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Study on oxidation mechanism and kinetics of MoO_2 to MoO_3 in air atmosphere

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ABSTRACT

The oxidation mechanism and kinetics of MoO_2 to MoO_3 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 MoO_3 has a tendency to form a 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 MoO_3 become rough and irregular. The intermediate product Mo_4O_{11} 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 MoO_2 to Mo_4O_{11}) and diffusion (from Mo_4O_{11} to MoO_3), 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 MoO_2 to MoO_3 directly) was controlled by the diffusion model.

1. Introduction

Transition metal oxides such as CrO_3, V_2O_5, WO_3 and MoO_3 have been subjected to numerous investigations owing to their considerable industrial importances [1,2]. Among these, MoO_3 is one of the most interesting intercalation materials for ambient temperature solid-state lithium batteries [3]. Moreover, MoO_3 is usually used as the basic starting material for the preparation of most of the industrial molybdenum products such as molybdenum metal, ferromolybdenum alloy and other pure chemical molybdenum compounds. The production of industrial grade MoO_3 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 show that the oxidation process proceeds through the intermediate product MoO_2, and the corresponding oxidation processes can be described as follows,

$$MoS_2+3O_2= MoO_2+2SO_2 \tag{1}$$

$$MoO_2 + 0.5O_2= MoO_3. \tag{2}$$

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 MoO_2 during the roasting process of molybdenite concentrate, which can contribute to a better understanding on the roasting mechanism of molybdenite concentrate.

What is more, several phases with different stoichiometric ratios of Mo:O are existing, such as MoO_3, MoO_2, Mo_4O_{11}, Mo_5O_{14}, Mo_8O_{23}, $Mo_{17}O_{47}$, $Mo_{18}O_{52}$, 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 $Mo_{18}O_{52}$ 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 $(Ea)_\alpha$ dependence on reaction extent (α)

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and a 2D (two-dimensional diffusion) mechanism with a variable activation energy value in the range of 110–200 kJ/mol was obtained.

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

2. Materials and experimental procedures

2.1. Materials

Commercially 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 ± 1 μg, 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.

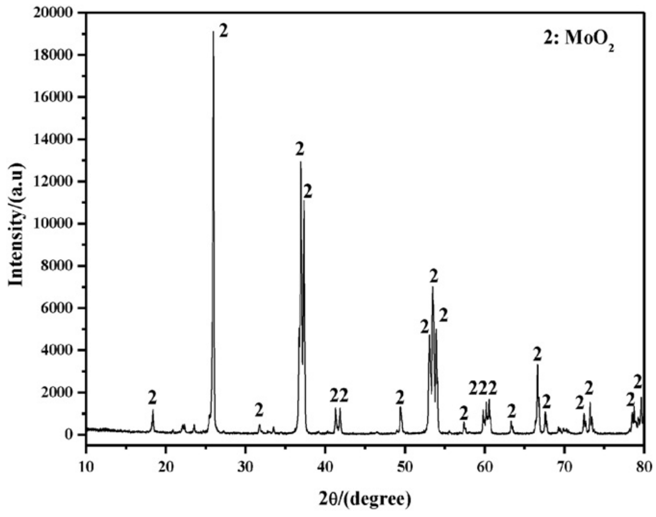

Fig. 1. XRD patterns of studied MoO_2 powders.

3. Results

3.1. Isothermal oxidation kinetics

The reaction extent (α) of MoO_2 powders by air was calculated as the ratio of weight gain W_t to the theoretical maximum weight gain W_{max} as shown in Eq. (3),

$$\alpha = \frac{W_t}{W_{max}} \times 100\%. \tag{3}$$

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 of 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 MoO_2 and final products MoO_3 are decreased and increased, respectively. However, the peaks for Mo_4O_{11} are also detected, which can be more obviously seen from Fig. 5(b). It is indicated that Mo_4O_{11} as an intermediate product is formed during the oxidation process. In the meantime, the amount of Mo_4O_{11} increases at first and then goes down gradually until disappearance. In addition, it is found that the final products MoO_3 show a predominantly (0k0) orientation, and lines at (020), (040) and (060) are clearly observed, which indicated the anisotropic growth of the final MoO_3.

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 Mo_4O_{11} are also detected, which suggests that the intermediate products Mo_4O_{11} are also formed during the oxidation process even though the amount is 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 Figs. 7 and 8, respectively. It can be obviously seen that MoO_2 is 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 the 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 result 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 a one-step process. Exact reasons need to be further explored in the future.