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Preparation of High-Surface-Area Transition-Metal Nitrides: Mo_2N and MoN

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The reactions of ammonia with MoO_3, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $(NH_4)_2MoO_4$, and H_xMoO_3 to produce MoN and Mo_2N with high surface areas have been studied. Thermogravimetric analysis (TGA) and in situ X-ray diffraction (XRD) were used to follow the reaction pathway and determine the structure of the reaction intermediates and products. The surface areas of the starting materials, intermediates, and products were determined by using the BET method. The results show that all four reactants form the same oxynitride intermediate; this oxynitride converts directly to a nitride. The temperature at which the oxynitride reacts to form the nitride determines the phase; fcc Mo_2N is formed at higher temperatures than hexagonal MoN. When the reactants and products are pseudomorphous, the products have a high surface area, near 57 m^2/g. This is the case for the reactions of MoO_3 and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ with ammonia. In contrast, the product from the reaction of $(NH_4)_2MoO_4$ with ammonia has a surface area of only 17 m^2/g. H_xMoO_3 reacts with ammonia to form nitride products with higher surface areas (between 65 and 84 m^2/g) compared with MoO_3. In addition, MoO_2 is not formed when H_xMoO_3 reacts with ammonia, in contrast to MoO_3.

Introduction

Transition-metal carbides and nitrides have catalytic activity for ammonia synthesis[1] and for reactions traditionally catalyzed by noble metals.[2–6] In addition, recent research indicates that nitrides, such as Mo_2N, show promise as hydrodenitrogenation catalysts.[7] For these reasons, carbides and nitrides have attracted attention as alternatives to noble-metal catalysts. If these materials are to be used as catalysts, they must be prepared with high surface areas. Unfortunately, transition-metal carbides and nitrides prepared by classical high-temperature synthesis routes[8] have very low surface areas, typically less than 1 m^2/g. In this paper, synthetic routes that yield molybdenum nitrides with high surface areas are described.

Recently, Boudart[9] reported that the reaction of MoO_3 with ammonia can produce Mo_2N with a surface area in excess of 200 m^2/g. He described the reaction as a "topotactic transformation" with conservation of the two-dimensional layers of the oxide precursor in the nitride product. This description is not complete, as the reaction involves the breaking of all of the intralayer bonds to remove the oxygen. In this study, the reaction of ammonia with MoO_3 is investigated further and is compared with the reactions of ammonia with related starting materials, including $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (ammonium paramolybdate), $(NH_4)_2MoO_4$ (diammonium molybdate), and H_xMoO_3 (hydrogen molybdenum bronze). The primary interest is to compare the reaction pathways to determine the relationships between the structure and stoichiometry of the starting materials and intermediates and the phase, surface area, and morphology of the product.

The products of traditional routes for synthesizing nitrides[8] are materials with low surface areas because of sintering at the high reaction temperatures. To avoid sintering, it is desirable to form the nitrides at low temperatures. For this purpose, the starting materials were chosen because they readily intercalate and/or react with ammonia at low temperatures. Indeed MoO_3, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and $(NH_4)_2MoO_4$ have been shown to react with ammonia at room temperature.[10–12] Because ammonia has a high mobility in these three reactants, the reaction with ammonia to form the nitride should occur homogeneously within the reactant particles. In contrast, classical high-temperature synthesis routes occur inhomogeneously and are limited to the surfaces of the reactant particles; higher temperatures and longer times are required for complete reaction.

Previous work has shown that the reaction between the starting materials chosen for this study with ammonia yields molybdenum nitrides. Hegedus et al.[13] reported the formation of molybdenum nitride phases from the reaction of MoO_3 and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ with ammonia. Lyutaya reported that the nitridification of MoO_3 with ammonia begins at temperatures under 400 °C. He found the formation of an oxynitride enroute to forming a nitride product.[14] Bliznakov et al.[15] discussed the nitriding of MoO_3, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and H_2MoO_4 with ammonia. The nitride phase depended on the temperature, duration of nitriding, and gas flow rate.

The formation of both fcc Mo_2N and hexagonal MoN by nitriding molybdenum oxides and ammonium oxides has been reported. As is evident from the binary phase diagram constructed by Hag,[16] these are the two stable nitrides of molybdenum at room temperature. Both phases have a narrow stoichiometry range, within 1–2 at. % nitrogen. In fcc Mo_2N, the metal atoms are arranged in a face-centered cubic array, with nitrogen atoms occupying half the octahedral holes randomly.[16] The molybdenum atoms in MoN are in a hexagonal array with nitrogen

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Table I. Products of the Reactions of Molybdenum Oxides, Ammonium Molybdates, and Hydrogen Molybdenum Bronzes with Ammonia

starting material	final product(s) (XRD)	final surface area, m^2/g
MoO_3	Mo_2N	57.2
$H_{0.04}MoO_3$	Mo_2N	57.5
$H_{0.13}MoO_3$	Mo_2N	65.0
$H_{0.31}MoO_3$	Mo_2N	65.5
$H_{0.80}MoO_3$	Mo_2N + MoN	83.8
$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	Mo_2N + MoN	56.9
$(NH_4)_2MoO_4$	MoN	16.5
MoO_2	Mo_2N + MoN	6.3

atoms in all the octahedral interstices.[17]

In this paper, our emphasis is on understanding the conditions necessary to produce nitrides with surface area in excess of 50 m^2/g. TGA/DTG, high-temperature XRD, BET surface-area analysis, and SEM were used to monitor the reaction pathways. The intermediates formed during the reactions and the products were identified by TGA/DTG and by XRD; powder X-ray diffraction patterns were obtained in situ as the reactants were exposed to ammonia at various temperatures. To determine when during the reaction the surface area increased from the low area of the reactant to the high area of the product, surface areas were measured as a function of reaction temperature. From these studies, we correlate the reaction pathway with the phase and surface area of the product and thereby evaluate the parameters that are important for the synthesis of high-surface-area materials. The reaction products and surface areas are summarized in Table I.

