Synthesis of Molybdenum Nitrides

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Abstract—We have studied the effect of precursors on the synthesis conditions and characteristics of molybdenum nitrides. Mo, MoO₃, and MgMoO₄ powders were nitrided in flowing ammonia at temperatures in the range 500–800°C. The use of molybdenum nanopowder as a precursor has made it possible to reduce the synthesis temperature and time. We have demonstrated the possibility of direct ammonolysis of the double oxide MgMoO₄. Using this molybdate, we have obtained a material with a specific surface area up to 29 m²/g, which is a factor of 2 to 3 larger than that reached by nitriding MoO₃. In all cases, the synthesis products consisted of the γ - and β -phases of Mo₂N, with cubic and tetragonal lattices, respectively.

Keywords: nitridation, molybdenum, molybdenum trioxide, magnesium molybdate, molybdenum nitride, ammonia

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INTRODUCTION

Technological progress is impossible without using novel functional materials, for example, such as transition metal nitrides [1]. One of them is molybdenum nitride, Mo₂N. It exists in two polymorphs: tetragonal (β) and face-centered cubic (γ) [2]. Mo₂N is thought to be a promising catalyst for a variety of processes, including ammonia synthesis, hydrodesulfurization (HDS) of fuel, and oil hydrodenitrogenation (HDN) [3–5].

There are several ways of preparing molybdenum nitride powders. Verkhoglyadova et al. [6] examined the feasibility of preparing nitrides via nitrogenation of metallic molybdenum powder with an average particle size in the range $2-7 \mu m$. An attempt to prepare nitrides in a nitrogen atmosphere at temperatures from 400 to 1000°C was unsuccessful. Nitrogenation in flowing ammonia for 4 h at a temperature of 700°C yielded the Mo₂N nitride containing 6.8% nitrogen. There are several processes for Mo₂N synthesis with the use of molybdenum pentachloride as a precursor [7–9]. O'Loughlin et al. [7] prepared γ -Mo₂N by reacting MoCl₅ with Ca₃N₂ at a pressure of 57 kbar. The addition of 3 mol NH₄Cl to the starting mixture allowed a crystalline nitride to be obtained at normal pressure. Nanocrystalline γ -Mo₂N with an average particle size of 30 nm was obtained by reacting metallic sodium with anhydrous MoCl₅ and NH₄Cl in an autoclave at a temperature of 550°C [8]. Choi and Kumta [9] synthesized MoN_x nanoparticles via ammonolysis of molybdenum pentachloride in dehydrated chloroform for 8 h. Next, the solvent was evaporated at a temperature of 100°C in flowing dry ammonia. The reaction product was heat-treated at temperatures from 600 to 800°C in an ammonia atmosphere for 10 h. As the heat treatment temperature was raised from 600 to 800°C, x decreased from 1.321 to 0.769 and the specific surface area of the material dropped from 49 to 16 m²/g.

Despite the diversity of approaches, the main process for the synthesis of molybdenum nitrides is MoO_3 ammonolysis because it is relatively easy to implement [10–13]. Choi et al. [10, 11] used a temperature-programmed reaction, that is, heating at a constant rate. MoO₃ was heated in flowing ammonia from room temperature to 623 K over a period of 0.5 h. The heating rate was 40 or 100 K/h from 623 to 732 K and 100 or 200 K/h at higher temperatures, up to 973 K. The holding time at the final temperature was 1 h. The resultant product was further heat-treated in flowing hydrogen at a temperature of 673 K for 3 h. It consisted of γ -Mo₂N powder, occasionally with a small amount of Mo or MoO₂ impurities. Its specific surface area varied from 4 to 116 m²/g, depending on ammonolysis conditions. Mckaya et al. [12] prepared the molybdenum nitrides $\gamma\text{-}Mo_2N$ and $\beta\text{-}Mo_2N_{0.78}$ using MoO_3 as a precursor. γ -Mo₂N was synthesized in flowing NH₃ at a heating rate of 5.6°C/min below 357°C, 0.5°C/min in the range 357–447°C, and 2.1°C/min at higher temperatures, up to 785°C. The holding time at



