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Preparation of high purity MoO_3 through volatilization of technical-grade Mo calcine in water vapor atmosphere

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ABSTRACT

Comparative experiment on MoO_3 preparation from a technical-grade Mo calcine by volatilizing in water vapor atmosphere and air atmosphere was investigated. MoO_3 deposition in the forms of strip-like α-MoO_3 and spherical β-MoO_3 were obtained at varying condensing temperatures. By adjusting the carrying gas from air to water vapor, MoO_3 separating rate and product purity were remarkably improved, which is attributed to the selectively intensified evaporation of MoO_3 from melted calcine. Specifically, MoO_3 purity was over 99.99% and its corresponding recovery reached 70.6% when the calcine was evaporated at 1050 °C within 10 min in the water vapor atmosphere. Mechanisms of MoO_3 separation from polynary system were furtherly explored and impurities including calcium, iron molybdates and silica were found to exert negative influence on MoO_3 separation.

1. Introduction

High-Purity MoO_3 has long been produced as a necessary intermediate material for preparing Mo metal powders, Mo-containing superalloys, catalysts, pigments, and smoke suppressors etc. [1–5]. For the current commercial production, high-purity MoO_3 is mainly produced by roasting the prefabricated ammonia molybdates [6–8]. By contrast, volatilization process, also known as sublimation or distillation process for preparing high-purity MoO_3 from roasted molybdenite concentrates emerged early but experienced a slow progress in the 20th century for the demerits of low metal recovery (65–85%) and poor adaptability of raw material. Thus, the volatilization process demands high-Mo-content calcine ($>$ 60%) with less volatile impurities [7, 9, 10].

However, on the one hand, the recent technological progress of flotation has enabled deep separation of gangue minerals such as galena, talc and calcite from molybdenite [11–13], offering opportunities to provide suitable raw materials for volatilization process. On the other hand, the demand for ultrafine MoO_3 is fast growing, which is stimulated by the downstream needs for producing nanosized M50 steel, $MoSi_2$ materials, coatings and high-density Mo compact [14–16], and the exploitation of new applications in nanocatalysis [17, 18], lithium batteries [19–21], organic solar cells [22, 23] etc. Thus, the application of volatilization process for high-purity and ultrafine MoO_3 production has raised considerable concern [24–27]. Besides, researches on novel one-step process of volatilization-reduction to obtain ultrafine Mo powders from pure MoO_3 or technical grade MoO_3 are also intensive [28, 29].

For the volatilization of Mo calcine, previous literatures usually focus on the formation and characterization of final products [27, 29], while ignore the separation stage which largely determines the energy consumption, product yield and purity. Besides, challenging issues on the increasing requirement for energy saving, environment protection and product quality are needed to be solved. Moreover, relevant theories on thermal behaviors of molybdates are incomplete and even contradictory. For instance, alumina molybdate was reported to decompose under thermal treatment [30], but also detected at high temperatures in another work [27]. Such discrepancies may misdirect the technic rules of ore pretreatment and volatilization, thereby are imperative to be clarified.

In this work, for the first time, water vapor was introduced to intensify MoO_3 separation and purification during the volatilization of technical-grade Mo calcine. Thermal behaviors of MoO_3 and impurities in vapor-melt-solid three-phase system were comprehensively discussed to provide an explicit understanding on the previous theories. We believe that the proposed novel strategy of introducing water vapor and insights in understanding the behaviors of MoO_3 separation and deposition will offer an important guidance in optimizing the volatilization process, thus attaining efficient utilization of high-grade molybdenite concentrates and valuable MoO_3 products with high purity

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Table 1
Main element contents in the technical molybdic oxide (wt%).

Mo	Si	Ca	Fe	Al	Mg	Cu	Pb	S	K	P	Na
60.47	1.46	1.14	0.70	0.21	0.047	0.087	0.088	0.14	0.081	0.023	0.003

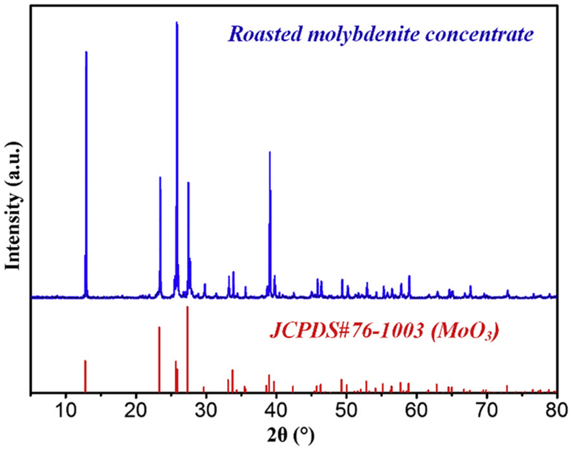

Fig. 1. XRD pattern of the roasted molybdenite concentrate.

and variable morphologies.