Experimental Section

Materials. MoO_3 (99.998%) and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (99.999%) were purchased from Alfa Chemicals and Mallinckrodt, Inc., respectively, and used without further purification. In addition, a sample of MoO_3 was synthesized by using the method described by Fransen et al.;[18] this sample was designated MoO_3–AM. MoO_2 was synthesized by the reduction of MoO_3 in a 3.55% H_2/Ar mixture at 600 °C for 1 day.[19] $(NH_4)_2MoO_4$ was prepared exposing MoO_3–AM to liquid ammonia in a dry ice-acetone bath for 4 h or to gaseous ammonia at 25 °C for 1 week. No H_2O was added to the NH_3 since the tank of high-purity ammonia (Matheson, 99.99%) was contaminated with enough water to produce the desired product. The X-ray powder pattern showed that the final product was homogeneous. A series of hydrogen molybdenum bronzes, H_xMoO_3, were prepared by the reduction of MoO_3 with Zn metal and HCl as originally described by Glemser et al.[20–23]

Elemental Analysis. Elemental analyses of the reactants and products for nitrogen, hydrogen, carbon, and molybdenum were performed by the Microanalytical Laboratory at the Department of Chemistry, University of California, Berkeley. Nitrogen, hydrogen, and carbon compositions were determined by using a combustion method and analyzing the effluent gas. Molybdenum analysis was performed by atomic absorption spectroscopy.

The elemental analyses of the nitride products were influenced by the absorption of water and ammonia that occurred during cooling of the samples and removal from the TGA apparatus. For this reason, elemental analysis was used only as a qualitative tool; the product compositions were determined from the final TGA weight and XRD.

TGA Apparatus. The reactions with NH_3 were carried out in a TGA system equipped with a Cahn RG microbalance. The glass vacuum system, which was connected to an oil diffusion pump backed by a rough pump, could achieve a dynamic vacuum of about 10^{-5} Torr. The system was designed such that either a furnace or a liquid nitrogen Dewar could be raised in place around the sample, allowing for both TGA studies and BET surface-area measurements to be made without exposing the sample to ambient atmosphere. The temperature was controlled with a programmable-temperature controller (LFE Model 2011), while the gas flow rates were controlled with rotameters (Matheson Series 600).

In each TGA experiment, 50–200 mg of sample was placed on a quartz pan suspended from the balance. Ammonia was flowed through the system at a constant rate of 100 cm^3/min (1 atm, 25 °C). Prior to use, the ammonia gas was dried with a Matheson type 452 molecular sieve purifier. In a typical experiment, the reaction temperature was raised linearly from 25 to 625 °C at 36 °C/h and held subsequently at 625 °C for several hours until no further weight change was observed. The sample weight and temperature were recorded continuously with an IBM compatible PC-XT microcomputer.

All TGA data are expressed as weight per mole of metal atoms in the starting material. This normalization is convenient for two reasons. First, the normalized weight of a given intermediate does not depend on the gross or molecular weight of the starting material. Thus two thermograms coincide when two reactions yield the same product. Also, the normalized weight change between plateaus in a thermogram can be related easily to the molecular weight of the species that are lost or gained during the reaction. For example, loss of 1 mol of NH_3/mol of molybdenum in the sample results in a reduction of the normalized weight by 17 g/mol.

BET Measurements. Sample surface areas were measured by static nitrogen adsorption at 77.4 K at pressures between 0.05 and 0.35 atm. The equilibrium nitrogen pressure was measured with a capacitance manometer (Type 600 Barocel Pressure Transducer with a 0–1000-Torr range), and the amount adsorbed was determined gravimetrically. Samples typically equilibrated in 30 min or less after a change in nitrogen pressure. Buoyancy effects were significant only at the higher nitrogen pressures for samples with surface areas smaller than 2 m^2/g. The monolayer surface coverage of nitrogen was estimated by the BET[24] method; the surface area was computed from the monolayer coverage by using a nitrogen cross section of 0.162 nm^2.

The evolution of surface area during reaction was determined by interrupting a TGA experiment at a particular temperature, cooling the sample rapidly in flowing ammonia, evacuating the sample, and then measuring the surface area by nitrogen adsorption at 77 K. Following the adsorption measurement, the sample was reheated in flowing ammonia to the previous reaction temperature, and the TGA experiment was continued to a higher temperature. This procedure was repeated at 25–100 °C intervals.

Powder X-ray Diffraction. A Picker Model 3488 diffractometer with a copper X-ray tube and equipped with an environmental hot stage was used to identify intermediates formed during the reaction with NH_3. The temperatures at which intermediates formed were determined by TGA, and XRD patterns were obtained at these temperatures. As in the TGA measurements, samples were heated at 1 °C/min in flowing dry ammonia. When a sample reached a measurement temperature, it was held for 30 min, and then an X-ray pattern was obtained over a range of 2θ from 10 to 80° at a scan rate of 1°/min. Following the scan, the sample was heated again at 1 °C/min to the next temperature. Finally, an X-ray pattern of the final product was measured after holding the sample for 12 h in flowing ammonia at 625 °C.

The starting materials, intermediates, and nitride products were identified by comparison with the patterns given in the following references: MoO_3,[25] H_xMoO_3,[26] MoO_2,[27] $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$,[28,29]

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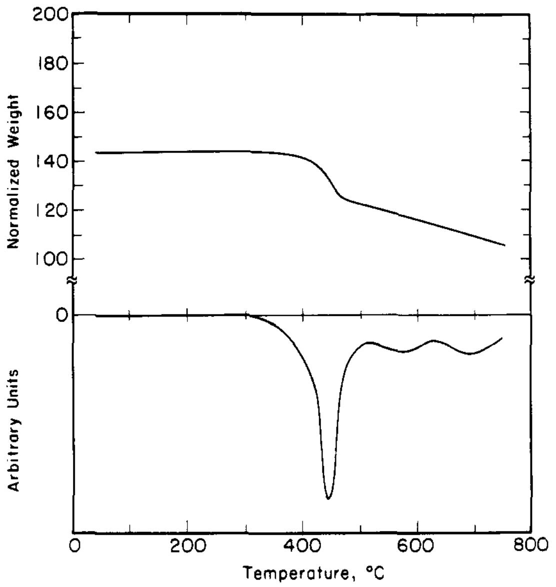


Figure 1. TGA/DTG of the reaction of molybdenum trioxide with ammonia (heating rate = 1 °C/min, 150 cm^3/min NH_3 at STP).