Fig. 1. Schematic of the experimental apparatus for nitridation: (1) ammonia cylinder, (2) pressure gage, (3) fine control valve, (4) rotameter, (5) quartz reactor, (6) boat containing the material, (7) resistance furnace, (8) ammonia inlet tube, (9) shields, (10) thermocouple, (11) Termodat-13K2, (12) flask, (13) water seal.

the final temperature was 5 h. The specific surface area of the resultant γ -Mo₂N was 85 m²/g. β -Mo₂N_{0.78} was synthesized by treating MoO₃ in a flowing mixture of H₂ and N₂ in the ratio 3 : 1 at a temperature of 700°C for 2 h. The specific surface area of the nitride thus obtained was 9 m²/g. The Mo₃N₂ nitride in the form of nanowire with a mesoporous structure and a specific surface area of 45 m²/g was prepared via ammonolysis of MoO₃ nanowire in a tubular furnace at a temperature of 700°C and holding time of 3 h [13]. According to Lee et al. [13], the mesoporous structure of the nitride was due to the transformation of the structure of the metal oxide to that of the nitride, which led to pore formation in the material.

The use of metal nanopowders as precursors for the synthesis of nitrides in flowing ammonia makes it possible to considerably lower the temperature of the process and reduce its duration [14, 15]. Because of this, it was of interest to study conditions for nitriding molybdenum nanopowders prepared via magnesio-thermic reduction of double molybdenum oxides [16] and examine the feasibility of preparing nitrides with an increased specific surface area via direct ammonolysis of a double molybdenum oxide.

EXPERIMENTAL

The starting chemicals used for nitridation were molybdenum powder with a specific surface area of $4.8 \text{ m}^2/\text{g}$ (calculated particle size of 130 nm), prepared by magnesiothermic reduction of calcium molybdate; the MgMoO₄ molybdate synthesized via sintering [17]; and reagent-grade MoO₃ as a reference precursor. The specific surface area of the MoO3 and MgMoO₄ was 0.4 and 1.5 m^2/g , respectively. We used a reactor (Fig. 1) in the form of a quartz ampule 40 mm in diameter and 700 mm in length. Quartz boats containing the material were placed in a uniformly heated zone of the furnace. The temperature was measured by a Chromel-Alumel thermocouple, whose hot junction was located over the boat containing the material. The temperature and heating rate were maintained constant by a Termodat-13K2 temperature controller. The experimental procedure was described in detail previously [14].

During the nitridation process, the temperature was raised to $500-800^{\circ}$ C at a rate of 8 K/min. The holding time at the highest temperature was varied from 1 to 5 h. The ammonia flow rate was 150–200 mL/min. After the heat treatment, the retort was withdrawn from the furnace and the reaction products



Fig. 2. (a) Nitrogen content and (b) specific surface area as functions of molybdenum powder nitridation temperature (holding for 1 h).

were cooled in flowing ammonia. Cooling to a temperature of 100°C took 15 min.

The residual MgO in the reaction products obtained with the use of MgMoO₄ as a precursor was removed by double leaching with a 10% HCl solution for 1.5 h in each step. The nitride powder was washed with distilled water until neutral solution pH was reached, and then dried at a temperature of 70°C for 8 h.

The phase composition of the reaction products was determined by X-ray diffraction on a DRF-2 diffractometer (Cu K_{α} radiation, graphite monochromator). The phases present were identified using the JCPDS-ICDD PDF-2 database (release 2002). Structural parameters were refined by the Rietveld method using a DRON-4 automatic X-ray diffractometer and the Inorganic Crystal Structure Database (ICSD) (Karlsruhe, release 2017). The specific surface area and porosity parameters were determined by static BET adsorption measurements and the Barrett-Joyner–Halenda (BJH) method, respectively, with a Micromeritics TriStar II 3020 analyzer. Oxygen and nitrogen concentrations were determined by gas adsorption chromatography in combination with pulsed heating on a K-671 analyzer.