2. Experimental

2.1. Materials

The technical-grade molybdic oxide used in the study was prepared by oxiditive roasting a high-grade molybdenite concentrate at 600 °C for 2 h. Main element contents of the calcine are listed in Table 1. It can be seen that the calcine is of high Mo (60.47 wt%) and low S (0.14 wt%) content, indicating that the molybdenite concentrate has been well oxidized. Impurities in the calcine mainly consist of Si (1.46 wt%), Ca (1.14 wt%) and Fe (0.70 wt%), which are common for most of molybdenite concentrates. XRD pattern presented in Fig. 1 shows that molybdenum all exists in form of trioxide while the impurities cannot be assayed due to their low contents.

Besides, compressed air with the purity > 99.99 vol% was applied to carrying the volatiles, and chemical reagents of Al_2O_3, Fe_2O_3, MoO_3 (99.9 wt%, Aladdin) were used for phase transformation studies, respectively.

2.2. Methods

2.2.1. MoO_3 volatilization and deposition

As depicted Fig. 2, volatilization tests were performed in assembled apparatus consisting of heating furnace and gas supply system. In each test, powdery samples charged in a quartz boat (50 × 25 × 15 mm) were transferred to the middle zone of the quartz tube where the temperature was accurately measured by a thermocouple. Once the temperature reached a certain value, air/steam was introduced in with a fixing rate of 300 L/h. The moment injecting the air/steam was considered as the starting point of volatilization. After volatilizing for a given period time, the quartz boat was quickly pulled out and immediately weighed. The residue was picked out and dried for subsequent analysis.

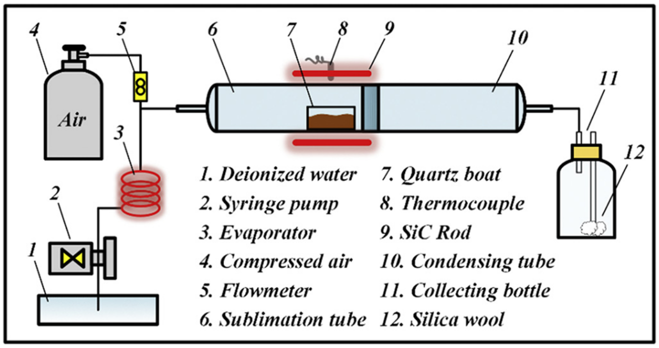

Fig. 2. Schematic for MoO_3 volatilization and products collection.

To collect the volatiles, an extra collecting tube followed by a bottle was joined together with the volatilization tube and silica wools were plugged into the outlet pipe to catch the fine powders. All the tubes, pipes and bottle were dunk in diluted nitric acid for 12 h and washed by deionized water for 3 times beforehand. The joints between tubes and pipes were sure to be completely tight. As volatilizing for a certain time, the gas supply system was closed up and simultaneously the collecting tube was pulled out. The volatiles in tubes, pipes and wools were flushed into the collecting bottle by deionized water. Then, volatiles mixed with water were dried for subsequent analysis.

2.2.2. Melting characteristics of the evaporation residue

Molten properties of volatilization residues were measured via a fusion tester (Fig. 3a). Residues were grinded, mixed with alcohol and shaped into uniform pyramids with the dimension of 5 × 5 × 5 × 12 mm by standard mold. Then, pyramids were placed in a grooved corundum plate and steady pushed into the middle of the fusion tester, which was set at the model of constant temperature. As samples heated up to the given temperature, the deformed pyramids were captured by a camera and compared with the standard molten states depicted in Fig. 3b. The heating process was operated in still air for about 2 min and each test adopted newly shaped pyramids so that compositions of the samples could be considered to be unchanged during the whole test.

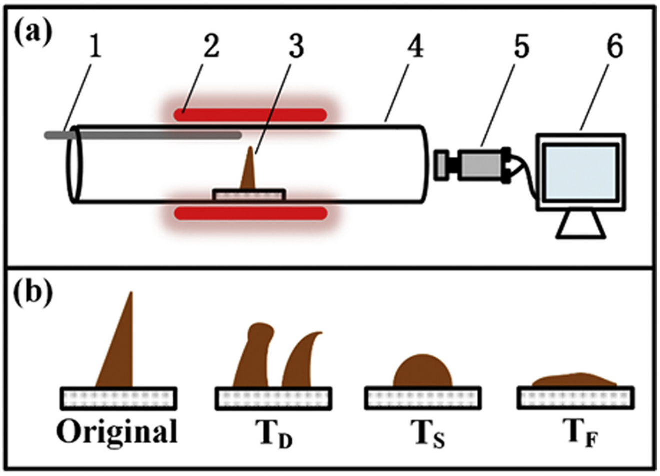

Fig. 3. Schematics of the fusion temperature tester and the standard states of the samples for measuring the characteristic temperatures. (a) 1. Thermocouple; 2. Elema; 3. Pyramid; 4. Corundum tube; 5. Camera; 6. Computer. (b) T_D—Deformation temperature; T_S—Sphere temperature; T_F—Flow temperature.

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