$(NH_4)_6Mo_7O_{24}$,[30] $(NH_4)_2O{\cdot}2.5MoO_3$,[31] $(NH_4)_2O{\cdot}3MoO_3$,[32] $(NH_4)_2O{\cdot}4MoO_3$,[33] $(NH_4)_2MoO_4$,[34] $MoO_3{\cdot}H_2O$,[35] MoO_xN_{1-x},[14] MoN,[17] and Mo_2N[16]. Listings of the *d* spacings for all the powder patterns obtained are published elsewhere.[36]

Scanning Electron Microscopy (SEM). Scanning electron microscopy was performed on several samples using an AMR 50 microscope made available through Lawrence Berkeley Laboratory. Typical magnifications used for this study were 1000–5000×.

Results and Discussion

The reactions of MoO_3, $(NH_4)_2MoO_4$, and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ with ammonia all proceed through different pathways. Of particular interest is the observation that all three reactants are converted to an fcc oxynitride intermediate, MoO_xN_{1-x}. Upon further reaction, this oxynitride converts directly to a nitride product: MoO_3 reacts to form Mo_2N; $(NH_4)_2MoO_4$ reacts to form MoN; $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ reacts to form a mixture of MoN and Mo_2N. The control of the stoichiometry of the nitride phase is examined below, and it is shown that the temperature at which the oxynitride reacts determines the phase of the nitride; fcc Mo_2N is formed at higher temperatures than those at which hexagonal MoN is formed. The control of the surface area of the nitride product is also discussed. High-surface-area products are generated only in pseudomorphic reactions. These pseudomorphic transformations occur when the precursor to the oxynitride contains edge-shared MoO_6 octahedra. The nitride products formed from the pseudomorphic transformation of MoO_3 and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ have surface areas near 60 m^2/g, while the product of the reaction of $(NH_4)_2MoO_4$, which is not pseudomorphous, is only 16.5 m^2/g. Finally, the reactions of H_xMoO_3 with ammonia are described. The partial reduction of MoO_3 by insertion of hydrogen results in products with higher surface areas.

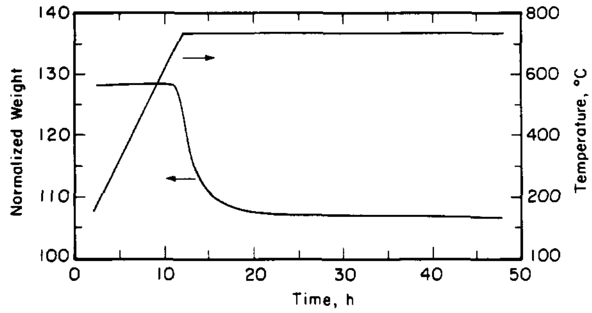
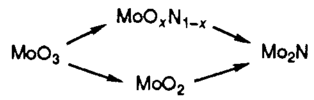


Figure 2. TGA of the reaction of molybdenum dioxide with ammonia (heating rate = 1 °C/min, 150 cm^3/min NH_3 at STP).

Reaction Pathways. Molybdenum trioxide: Molybdenum trioxide forms two intermediates in its reactions with ammonia to form molybdenum nitride. As shown by the TGA/DTG results in Figure 1, the reaction begins above 375 °C and proceeds in two steps at 460 and 595 °C, forming an intermediate at approximately 510 °C. A smaller third DTG peak is present at 695 °C. At 750 °C, the final weight loss after several hours of reaction is 28.1%, very close to the theoretical weight loss of 28.5% expected for the formation of Mo_2N. High-temperature XRD indicated that the intermediate formed near 535 °C is a mixture of MoO_2 and MoO_xN_{1-x} and that the final product was fcc Mo_2N. On the basis of the thermogravimetric and XRD data, we propose that the reaction of MoO_3 with ammonia proceeds through the following reaction pathway:



The high-temperature XRD results indicated that the main reaction of MoO_3 with ammonia to form Mo_2N is accompanied by a side reaction, the partial reduction of the trioxide to molydenum dioxide. XRD showed the presence of MoO_2 between 375 and 620 °C. TGA of the direct reaction of MoO_2 with ammonia, presented in Figure 2, shows that MoO_2 does not begin to lose weight until 688 °C and continues to lose weight appreciably at the final reaction temperature of 750 °C. The final product of this reaction is predominantly Mo_2N and a small amount of MoN, as determined by XRD. This shows that MoO_2 converts directly to a nitride product and suggests that the high-temperature DTG peak at 695 °C in Figure 1 corresponds to the nitridification of MoO_2. In addition, this indicates that the DTG peaks in the reaction of MoO_3 with ammonia below 688 °C are not produced by reaction of MoO_2. We conclude that MoO_2 plays only a spectator role at temperatures below 688 °C.

On the basis of XRD, the fcc intermediate formed at 535 °C along with MoO_2 could be Mo_2N[16] or the oxynitride MoO_xN_{1-x}.[14] The composition of the sample at 535 °C can be estimated as follows: Assuming that the only phases present at 625 °C are MoO_2 and Mo_2N, then the TGA weight at 625 °C can be used to calculate the amount of MoO_2 formed through the side reaction; we estimate this to be approximately 15 wt %. This is an upper limit on the amount of MoO_2 that can be present at 535 °C. If the intermediate at 535 °C contains 15 wt % MoO_2, then the fcc intermediate has a weight close to that expected for

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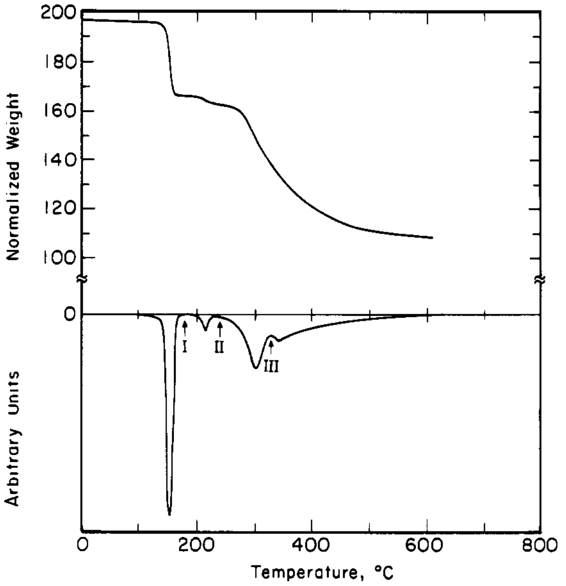

Figure 3. TGA/DTG of the reaction of diammonium molybdate with ammonia (heating rate = 1 °C/min, 150 cm^3/min NH_3 at STP).