RESULTS AND DISCUSSION

Reactions of molybdenum powder and molybdenum oxide compounds with ammonia can proceed according to the following schemes:

$$8Mo + 4NH_3 = 4Mo_2N + 6H_2^{\dagger},$$
(1)

$$2Mo + 2NH_3 = 2MoN + 3H_2^{\dagger}$$
, (2)

$$4\text{MoO}_3 + 8\text{NH}_3 = 2\text{Mo}_2\text{N} + 12\text{H}_2\text{O} + 3\text{N}_2^{\dagger}, \quad (3)$$

$$4MgMoO_4 + 8NH_3 = 2Mo_2N + 4MgO + 12H_2O + 3N_2^{\uparrow}.$$
(4)

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Nitridation of molybdenum powder. Figure 2 shows the percentage of nitrogen in the molybdenum powder nitridation products and their specific surface area as functions of process temperature. The nitrogen content of the powder was 3.9% after just 1 h of nitrogenation at a temperature of 500°C and reached a maximum as the synthesis temperature was raised to 600°C (Fig. 2a). The specific surface area of the nitrides synthesized in the range 500-700°C was at the level of the starting molybdenum powder and decreased slightly as the temperature was raised to 800°C (Fig. 2b). Figure 3 shows X-ray diffraction patterns of the starting molybdenum powder and the synthesis products obtained at different temperatures. Even after nitrogenation for 1 h at a temperature of 500°C, we observed weak, broad peaks of new phases: tetragonal phase β -Mo₂N and face-centered cubic phase γ -Mo₂N (Fig. 3, scan 2). With increasing nitrogenation time and temperature, the intensity of the reflections from the nitride phases increased, and that of the reflections from Mo decreased. After nitrogenation for 3 h at a temperature of 800°C, no peaks corresponding to Mo were detected (Fig. 3, scan 5).

Table 1 summarizes data on the structure and phase composition of the Mo nitrogenation products in relation to synthesis conditions. The absence of the β -Mo₂N phase in the sample obtained by nitrogenation for 2 h at a temperature of 800°C can be accounted for by the fact that it contains 9% nitrogen. A second phase in it is the hexagonal nitride δ_3 -MoN. Its structure is distinctive in that is contains ordered defects in the nitrogen sublattice. The nitrogen atoms occupy every other trigonal prismatic interstice built from layers of metal atoms. The presence of such defects is evidenced by the superstructure reflections from this phase, marked by arrows, in scan 5 (Fig. 3) [18].

Nitridation of oxide compounds. Table 2 presents the percentages of nitrogen and oxygen in the samples obtained by nitriding MoO_3 and $MgMoO_4$ and their



Fig. 3. X-ray diffraction patterns of the Mo powder (1) and the samples obtained by nitriding it at 500 (2, 3) and 800°C (4, 5) for 1 (2, 4) and 3 h (3, 5).

specific surface area (*S*) and phase composition in relation to process conditions. Their X-ray diffraction patterns are shown in Figs. 4 and 5. The composition of the samples obtained by nitriding MoO_3 at a temperature of 600°C suggests that the process involves two steps. First, the hydrogen released as a result of ammonia decomposition reduces MoO_3 to MoO_2 , and then nitrogen substitutes for the oxygen in this oxide. Table 3 presents detailed data on the structure and phase composition of the samples obtained by MoO_3 ammonolysis.

Nitriding MgMoO₄ at a temperature of 500°C for 2 h produced no changes in the phase composition of the starting material (Table 2). At the same time, the reaction products obtained by nitridation at a temperature of 600°C for just 1 h contained the Mo₂N phase (Fig. 5a, scan 1). After the nitridation time was increased to 2 h, all of the molybdenum in the composition of the compound formed the γ -Mo₂N nitride (Fig. 5a, scan 2). The X-ray diffraction patterns of the samples obtained at a higher temperature are shown in Fig. 5b. The Rietveld-refined phase composition and lattice parameters of the samples obtained by nitriding MgMoO₄ are presented in Table 3.

Analysis of characteristics of the samples obtained by nitriding all three precursors indicated that essentially all of them consisted of a mixture of the β - and γ -Mo₂N phases. The high-temperature phase γ -Mo₂N is present even in the samples prepared by nitriding the molybdenum powder at a temperature of 500°C. This is consistent with data reported by Ettmayer [19], who showed that increasing the nitrogen content of the nitride from 28.7 to 34.5 at % (from 5.54 to 7.13 wt %) led to a decrease in the temperature of the β -Mo₂N \leftrightarrow γ -Mo₂N phase transition from 800 to 400°C. The presence of the high-temperature phase γ -Mo₂N can be accounted for by two factors: the slow kinetics of the transformation of the γ -phase to the β -phase and the decrease in the degree of order in the nitrogen sublattice with increasing nitrogen content. At 34.5 at % N, the tetragonal lattice of the nitride transforms into a cubic one [19].

