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A facile and reliable route to prepare highly dispersive ammonium dimolybdate uniform crystals from commercial molybdenum oxide

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ABSTRACT

Highly dispersive ammonium dimolybdate crystals with high purity have been prepared through reaction–evaporation–crystallization united route using commercial molybdenum oxide as starting material. The as-prepared ammonium dimolybdate uniform crystals were systematically characterized by X-ray powder diffraction, transmission-reflection optical microscope, Fourier transform infrared spectroscopy and TG-DSC thermal analysis. The Fsss grain diameter, loose packed density, and crystal-grain size distribution were also measured by the Malvern laser particle sizer. These collective characterization and analysis reveal that the ammonium dimolybdate grains are non-agglomerated uniform crystals with well normal distribution and geometric shape. The average Fsss diameter, $d_{(0.5)}$ and loose packed density are 433.316 μm, 470.981 μm and 1.592 g cm^{-3}, respectively, which could well meet the quality requirements for the subsequent production of molybdenum powders.

1. Introduction

Ammonium molybdate belongs to typical isopolymolybdate, commonly including ammonium dimolybdate (abbreviated as ADM), ammonium tetramolybdate, ammonium heptamolybdate, ammonium octamolybdate, twelve ammonium molybdate and beta-ammonium tetramolybdate [1]. The molybdates used in current industry are mostly the mixture of the above-mentioned ammonium molybdates with different proportions. The crystal structure, grain diameter, size distribution and flowability of the ammonium molybdates have great impact on the physical and chemical properties of the molybdenum powders derived from the reduction of the ammonium molybdates [2,3]. Therefore, the preparation of non-agglomerated ammonium molybdates with the pure crystal phase, high dispersity, uniform size has attracted wide attention in recent years. It has been proved [4] that the uniformly crystalline ADM possesses such advantages as the high purity, perfect size distribution, suitable flowability and so on. The uniform ADM crystal grains are relatively unbreakable in the process of dynamic pyrolysis reduction, leading to the formation of high-class molybdenum powders. In addition, the reduction temperature is easily controlled, and the yield of molybdenum powders is relatively high. For these reasons, the uniform ADM crystals have become preferable raw-material for production of high-quality molybdenum powder. Thus, it is of much significance to intensively study the preparation technique for ADM crystals with high purity and dispersity [5–8].

2. Experimental

2.1. Raw materials and instruments

Commercial molybdenum oxide (principal component MoO_3, total Mo $\geq$ 42%, insoluble Mo < 1%, 40 mesh screen sifting) was purchased from local molybdenum company, and sintered at 500 °C for 3 h before used. Aqueous ammonia ($NH_3{\cdot}H_2O$, 28%), sulfuric acid (H_2SO_4, 98%), ammonium sulfate ($(NH_4)_2SO_4$, 99%), ammonium persulfate ($(NH_4)_2S_2O_8$, 98%) and ammonium sulfide ($(NH_4)_2S$, aqueous, sulfur content $\geq$ 8%), are all analytically pure reagents. The phase composition and structure of the products were analyzed via an X-ray diffractometer (Advance-D8, Bruker, Germany) under the following conditions: graphite monochromatic copper radiation (Cu-Kα, λ = 0.15406 nm), scanning step of 0.02° min^{-1}, 2θ range from 10° to 70°. The FT-IR spectra were recorded on an infrared spectrometer (VERTEX70, Bruker, Germany) with KBr wafer in 100–4000 cm^{-1} wave number. The laser Raman spectrometer (HR800, GLY, French) was employed for the record of Raman spectra under the stimulation wavelength of 514 nm and optical grating of 1800 mm. The thermal analysis of the ADM samples was carried out by

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differential thermal analysis (DTA) and thermogravimetric analysis (TG) using a Netzsch STA409PC thermoanalyzer (Germany) with heating rate of 10 °C min^{-1} under argon protection. The morphology and size were studied using an optical microscope (OM) (BM-12, Shanghai, China). The grain diameter and size distribution were measured via a laser particle analyzer (Mastersizer 2000, Malvern, England).