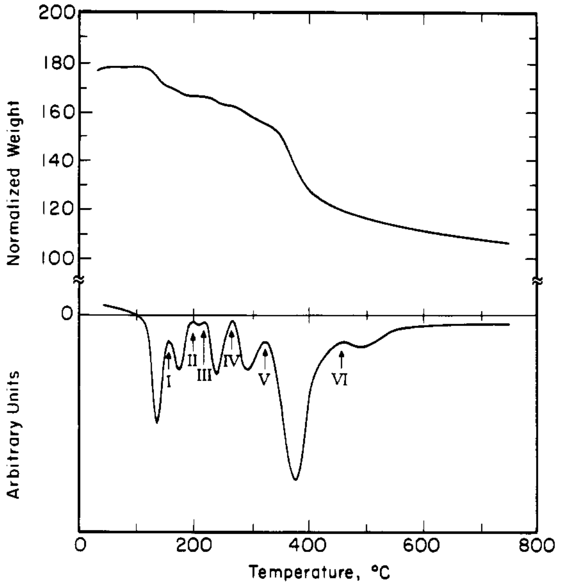

Figure 4. TGA/DTG of the reaction of ammonium paramolybdate with ammonia (heating rate = 1 °C/min, 150 cm^3/min NH_3 at STP).

Table II. Proposed Reaction Intermediates in the Reaction of Ammonium Paramolybdate with Ammonia

intermediate	XRD structure	TGA temp, °C	normalized wt	
			actual	theor
I	$(NH_4)_6Mo_7O_{24}\cdot 2H_2O^a$	140	171.96	171.43
II	$(NH_4)_6Mo_7O_{24}$	165	165.96	166.31
III	$(NH_4)_8Mo_{10}O_{34}$	185	164.72	164.72
IV	$(NH_4)_2O\cdot 3MoO_3$	245	160.13	161.37
V	$(NH_4)_4Mo_8O_{26}$	300	156.78	156.95
VI	MoO_xN_{1-x}	450		

[a] Not identified by XRD but proposed on the basis of its weight.

MoN; this weight is too large for 85% of the sample to be Mo_2N. However, MoN is hexagonal, and for this reason we propose that the fcc intermediate still contains oxygen and is the oxynitride MoO_xN_{1-x}. The reaction of this oxynitride to form the nitride is represented by the DTG peak at 595 °C. The final product is fcc Mo_2N, as determined by TGA/DTG and XRD.

The formation of an oxynitride intermediate is consistent with the results of Lyutaya,[14] who determined the activation energies of formation of MoO_xN_{1-x} and Mo_2N for the reaction of MoO_3 with ammonia. The formation of the oxynitride has a lower energy of activation (16.8 kcal/mol) than the activation energy for the formation of the nitride Mo_2N (22.2 kcal/mol). This indicates that at lower temperatures the formation of an oxynitride intermediate should be favored over the nitride.

Diammonium molybdate: Diammonium molybdate, $(NH_4)_2MoO_4$, reacts with ammonia through a different reaction pathway than MoO_3 yet still forms the same fcc oxynitride MoO_xN_{1-x} as a precursor to the nitride product. The TGA/DTG results shown in Figure 3 indicate a reaction pathway with four reaction steps, resulting in the formation of three reaction intermediates. These steps are represented by DTG peaks at 150, 210, 305, and 350 °C, while intermediates I, II, and III are formed at 165, 225, and 330 °C, respectively. The normalized weights of intermediates I, II, and III to the starting material are 165.83, 162.10, and 126.04, respectively, while the final weight of 108.00 is close to the theoretical value of 109.96 for a pure MoN product. On the bais of the TGA/DTG and high-temperature X-ray diffraction results, the following reaction pathway is proposed:

$$(NH_4)_2MoO_4 \rightarrow MoO_3\cdot 1.29NH_3 \rightarrow MoO_3\cdot NH_3 \rightarrow MoO_xN_{1-x} \rightarrow MoN$$

The two materials $MoO_3\cdot 1.29NH_3$ and $MoO_3\cdot NH_3$, proposed as the first two intermediates formed during the reaction of $(NH_4)_2MoO_4$ with NH_3, have not been reported previously. The weight loss at 225 °C, which is associated with these first two reaction steps, suggests that 2 mol of a mixture of NH_3 and H_2O is lost per mole of $(NH_4)_2MoO_4$. The X-ray diffraction patterns at both 175 and 275 °C are a mixture of those of the starting material $(NH_4)_2MoO_4$[34] and a phase that has a structure similar to yellow $MoO_3\cdot H_2O$.[35] Since $MoO_3\cdot H_2O$ loses water in air between 110 and 130 °C,[35] it is unlikely that the intermediate present between 175 and 275 °C is $MoO_3\cdot H_2O$. We propose that the second intermediate is a new phase, $MoO_3\cdot NH_3$, containing NH_3 instead of H_2O and possessing a structure similar to yellow $MoO_3\cdot H_2O$. The first intermediate has a weight corresponding to $MoO_3\cdot 1.29NH_3$. An XRD pattern of this intermediate was not obtained; it is possible that the material is amorphous.

Above 245 °C, the $MoO_3\cdot NH_3$ reacts to form intermediate III, which exhibits diffraction lines that are characteristic of the fcc structure; this intermediate could be either MoO_xN_y or Mo_2N. The XRD of the final product indicates that it is hexagonal MoN. As observed in the reaction of MoO_3 with ammonia, the weight loss is not sufficient for the fcc intermediate to be Mo_2N. Furthermore, we have found that it is not possible to convert fcc Mo_2N to hexagonal MoN at temperatures between 450 and 750 °C. This is strong evidence that the fcc intermediate cannot be Mo_2N. We conclude that the intermediate still contains oxygen and is the fcc oxynitride MoO_xN_{1-x}.