We call attention to the high oxygen content, especially in the molybdate nitridation products. At the same time, no oxide phases were detected. It seems likely that a considerable fraction of the oxygen detected by analysis was sorbed on the surface of the nitride powder. This is confirmed by the fact that the lattice parameters of the nitrides are similar to those of references. In addition, nitrogen sorption on the surface is probably responsible for the fact that, despite the presence of excess nitrogen with respect to the Mo_2N nitride in a number of samples, no MoN was detected.

The pore structure of the synthesized samples depends significantly on the precursor used. Figure 6 shows typical sorption curves. The curves of the samples obtained by nitriding Mo and MoO₃ (Figs. 6b, 6c) are similar in shape to type II in the IUPAC classification, characteristic of macroporous materials [20]. The hysteresis loop is similar in shape to type *D*, typical of materials containing V-shaped pores. The samples prepared by MgMoO₄ ammonolysis have a radically different pore structure. Their sorption curves

SYNTHESIS OF MOLYBDENUM NITRIDES

Phase	ICSD no.	Sp. gr.	a, Å		<i>c</i> , Å					
			ICSD	meas	ICSD	meas	WT %			
Starting Mo										
Мо	52267	Im3m	3.14737	3.146	-	_	100			
Nitrogenation at 500°C, 1 h										
Мо	52267	Im3m	3.14737	3.1460(6)	-	-	71			
β -Mo ₂ N	30 5 9 3	$I4_1/amd$	4.2	4.2318(2)	8.0	7.9451(2)	16			
γ -Mo ₂ N	172802	Fm3m	4.16158	4.1714(5)	-	· —	13			
Nitrogenation at 500°C, 5 h										
Мо	52267	Im3m	3.14737	3.1424(8)	-	_	58			
$\beta - Mo_2N$	30 5 9 3	$I4_1/amd$	4.2	4.2261(8)	8.0	7.9798(1)	21			
γ -Mo ₂ N	172802	Fm3m	4.16158	4.1887(9)	-	-	21			
Nitrogenation at 800°C, 1 h										
Мо	52267	Im3m	3.14737	3.1468(9)	-	_	3			
β -Mo ₂ N	30 5 9 3	$I4_1/amd$	4.2	4.2126(1)	8.0	8.0443(4)	29			
γ -Mo ₂ N	172802	Fm3m	4.16158	4.1828(5)	-	-	68			
Nitrogenation at 80°C, 2 h										
γ -Mo ₂ N	172802	Fm3m	4.16158	4.1710(2)	-	_	70			
δ_3 -MoN	99452	<i>P</i> 6 ₃ <i>mc</i>	5.73659	5.7424(3)	5.6188(4)	5.6205(7)	30			

Table 1. Phase composition and structural parameters of the molybdenum powder nitrogenation products

Table 2. Composition of the samples obtained by nitriding MoO_3 and $MgMoO_4$

Precursor	t, °C	τ, h	wt % N	wt % O	<i>S</i> , m ² /g	Phases
	600	1	_	_	_	MoO ₂
		3	2.5	>12	2.6	MoO ₂ , Mo ₂ N
MoO ₃	700	1	7.2	_	6.6	Mo ₂ N, MoN
		3	6.9	_	_	Mo ₂ N, MoN
	800	2	6.5	2.1	11	Mo ₂ N, Mo
	500	2	_	_	_	MgMoO ₄ *
	600	1	_	_	_	MgMoO ₄ *, MgO, Mo ₂ N
MgMoO	600	2	4.2	5.2	_	Mo ₂ N
Wigivio04	700	2	7.7	8.1	14.3	Mo ₂ N
	800	1	8.1	3.4	22.3	Mo ₂ N
	800	2	5.6	5.1	29	Mo ₂ N

* Phase composition of the reaction products before leaching.



