxidation kinetics curves of MoO_2 to MoO_3 by air.

Fig. 5. XRD patterns of oxidation products of MoO_2 powders oxidized by air at 902 K. (a) for different reaction extents; (b) amplified XRD patterns. (α represents the reaction extent).

Fig. 6. XRD patterns of oxidation products of MoO_2 powders oxidized by air at 810 K. (a) for different reaction extents; (b) amplified XRD patterns. (α represents the reaction extent).

Fig. 7. XRD patterns of oxidation products of MoO_2 powders oxidized by air at 779 K for different reaction extents.

Fig. 8. XRD patterns of oxidation products of MoO_2 powders oxidized by air at 750 K for different reaction extents.

Fig. 9. FE-SEM micrographs of MoO_2 powders oxidized by air at 902 K for different reaction extents. (a) and (A) $\alpha=0.3381$; (b) and (B) $\alpha=0.5322$; (c) and (C) $\alpha=0.7849$; (d) and (D) $\alpha=0.9130$; (e) and (E) $\alpha=1$. (α represents the reaction extent, and the Figs marked with capitals are the amplified images of the parts of red rectangles in Figs marked with lowercase, respectively).

Fig. 10. FE-SEM micrographs of MoO_2 powders oxidized by air at 750 K for different reaction extents. (a) $\alpha=0.2801$; (b) $\alpha=0.5806$; (c) $\alpha=0.8037$; (d) $\alpha=1$; (e) $\alpha=0.8037$; (f) $\alpha=0.8037$. (α represents the reaction extent, Fig. f is the amplified image of the red rectangle marked in Fig. e).

Fig. 11. Crystal structure of orthorhombic molybdenum trioxide ($\alpha\text{-MoO}_3$). (O_1 represents the terminal oxygen; O_2 represents the asymmetric bridging oxygen; O_3 represents the symmetric bridging oxygen).

Fig. 12. FE-SEM micrographs of MoO_2 powders oxidized by air at 902 K for different reaction extents. (A) $\alpha=0.5322$; (B) $\alpha=0.7849$; (C) and (D) $\alpha=0.9130$. (α represents the reaction extent, and Fig. D is the amplified image of the parts of the red rectangles in Fig. C).

Fig. 13. Comparisons of calculated and measured reaction extent vs reaction time curves for the oxidation of MoO_2 to MoO_3 by air at temperatures of 810 K, 840 K, 870 K, and 902 K. (R represents the correlation coefficient).

Fig. 14. Comparisons of calculated and measured reaction extent vs reaction time curves for the oxidation of MoO_2 to MoO_3 by air at temperatures of 750 K, 760 K and 779 K. (R represents the correlation coefficient).

Table 1 Molar Volume of Mo-O Species.

Table 2 List of the rate expressions of different gas-solid reaction kinetic models.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.

Fig. 10.

Fig. 11.

Fig. 12.

Fig. 13.

Fig. 14.

Table 1

Species	Molar Weight(g/mol)	Density(g/cm ³)	Molar Volume(cm ³ /mol)
MoO ₂	127.94	6.47	19.77
Mo ₄ O ₁₁ /MoO _{2.75}	559.76/139.94	4.17	134.24/33.56
MoO ₃	143.94	4.692	30.68

Table 2

Model	Integral form $g(\alpha)=kt$	Explicit form (α)
Geometrical contraction models		
1. Contracting area(R2)	$1-(1-\alpha)^{1/2}$	$\alpha=1-(1-kt)^2$
2. Contracting volume(R3)	$1-(1-\alpha)^{1/3}$	$\alpha=1-(1-kt)^3$
Reaction-order models		
3. Zero-order(F0/R1)	α	$\alpha=kt$
4. First-order (Mampel) (F1)	$-\ln(1-\alpha)$	$\alpha=1-\exp(-kt)$
5. Second-order(F2)	$(1-\alpha)^{-1}-1$	$\alpha=1-(1+kt)^{-1}$
6. Third-order(F3)	$0.5[(1-\alpha)^{-2}-1]$	$\alpha=1-(1+2kt)^{-1/2}$
Diffusion models		
7. Jander equation(2D, n=1/2)	$[1-(1-\alpha)^{1/2}]^{1/2}$	$\alpha=1-[1-(kt)^2]^2$
8. Jander equation(2D, n=2)	$[1-(1-\alpha)^{1/2}]^2$	$\alpha=1-[1-(kt)^{1/2}]^2$
9. Jander equation(3D, n=1/2)	$[1-(1-\alpha)^{1/3}]^{1/2}$	$\alpha=1-[1-(kt)^2]^3$
10. Jander equation(3D, n=2)	$[1-(1-\alpha)^{1/3}]^2$	$\alpha=1-[1-(kt)^{1/2}]^3$
Nucleation and growth models		
11. Power law(P2)	$\alpha^{1/2}$	$\alpha=(kt)^2$
12. Power law(P3)	$\alpha^{1/3}$	$\alpha=(kt)^3$
13. Avrami-Erofe'ev(A1.5)	$[-\ln(1-\alpha)]^{2/3}$	$\alpha=1-\exp[-(kt)^{3/2}]$
14. Avrami-Erofe'ev(A2)	$[-\ln(1-\alpha)]^{1/2}$	$\alpha=1-\exp[-(kt)^2]$
15. Avrami-Erofe'ev(A3)	$[-\ln(1-\alpha)]^{1/3}$	$\alpha=1-\exp[-(kt)^3]$
16. Avrami-Erofe'ev(A4)	$[-\ln(1-\alpha)]^{1/4}$	$\alpha=1-\exp[-(kt)^4]$