Ammonium paramolybdate: The reaction of ammonium paramolybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, with ammonia involves a more complex reaction pathway. In this reaction, NH_3 and H_2O are lost sequentially in several steps. However, like the reactions of MoO_3 and $(NH_4)_2MoO_4$ with ammonia, an fcc oxynitride intermediate is formed as the precursor to the nitride product.

The reaction involves seven reaction steps, represented by DTG peaks at 120, 155, 175, 220, 275, 370, and 500 °C; the TGA/DTG results are shown in Figure 4. Six intermediate phases are formed at 140, 165, 185, 245, 300, and ~450 °C. Identification of these intermediates was made using high-temperature XRD and/or weights obtained from TGA; the intemediates are listed in Table II. On the basis of these results, the following reaction pathway is proposed:

$$(NH_4)_6Mo_7O_{24}{\cdot}4H_2O \rightarrow (NH_4)_6Mo_7O_{24}{\cdot}2H_2O \rightarrow (NH_4)_6Mo_7O_{24} \rightarrow (NH_4)_8Mo_{10}O_{34} \rightarrow (NH_4)_2O{\cdot}3MoO_3 \rightarrow (NH_4)_4Mo_8O_{26} \rightarrow MoO_xN_{1-x} \rightarrow MoN + Mo_2N$$

XRD confirms the presence of all the intermediates except the dihydrate, $(NH_4)_6Mo_7O_{24}{\cdot}2H_2O$. This is probably due to the close proximity of the two weight-loss steps, indicating that a stable intermediate with uniform composition may not form in the XRD experiment. The TGA/DTG results, however, do suggest the formation of the dihydrate intermediate; the DTG clearly shows the presence of two reaction peaks before the formation of intermediate II, and the weight loss associated with the minimum between these peaks is consistent with the weight loss expected for the formation of the dihydrate. TGA and XRD confirm that the starting material loses four water molecules to form intermediate II, $(NH_4)_6Mo_7O_{24}$.[30] This loss of water in two equal steps at 120 and 155 °C agrees with previous reports that two of the four water molecules of hydration act as a "bridge" between a pair of ammonium ions lying between adjacent heptamolybdate ions. The other two water molecuels are situated elsewhere, each bonded to a pair of cations, and are not as strongly bonded in the structure.[28] This loss of water in two stages was also observed for potassium hepatomolybdate tetrahydrate, $K_6Mo_7O_{24}{\cdot}4H_2O$, which is isomorphous with ammonium paramolybdate.[28]

After the initial loss of the four water molecules of hydration, the reaction proceeds through several molybdate intermediates. This reaction pathway is similar to the polycondensation reactions observed for the decomposition of several molybdates to form molybdenum trioxide.[30-32,37-45] The sample loses ammonia and water simultaneously in the ratio 2:1.[42] The two ammonia and one water molecules have been shown to be bonded together as $(NH_4)_2O$ groups between the heptamolybdate ions in ammonium paramolybdate.[28] The final molybdate structure detected before the formation of the oxynitride intermediate is ammonium octamolybdate, $(NH_4)_4Mo_8O_{26}$.[33] In comparison, when ammonium paramolybdate decomposes in air, it does not lose the four waters of hydration in a separate series of reactions; rather, it decomposes directly to ammonium decamolybbdate, $(NH_4)_8Mo_{10}O_{34}$, which is the third intermediate formed in the reaction with ammonia.[32]

Above 325 °C, $(NH_4)_4Mo_8O_{26}$ reacts to form a fcc crystal structure before hexagonal MoN is formed. Although the proposed fcc oxynitride MoO_xN_{1-x} has the same X-ray diffraction pattern as the fcc nitride Mo_2N, the temperature at which this intermediate is detected by XRD corresponds to a sample weight that is much too high for the bulk of the sample to be Mo_2N. It is therefore concluded that the intermediate still contains oxygen. As the temperature is increased, the sample loses weight continuously. At temperatures above 625 °C, the hexagonal MoN phase is present in the XRD patterns, as well as fcc Mo_2N. The ratio of MoN to Mo_2N depends on the temperature of the reaction as discussed below.

Table III. Dependence of Nitride Stoichiometry on the Precursor to and Formation Temperature of the Oxynitride Intermediate

starting material	oxynitride precursor	oxynitride formation temp, °C	ultimate product(s)
MoO_3	MoO_3	510	Mo_2N
$(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$	$(NH_4)_4Mo_8O_{26}$	450	Mo_2N + MoN
$(NH_4)_2MoO_4$	$MoO_3{\cdot}NH_3$	325	MoN

Control of the Nitride Phase. MoO_3, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, and $(NH_4)_2MoO_4$ react to form different nitride phases or mixtures of phases, although each reaction involves the same fcc oxynitride intermediate. The temperature at which this oxynitride is formed, however, depends on the reaction pathway and, in particular, on the oxynitride precursor. Since in each case the oxynitride reacts readily to form the nitride product, it is the temperature of formation of the oxynitride which influences the final nitride phase. Table III summarizes these results.

The temperature dependence of the reaction of the oxynitride to form different nitride products is consistent with the results of Lyutaya.[14] He showed that the nitridification of activated Mo metal with ammonia at 450 °C yielded MoN, while reacting at 700 °C produced Mo_2N. A similar trend is present in the nitridification of the fcc oxynitride: at 325 °C, MoN is formed; at 535 °C, Mo_2N is formed; and between these temperatures a mixture of the nitrides is formed. Attempts to convert Mo_2N to MoN in ammonia from 450 to 750 °C were unsuccessful. Additionally, the MoN product from the reaction of diammonium molybdate with ammonia is not converted to Mo_2N at temperatures below 750 °C. Therefore, the two nitrides must be produced from the oxynitride in parallel, with the relative rates of reaction depending upon the temperature.