Fig. 4. X-ray diffraction patterns of the samples obtained by nitriding MoO_3 (*1*) at 600 °C for 3 h, (*2*) at 700°C for 1 h, and (*3*) at 800°C for 3 h.



Fig. 5. X-ray diffraction patterns of the samples obtained by nitriding MgMoO₄ at temperatures of (a) 600 and (b) 800°C for (1) 1 and (2) 2 h.

SYNTHESIS OF MOLYBDENUM NITRIDES

Phase	ICSD no.	Sp. gr.	<i>a</i> , Å		<i>c</i> , Å		wt %		
Thase			ICSD	meas	ICSD	meas	vvi /0		
Nitrogenation of MoO ₃ , 700°C, 1 h									
γ -Mo ₂ N	172802	$Fm\overline{3}m$	4.16158	4.16669	-	_	91		
$\delta_3\text{-}Mo_2N$	99452	$P6_3mc$	5.73659	5.73652	5.6188(4)	5.60233	9		
Nitrogenation of MoO ₃ , 800°C, 2 h									
Mo	52267	Im3m	3.14737	3.14873	-	_	3		
γ -Mo ₂ N	172802	$Fm\overline{3}m$	4.16158	4.17926	-	-	97		
Nitrogenation of MgMoO ₄ , 800°C, 1 h									
γ -Mo ₂ N	172802	Fm3m	4.16158	4.1768(5)	-	_	100		
Nitrogenation of MgMoO ₄ , 800°C, 3 h									
β -Mo ₂ N	30 5 9 3	$I4_1/amd$	4.2	4.2006(3)	8.0	8.0739(2)	35		
γ -Mo ₂ N	172802	$Fm\overline{3}m$	4.16158	4.1725(6)	-	-	65		

Table 3. Phase composition and structural parameters of the MoO₃ and MgMoO₄ nitridation products



Fig. 6. Sorption curves of the Mo powder (a) and the nitrides obtained under standard conditions using Mo (b), MoO_3 (c), and $MgMoO_4$ (d) as precursors.

also correspond to type II, but there is negligible hysteresis (Fig. 6d). The pore volume ranges from 0.1 to $0.18 \text{ cm}^3/\text{g}$. This is more than five times the pore volume in the samples prepared by nitriding Mo and MoO₃. The distinction is due to the additional macropores produced by the leaching of the magnesium oxide in the composition of the molybdate.

CONCLUSIONS

We have studied the composition of materials prepared by nitriding metallic molybdenum powder, molybdenum trioxide, and the MgMoO₄ molybdate in flowing ammonia between 500 and 800°C. The use of molybdenum nanopowder with a specific surface area of 4.8 m²/g (calculated particle size of 130 nm) as a precursor has made it possible to prepare a material containing on the order of 8% nitrogen by nitrogenation at a temperature of 600°C for just 1 h. This result demonstrates an advantage of the method used: in the case of molybdenum powder ranging in particle size from 2 to 7 μ m, nitrogenation for 4 h at a temperature of 700°C was needed [6].

Ammonolysis of the MoO_3 oxide has been shown to involve two steps. First, it is reduced to MoO_2 , and then nitrogen substitutes for the oxygen in this oxide to give a nitride. A material containing 7% nitrogen was obtained by nitrogenation for 1 h at a temperature of 700°C. The sorption curves of the nitrides obtained by nitriding Mo and MoO_3 are similar in shape to type II in the IUPAC classification, characteristic of macroporous materials.

The present results demonstrate for the first time the feasibility of preparing molybdenum nitrides by nitriding the double oxide MgMoO₄ in flowing ammonia. Using this oxide as a precursor instead of MoO₃ has made it possible to increase the specific surface area of the nitridation products by a factor of 2 to 3. The presence of additional magnesium oxide layers in nitrided particles has led to changes in the pore structure of the nitride after leaching, an effect observed for the first time. The sorption curves of this material also correspond to type II, but there is negligible hysteresis.

The phase composition of the materials obtained at 700 and 800°C is typically a combination of the low-temperature tetragonal nitride β -Mo₂N and the high-temperature face-centered cubic phase γ -Mo₂N. The relative amounts of these phases depend on the synthesis temperature and the percentage of nitrogen in the nitride.

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