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Preparation of Mo nanopowders through hydrogen reduction of a combustion synthesized foam-like MoO_2 precursor

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ABSTRACT

In this work, Nano-sized Mo particles were fabricated by solution combustion synthesis (SCS) followed by hydrogen reduction. A foam-like MoO_2 precursor was first assembled using 20–30 nm nanoparticles generated by SCS. Subsequently, hydrogen reduction of the foam-like MoO_2 precursor was undertaken to prepare the nano-sized Mo particles. The reduction temperature of the final phases and morphologies of the Mo products were then systematically investigated. The hydrogen reduction mechanism of the foam-like MoO_2 precursor was analyzed using thermogravimetry analysis (TG) and H_2 temperature programmed reduction with MS analysis (H_2-TPR-MS). The results show that the nano-sized and irregularly-shaped 60–80 nm Mo particles were successfully synthesized at 600 °C for 2 h. Increasing the temperature to 650 °C–700 °C produced larger Mo particles due to sintering of the Mo powder at a higher reduction temperature. Additionally, a Mo_2C impurity formed as a result of the carbon-thermal reaction between residual carbon and MoO_2 in the presence of hydrogen.

1. Introduction

Molybdenum (Mo) is widely used as an alloying agent for manufacturing steel, cast iron, structural and electronic materials, and superalloys due to its high temperature strength, creep resistance, low coefficient of thermal expansion, and high thermal conductivity. For this reason, the fabrication of molybdenum powders with suitable morphology, size, and purity has been extensively studied in an effort to obtain materials with better performance. In recent years, nano-sized Mo powder has been reported to exhibit attractive properties due to its ultrahigh specific surface area and instability of free surface [1–4]. To form nano-sized Mo powder, many advanced synthesis strategies have been applied, such as a molten salt technique [5], carbothermal reduction [6], hydrogen reduction [7, 8], microwave assisted combustive reduction [9], and electroreduction [10]. Huang et al. reported a novel molten salt technique to synthesize pure molybdenum nanoparticles (NPs) with a crystalline size of roughly 46 nm [5]. Hoseinpur et al. prepared nano-sized Mo nanoparticles by zincothermic reduction of MoO_3 [9, 11]. However, these techniques are complicated and costly to perform due to multi-step procedures, the need for specialized equipment, and a high reduction temperature. Therefore, low temperature, facile methods for the synthesis of nano-sized Mo powder are highly desirable.

Solution combustion synthesis (SCS) is a versatile, energy-efficient, and mass production method that has been used to fabricate several types of nano-sized oxides with different physical and chemical properties [12–15]. Recently, 20–30 nm particle size tungsten nanopowder was prepared by SCS and hydrogen reduction [16]. In our previous work, foam-like MoO_2 nanoparticles assembled by 20–30 nm nanoparticles were successfully fabricated by SCS [17]. To the best of our knowledge, the synthesis of nano-sized Mo powder using a MoO_2 precursor obtained by SCS has not been reported. Thus, herein, we propose a facile SCS method, followed by hydrogen reduction strategy to synthesize nano-sized Mo powder. First, foam-like MoO_2 precursor assembles with nanoparticles were fabricated by SCS. Subsequently, hydrogen reduction with different temperatures was performed to prepare the Mo products. Finally, the hydrogen reduction mechanism is analyzed to shed light on the hydrogen reduction process.

2. Experimental section

2.1. Starting materials

Hexaammonium molybdate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, AHM), ammonium nitrate (NH_4NO_3), and glycine were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All chemicals were of analytical

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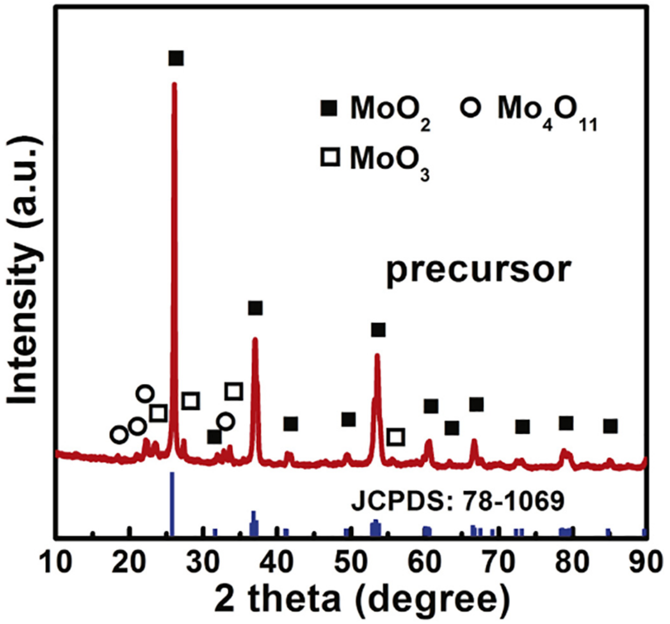

Fig. 1. XRD patterns of foam-like MoO_2 precursor synthesized by SCS.

grade, commercially available, and used as received without further purification.