The fact that the two nitride phases are formed in parallel implies that the Mo_2N/MoN ratio should depend on the heating rate and final reaction temperature. Since our heating rate is comparable to the rate of conversion of the oxynitride, the Mo_2N/MoN ratio should increase as the final reaction temperature is increased. This has been observed for the reaction of ammonium paramolybdate with ammonia. The XRD patterns of the nitride at final reaction temperatures of 625 and 750 °C showed that both phases were present. The product obtained at 750 °C contained a higher Mo_2N/MoN ratio than that obtained at 625 °C. On the basis of the final weights, it can be calculated that the product at 625 °C contained 32.1 mol % Mo_2N and 67.9 mol % MoN, while the product at 750 °C contained 72.5 mol % Mo_2N and 27.5 mol % MoN. Also, the presence of a higher concentration of MoN in the product at 625 °C is supported by the XRD data, on the basis of the ratio of the [202] diffraction peak of MoN to the [200] peak of Mo_2N. These two peaks were chosen since they do not overlap, thereby presenting a fair representation of the relative (but not absolute) concentrations of the two phases. This ratio, $MoN_{[202]}/Mo_2N_{[200]}$, was 0.89 for a final reaction temperature of 625 °C and dropped to 0.32 at 750 °C.

Control of Surface Area. Pseudomorphism of reactants and products: Figure 5 shows the development of surface area in the reactions of MoO_3 and the molybdates with ammonia. MoO_3 and $(NH_4)_6Mo_7O_{24}{\cdot}$

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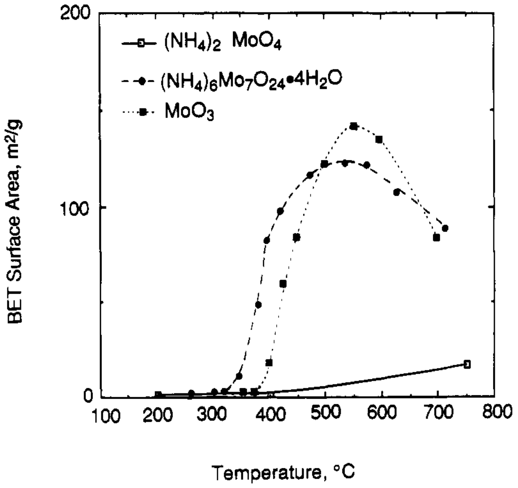

Figure 5. Surface-area development during the synthesis of molybdenum nitrides from MoO_3, ammonium paramolybdate, and diammonium molybdate.

$4H_2O$ behave similarly. A large increase in surface area occurs during the formation of the oxynitride intermediate; the surface area peaks above 100 m^2/g at 550 °C and decreases to approximately 80 m^2/g at 700 °C. In contrast, the reaction of $(NH_4)_2MoO_4$ with ammonia exhibits a gradual, monatomic increase in surface area to 16.5 m^2/g. Since all three reactions proceed through the same oxynitride intermediate, we believe that the structure of the precursor to this intermediate plays a key role in determining the ultimate surface area of the nitride product.

An important characteristic of the high-surface-area nitrides formed from MoO_3 and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ is that they are pseudomorphous with the reactants. SEM photographs of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and the nitride product in Figure 6 show that the product exhibited the same fracturing along layers that was present in $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, even though MoN is not a layered material. Previous studies of the reaction of MoO_3 with ammonia by Boudart et al.[9] showed that the final product also retained the particle morphology of the starting material. Although SEM photographs for $(NH_4)_2MoO_4$ could not be obtained due to loss of ammonia upon placement in the vacuum chamber, photographs of the nitride product were obtained and are shown also in Figure 6. By comparison to the high-surface-area nitrides, it is evident that the particles have totally different morphologies.

The pseudomorphism of the starting materials and the final products apparently contributes to the high-surface-area of the nitride products. During the reactions of MoO_3 and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ with ammonia, the density of the sample increases 400–500%. However, the gross particle size and shape are unchanged. Therefore, these materials must develop cracks to accommodate this increase in density; this yields microporous particles with high specific surface areas. This hypothesis is supported by the nitrogen adsorption isotherms of the high-surface-area nitrides; a typical isotherm is shown in Figure 7. The isotherm is best described as a type II isotherm.[46] The small type B adsorption hysteresis[47] indicates the presence of slit-shapped pores or platelike particles.[9] In contrast, there is no evidence of a pore structure in the BET isotherms for the nitride phases generated in the reaction of $(NH_4)_2MoO_4$.

The pseudomorphism is apparently the result of a reaction mechanism in which the molydenum atoms are constrained during the formation of the oxynitride. We suggest that when a pseudomorphic transformation occurs with a concomitant change in density, a high-surface-area material will be produced. Although we do not know all the necessary criteria for a pseudomorphic transformation, it appears that the Mo–Mo distances in the precursor to the oxynitride are important. In the reactions of MoO_3, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and $(NH_4)_2MoO_4$, the oxynitride precursors are MoO_3, $(NH_4)_4Mo_8O_{26}$, and $MoO_3\cdot NH_3$, respectively. $(NH_4)_4Mo_8O_{26}$ consists of isolated $Mo_8O_{26}{}^{4-}$ clusters linked by $NH_4{}^+$ cations. MoO_3 and $MoO_3\cdot NH_3$ are both layered; MoO_3 consists of double-thick layers of MoO_6 octahedra held loosely together by van der Waals interactions,[25] while $MoO_3\cdot NH_3$ presumably has monolayers of MoO_6 octahedra[35] with NH_3 between the layers. While $(NH_4)_4Mo_8O_{26}$ contains edge-shared MoO_6 octahedra and MoO_3 contains both edge- and corner-shared octahedra, the octahedra in $MoO_3\cdot NH_3$ are exclusively corner-shared. Therefore, the average Mo–Mo distances are comparatively longer in the latter compound. It is the two structures containing edge-shared MoO_6 octahedra that undergo pseudomorphic transformations; we speculate that the Mo atoms cannot rearrange as easily if the MoO_6 octahedra are edge-shared.