2.2. The preparation of uniform-crystal ADM grains

At room temperature, 1000 g commercial molybdenum oxide, 30 g ammonium sulfate and 10 g ammonium persulfate were put into 2500 ml water, followed by drop-by-drop addition of 160 ml sulfuric acid under stirring until well dissolution. The resulting solution was heated to 75 °C, continually reacted for 0.5 h at that temperature, and then filtered and alternately washed with 1 wt% dilute sulfuric acid (at 75 °C, heated in advance) and water three times each. The collected 1100 g filter cake (water content ca.10 wt%) was dissolved in 1000 ml diluted aqueous ammonia (15 wt%) under stirring, and the solution temperature was kept at 50 °C for 30 min, during which the pH of the solution was regulated at 8 using the diluted aqueous ammonia. While it is hot, the solution was suction-filtered, and transparent filtrate with light blue color could be obtained. Into the filtrate that has been heated to 80 °C was dropwise added 1 ml aqueous ammonium sulfide (8 wt%), followed by reacting for 30 min and resting for 6 h at ambient temperature. After suck filtration the purified filtrate was collected. At 70 °C, the filtrate was isothermally evaporated and condensed under continuous stirring. When the density of the concentrated solution approached to 1.30 g ml^{-1} and the pH value to 6, the careful observation to the solution was required. Once plenty of superfine crystal grains were found and the solution turned to milky white suspension, it was necessary to immediately add proper quantity of the diluted aqueous ammonia so as to eliminate the milky white appearance, until transparent fine crystal grains were clearly seen. During the crystallizing process, repeatedly adding aqueous ammonia was required according to the solution change. As the volume of the condensed solution dropped to 60% with respect to the initial amount, the evaporation–crystallization course was terminated. At that moment, the addition of the diluted aqueous ammonia for the last time was carried out, and the added amount was about 1% of the current volume of the condensed solution. After vacuum filtration, the collected filter cake was dried at 80 °C for 5 h, and transparent crystals were achieved. The direct recovery efficiency of ADM was up to 80–90%.

3. Results and discussion

3.1. XRD analysis of the ADM samples

Fig. 1 gives XRD patterns of as-prepared ADM samples. It is found that the XRD patterns are consistent with the standard powder diffraction file card (ICDD PDF card No. 37–0379) of ADM. The corresponding diffraction peaks can be indexed, just as shown in Fig. 1. Among them the crystal face indexes (1 0 0), (−1 0 1), (1 1 −1), (1 1 1), (2 1 0), (−2 2 1), (0 −2 1), (0 −1 2) and (3 2 −2) stand for the characteristic diffraction peaks of ADM crystals. No other peaks stemmed from impurities appear. Moreover, the strong, sharp diffraction peaks imply the well-crystallized ADM crystal that is assigned to triclinic system (P-1 (2)). According to Scherer's formula: $d = K\lambda/(B\cos\theta)$, where λ is wavelength of X-ray; θ and B are Bragg diffraction angle and FWHM of (−1 0 1) crystal face, respectively; K is constant (0.89), the mean size of ADM crystal grains is calculated to be ca. 340 μm.

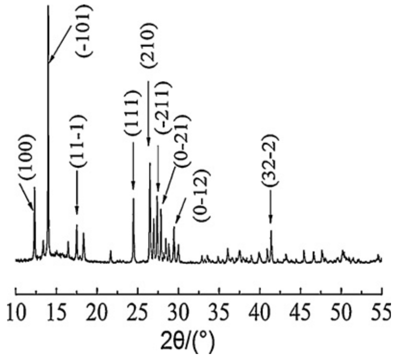

Fig. 1. XRD patterns of the ADM sample.

3.2. Morphology of the ADM samples

Fig. 2 shows the optical micrographs of the ADM samples. It is clearly seen that the sample is transparent crystal with relatively regular geometric shape and clear interface. In addition, the crystals are well dispersed. The statistical average of crystal size is about 330 μm, which is consistent with the calculated values from XRD patterns.

3.3. FT-IR analysis of the ADM samples

Fig. 3 displays the FT-IR spectra of the uniform-crystal ADM samples. The analysis based on the spectra and related literatures [9,10] suggests that two weak absorption peaks at 3446 cm^{-1} and 1662 cm^{-1} can be respectively attributed to stretching and bending vibration absorption of H–O–H bond from trace water contained in the samples. Both 3170 cm^{-1} and 3022 cm^{-1} peaks are ascribed to the stretching vibration of N–H bond in NH_4^+ group, but the strong peak at 1394 cm^{-1} results from the N–H bending vibration. In fingerprint region from 470 cm^{-1} to 1000 cm^{-1} some characteristic peaks relating to isopolymolybdate $Mo_2O_7^{2-}$, such as 884 cm^{-1}, 682 cm^{-1} and 476 cm^{-1} peaks, simultaneously arise, even though they are weak. Among them, the former stems from the stretching vibration of Mo=O (terminal group), and the latter both should be assigned to the flexural vibration of Mo–O–Mo group.

3.4. Thermal analysis of ADM samples

During heating reduction process of ADM, different pyrolysis reactions will take place, resulting in emergence of diverse intermediates, also affecting the physicochemical properties of the end product-molybdenum powders. Therefore, extensive

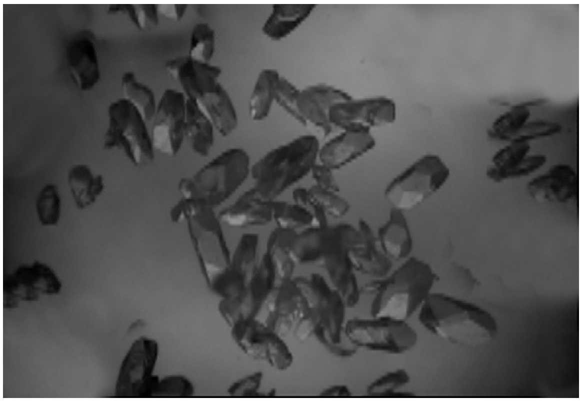

Fig. 2. The OM picture of the ADM sample.