2.2. Synthesis of MoO_2 precursor

The precursor was synthesized using a solution combustion synthesis method. First, 0.01 mol AHM, 0.2 mol NH_4NO_3, and 0.10 mol glycine were dissolved in 100 mL deionized water with magnetic stirring until a homogeneous solution was obtained. The solution was then poured into a 1000 mL beaker and heated in air using a temperature-controlled electric heating furnace. During heating, the solution evaporated and a gelatinous mass formed. With further heating, the gelatinous mass expanded and a smoldering combustion reaction occurred, accompanied by the evolution of gas. After several minutes, the black, foam-like MoO_2 precursor was obtained. The synthesis process mentioned above was well in accordance with previous report [17].

2.3. Hydrogen reduction process

Mo powders were prepared from the foam-like MoO_2 precursor by a one-step hydrogen reduction process in a tubular furnace. A strict temperature program was followed in all runs with a constant heating rate (10 °C/min) up to a target temperature (500 °C, 550 °C, 600 °C, 650 °C, and 700 °C). The dwelling time at the target temperature was 2 h. Subsequently, the reduced precursors were cooled naturally to room temperature. In all experimental runs, 100 mL/min of H_2 (99.99%) was maintained during hydrogen reduction.

2.4. Characterization

The crystalline nature of the products were confirmed using an X-ray diffractometer (Rigaku, D/max-RB12, Japan) with Cu $K\alpha$ radiation, and a 2θ angle from 10° to 90° with 0.02° increments. The resulting XRD patterns of the precursor and the products reduced at 600 °C, 650 °C, and 700 °C were refined by Rietveld method using the GSAS and EXPGUI software [18, 19]. Thermogravimetry analysis (TG) was performed on a TG instrument (NETZSCH, STA 449F3, German) using approximately 20 mg of product with a heating rate of 10 °C/min in 20 mL/min H_2. The morphology and size distribution of the products were characterized by field emission scanning electron microscopy (Zeiss, ULTRA 55, German). Transmission electron microscopic images (TEM) and high resolution transmission electron microscopic images (HRTEM) were taken on a transmission electron microscope (FEI, Tecnai G2 F20, USA) with an acceleration voltage of 200 kV. The carbon content in the precursor and Mo products were measured with a Carbon/Sulfur analyzer (LECO TC-436), and their oxygen content was determined with an Oxygen/Nitrogen analyzer (LECO CS-444). H_2 temperature programmed reduction experiments (H_2-TPR-MS) were conducted on a Micromeritics AutoChem II 2920 Chemisorption Analyzer equipped with a TCD detector and mass spectrometer using hydrogen with a flowing rate of 20 mL/min from room temperature to 780 °C.

3. Results and discussion

3.1. Phases and morphology of precursor

Fig. 1 shows the XRD patterns of the precursor synthesized by SCS. The main diffraction peaks can be readily indexed as monoclinic MoO_2 (JCPDS: 78–1069). The sharp and intense nature of the peaks suggests that the material is highly crystalline. Trace Bragg reflections corresponding with MoO_3 and Mo_4O_{11} are also observed in the XRD patterns, which may have formed as a result of oxidation at the MoO_2 particle surface in air. XRD patterns of the foam-like MoO_2 precursor are also analyzed using the Rietveld refinement method. Fig. 4(a) shows the Rietveld refined XRD patterns for the precursor. The results of refinement are listed in Table 1. The low values of R_{wp}, R_p, and x^2 indicate a good fit in final refinement. The phase fraction of MoO_2 in the precursor based on the refined scale factors is 89.2 wt%. The refined lattice parameters and unit volume are $a = 5.624\,Å$, $b = 4.852\,Å$, $c = 5.545\,Å$, $\alpha = \gamma = 90°$, $\beta = 119.56°$, and $V = 131.639\,Å^3$, which are in good agreement with previous report [20]. As shown in Table. 2, the grain sizes of the MoO_2 precursor calculated using Scherrer's equation and Rietveld method are 21.7 nm and 17.6 nm, respectively.

To further study the morphologies and microstructures of the synthesized precursor, FE-SEM and TEM measurements were undertaken, the results of which are shown in Fig. 2. The precursor has a foam-like morphology as shown in Fig. 2(a), which is characteristic of products

Table 1
Phase fraction, lattice parameters, unit volume and refinement factors of MoO_2 precursor and Mo products obtained using the Rietveld refinement method.

Sample	MoO_2 precursor	Products reduced at different temperatures		
		600 °C	650 °C	700 °C
Phase fraction	MoO_2 = 83.6 wt%	Mo = 100 wt%	Mo = 87.6 wt%	Mo = 87.8 wt%
a, b, c (Å)	5.624, 4.852, 5.545	3.146, 3.146, 3.146	3.152, 3.152, 3.152	3.153, 3.153, 3.153
α, β, γ (°)	90, 119.56, 90	90, 90, 90	90, 90, 90	90, 90, 90
Unit volume (Å^3)	131.639	31.143	31.333	31.344
R_{wp}	0.0789	0.0805	0.1103	0.1061
R_p	0.0592	0.0614	0.0924	0.0851
x^2	2.091	1.839	1.941	1.438