The possibility that the low surface area in the product of the reaction of $(NH_4)_2MoO_4$ results from hydrothermal sintering can be ruled out. Varying the flow rates and heating rates to reduce the gas-phase water concentration had no effect on the product surface area. In addition, the temperature region in which the oxynitride forms, 325–500 °C, is too low for hydrothermal sintering.[48]

The reaction of MoO_2 with ammonia involves a completely different reaction mechanism than MoO_3 and the ammonium molybdates. Unlike these compounds, the dioxide does not intercalate or react with ammonia at low temperatures, nor does it form the oxynitride intermediate. Instead, it reacts directly to form the nitride at high temperatures. This is analogous to typical high-temperature synthesis routes, and for this reason MoO_2 reacts to form a low-surface-area nitride.[8]

Maximum in surface area generation: It can be seen in Figure 5 that the surface areas of the MoO_3 and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ samples pass through a maximum at 550 °C. The decrease in surface area at high temperatures is attributed to hydrothermal sintering, since water is formed as a product of these reactions. This conclusion is supported by the observation that if the heating rate is raised from 1 to 5 °C/min, the surface area of the products is dramatically reduced; increasing the heating rate increases the rate of water production, thereby accelerating the rate of sintering. Similarly, the surface area varied with ammonia flow rate; it was necessary to keep the ammonia flow rate high enough for water removal. This study did not quantify these effects, nor did it attempt to optimize the reaction conditions. Other authors discuss hydrothermal sintering,[48] and Oyama et al.[7] discuss the importance of superficial gas velocity in the synthesis of transition-metal nitrides.

Hydrogen Molybdenum Bronzes. The reactions of ammonia with H_xMoO_3 (hydrogen molybdenum bronzes) offer an interesting comparison to the reactions of MoO_3 with ammonia. The bronzes are produced by topotactic insertion of hydrogen between the loosely held layers of the parent compound, MoO_3. The hydrogen reduces the

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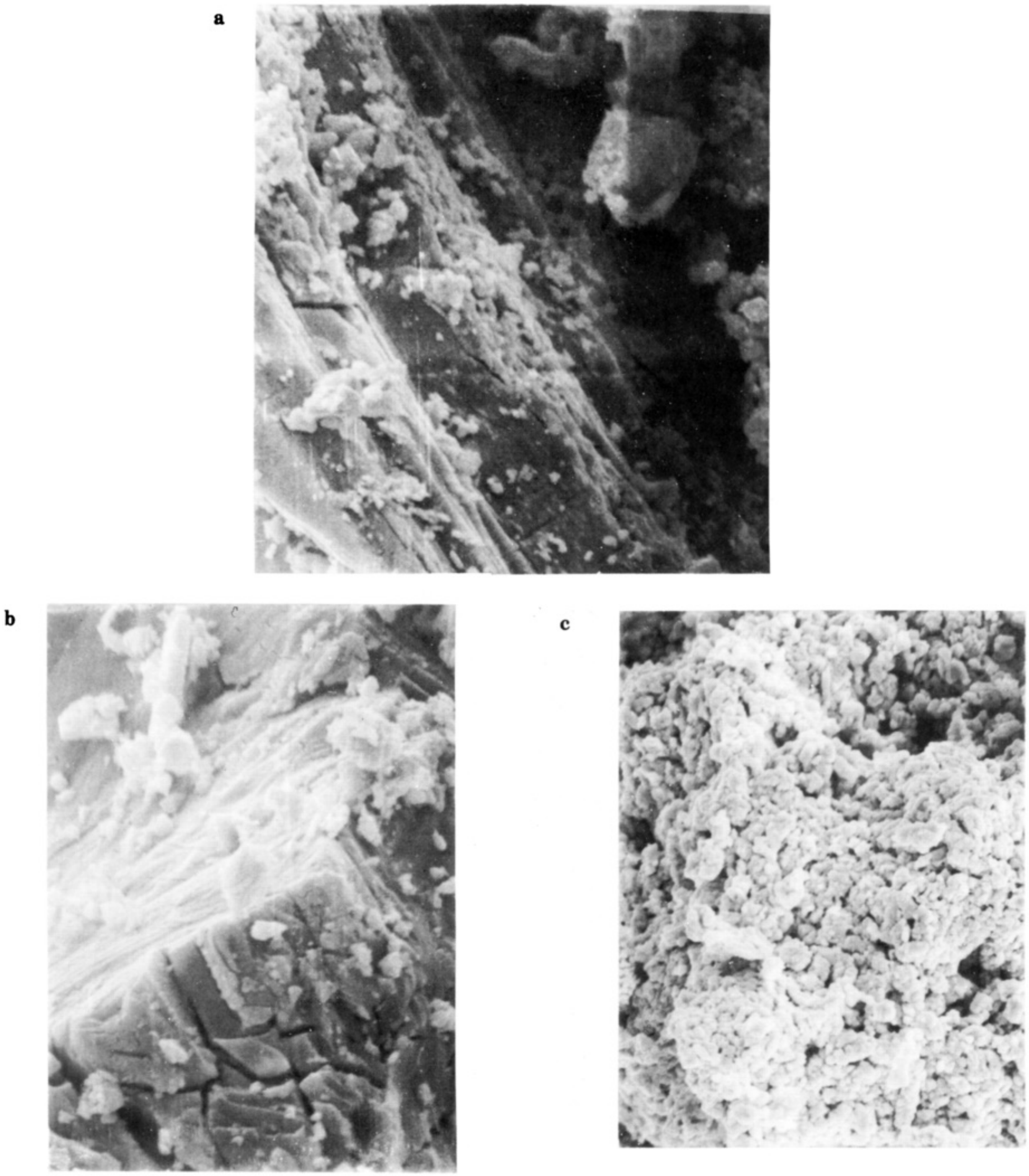

Figure 6. (a) SEM of ammonium paramolybdate (magnification = 1500×); (b) SEM of product from ammonium paramolybdate/ammonia reaction (magnification = 1500×); (c) SEM of MoN product from diammonium molybdate/ammonia reaction (magnification = 1500×).

molybdenum ions without altering the structure of the parent oxide significantly; the value of x can be as large as 2, corresponding to a reduction from Mo(VI) to Mo(IV). Due to the structural similarity, the bronzes allow the study of the effect of partially reducing the metal ions on the reaction pathway, ultimate nitride phase, and product surface area.

A series of hydrogen molydenum bronzes, H_xMoO_3 with $x = 0, 0.04, 0.13, 0.31$, and 0.80, were reacted with ammonia, and the TGA/DTG of these reactions are compared in Figure 8. The reactions of the bronzes with $x < 0.3$ are characterized by two DTG peaks. These are associated with the formation of the fcc oxynitride MoO_xN_{1-x} and its subsequent reaction to form single-phase Mo_2N; this is the same pathway as the reaction between MoO_3 and ammonia. As shown in Table IV, both DTG peak temperatures for H_xMoO_3, decrease monotonically with increasing hydrogen content.

Table IV. DTG Peak Temperatures in the Reactions of MoO_3 and H_xMoO_3 with NH_3

		DTG peaks,[a] °C		
starting material	T_{onset}, °C	1	2	3
MoO_3	375	460	595	695
$H_{0.04}MoO_3$	350	440	590	
$H_{0.13}MoO_3$	310	425	590	
$H_{0.31}MoO_3$	300	405	550	

[a] Reaction 1: $H_xMoO_3 \rightarrow MoO_xN_{1-x}$. Reaction 2: $MoO_xN_{1-x} \rightarrow Mo_2N$. Reaction 3: $MoO_2 \rightarrow Mo_2N$.

The reaction of $H_{0.80}MoO_3$ with ammonia differs from the other bronzes as it exhibits three DTG peaks at 285, 495, and 595 °C; we are unable to assign these peaks.

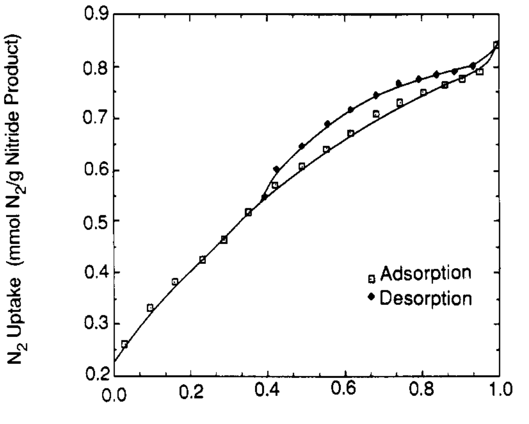

Figure 7. BET isotherm of the MoN/Mo_2N mixture formed by reacting ammonium paramolybdate with ammonia.

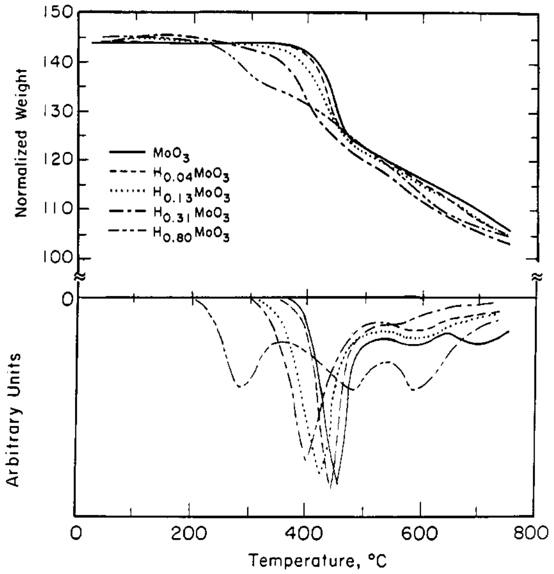

Figure 8. Comparison of TGA/DTG of the reactions of hydrogen molybdenum bronzes with ammonia (heating rate = 1 °C/min, 150 cm^3/min NH_3 at STP).

However, since the structure of $H_{0.80}MoO_3$ is not the same as that observed for the compounds with $x < 0.30$, it is not surprising that the reaction pathway for $H_{0.80}MoO_3$ is different. The blue orthorhombic form is stable for $0.23 < x < 0.4$, while compositions near $x = 0.8$ are monoclinic.[49] In the orthorhombic form, the hydrogen atoms are present as $-OH$ groups, but the monoclinic form contains $-OH_2$ groups.[50] It is interesting to note that the product of the reaction of $H_{0.80}MoO_3$ is a mixture of both MoN and Mo_2N as shown by XRD; for the other bronzes studied, only Mo_2N was formed. The formation of MoN is consistent with the fact that the reaction of $H_{0.80}MoO_3$ with ammonia begins at lower temperature.

The reaction of hydrogen molybdenum bronzes with ammonia eliminates the formation of MoO_2. As shown in Figure 8, the DTG peak at 695 °C observed in the reaction of MoO_3 with ammonia is not present in the DTG of the bronzes; this peak is associated with the reaction of MoO_2 with ammonia. Additionally, X-ray diffraction patterns obtained at 500 °C during the reaction of $H_{0.31}MoO_3$ with ammonia do not show the presence of MoO_2. This result suggests that it is possible to fully nitride the bronzes at lower temperatures than MoO_3 by avoiding the formation of MoO_2, and this should reduce the hydrothermal sintering that occurs at higher temperatures. Indeed, the molydenum bronzes produce nitrides with higher surface areas than those produced by the reaction of MoO_3 with ammonia.

Conclusions

The synthesis of molybdenum nitrides from oxide and ammonium oxide precursors can be summarized as follows:

An oxynitride intermediate MoO_xN_{1-x} with a fcc structure is formed during the reactions of MoO_3, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, $(NH_4)_2MoO_4$, and H_xMoO_3 with ammonia; this oxynitride converts directly to a nitride.

The temperature at which the oxynitride reacts to form the nitride determines the phase of the nitride: fcc Mo_2N is formed at temperatures higher than those at which hexagonal MoN is formed.

When the reactant and products are pseudomorphous, the products have a high surface area. This is the case for the reactions of MoO_3 and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ with ammonia.

H_xMoO_3 reacts with ammonia to form nitride products with higher surface areas as compared with MoO_3. In addition, the bronzes do not form MoO_2 when they react with ammonia, in contrast to MoO_3.

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