Inorg. Chem. **2002**, *41*, 5317–5319

Inorganic Chemistry
Communication

New Single Source Route to the Molybdenum Nitride Mo_2N

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Received February 26, 2002

Dispersed Mo_2N with lamellar morphology and high specific surface area was obtained from the decomposition of the $(HMT)_2(NH_4)_4Mo_7O_{24}$ salt (HMT = hexamethylentertramine) in the temperature range 550–800 °C. During the thermal decomposition, reduction of Mo species by carbon from the HMT ligand occurs, with release of CO gas.

Inorganic nitrides play an important role in advanced technology because of their applications for electronic devices, light emitting diodes and lasers, solid-state sensors, and others.

The existing methods of nitride synthesis include high-temperature solid−gas reactions of metals or oxides with ammonia or molecular nitrogen.[1] To improve control of nitride properties and to extend the number of binary and ternary nitrides available, new methods are being developed using lower temperatures compared to those required by conventional solid-state methods, for example, reactions of nitrogen with the solutions of metals in liquid zinc,[2] ammonothermal synthesis,[3] solid-state metathesis,[4] or metathesis between halogenides and lithium nitride in benzene,[5] as well as pyrolysis of azide or azane precursons,[6] CVD, or ion beam sputtering.[7]

Since the synthesis methods for the high surface area molybdenum nitrides were reported,[8,9] these solids have been used as the catalysts for many reactions such as ammonia synthesis,[10] hydrotreating,[11] or isomerization.[12]

The synthesis conditions have a strong influence on the molybdenum nitride catalytic activity.[13] In the previously reported preparations, mostly solid−gas reactions have been used to prepare Mo_2N. Here, we report on the Mo_2N synthesis by means of thermal decomposition of a chemically homogeneous molecular precursor, which is a mixed ammonium and hexamethylentetramine (HMT) molybdate salt. The precursor was prepared by mixing of 3.5 g of $(NH_4)_4Mo_7O_{24}\cdot 4H_2O$ dissolved in 50 mL of distilled water with 6 g of HMT dissolved in 50 mL of water (both reagents high purity grade from Aldrich). After several hours of staying in air at ambient conditions, colorless crystals precipitated. The crystals (further designated as solid **I**) were collected, washed with a small amount of distilled water, and dried in air.

Chemical analysis showed that solid **I** contains 11.7 wt % of N, 10.1% of C, and 45.9% of Mo, in agreement with the stoichiometric composition $(HMT)_2(NH_4)_4Mo_7O_{24}\cdot 2H_2O$. Powder X-ray diffraction (XRD) of **I** suggests that this solid has a complex low symmetry cell. The cell refinement and determination of the crystalline structure of starting compound **I** is beyond the scope of this paper and will be published elsewhere. Scanning electron microscopy of **I** showed homogeneous rodlike crystals.

Solid **I** was heated in a quartz reactor under a flow of argon, at a mass rate 3 h^{-1}. The temperature was increased linearly at a rate 10 °C min^{-1} and then kept at a given value for 2 h. The product was cooled and further handled under argon. Three samples have been obtained from heating at 550, 650, and 800 °C, designated, respectively, as **I**-550, **I**-650, and **I**-800 (Table 1).

The XRD patterns (Figure 1) show that the **I**-550 solid is completely amorphous, whereas **I**-650 and **I**-800 demonstrate the broad peaks of the Mo_2N fcc phase.

Chemical analyses of the products (Table 1) show that, at 550°C, considerable amounts of carbon and oxygen still remained in the solid but are eliminated at higher temperatures. The nitrogen amount also decreases with temperature

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10.1021/ic025564d CCC: $22.00

Table 1. Chemical Composition, Specific Surface Area (S_{BET}), and Surface Atomic Ratios Calculated from the XPS Data for the Products of Thermal Decomposition of Solid **I**

sample	composition $Mo_2N_xC_yO_z$	S_{BET} m^2/g	O/Mo, XPS	Mo(IV)/Mo(II)
I-550	$Mo_2N_{0.71}C_{0.43}O_{0.38}$	158	0.5	0.3
I-650	$Mo_2N_{0.88}C_{0.06}O_{0.09}$	139	0.23	0.12
I-800	$Mo_2N_{0.96}C_{0.01}O_{0.05}$	71	0.14	0.05

but is subjected to much less change. The **I**-800 solid is almost pure Mo_2N phase, which is obtained with a quantitative yield.

The XPS Mo $3d_{5/2}$ binding energy (BE) in all three samples was 228.3 ± 0.2 eV, corresponding to that reported earlier in the Mo_2N nitride.[14] Beside the main peak, there is a shoulder at higher BE (Mo $3d_{5/2} \approx 230 \pm 0.2$ eV), which corresponds to Mo(IV) in the MoO_2 oxide. The intensity of the Mo(IV) peak decreased with the increase of the treatment temperature. At the same time, the O1s peak was present in all the samples. The surface atomic ratio O/Mo determined from the XPS data decreased with the increase in the heating temperature (Table 1). The results of the XPS study demonstrate that the majority of Mo is present on the surface in the form of nitride even for the amorphous **I**-550 solid.

The mass spectra of gaseous products of the decomposition of **I** during linear heating in argon were studied. Formation of gaseous products begins below 100 °C and is mostly completed at 600 °C. At low temperatures, dehydration and ammonia production occur. Formation of NH_3 goes mostly in step with dehydration. The release of water and ammonia have coinciding maxima at 200 and 280 °C (see Supporting Information). At higher temperatures, we observed the signal with the *m*/*z* value of 28. This signal can be attributed to CO. To confirm that mostly CO is evolved, we measured the IR spectrum of the trapped gas from decomposition of **I**. It shows two strong vibration−rotation group bands covering the approximate range 1950−2275 cm^{-1} and centered at 2143 cm^{-1}, which indicates the presence of CO in the gaseous products.

The ensemble of mass spectrometry, XPS, and chemical analysis data allows us to conclude that thermal decomposition of **I** proceeds as an internal oxidation−reduction process in which carbon reduces Mo(VI) and is eliminated as CO, whereas nitrogen remains mostly in the solid (eq 1). It was observed earlier that the intramolecular oxidation−reduction during the thermal decomposition of ammonium salts of transition metals may lead to the formation of reduced oxides. For example, Mo_5O_{11} or MoO_2 oxides are formed upon thermal decomposition of hydrated $(NH_4)_6Mo_7O_{24}$.[15]

$$C_{12}H_{44}O_{26}N_{12}Mo_7 \rightarrow 12CO + 14H_2O + 5.33NH_3 + 1.583N_2 + 3.5Mo_2N \quad (1)$$

As we see CO as a main gaseous product, the analogy might be relevant between the method reported here and the carbothermal preparations of nitrides in which formation of nitride is assisted by the reduction of oxide with carbon, present either as an organic ligand[16] or as graphite mixed with the precursor oxide.[17] In our case, however, both carbon and nitrogen are initially contained in the precursor, thus allowing us to obtain nitride at a relatively low temperature.

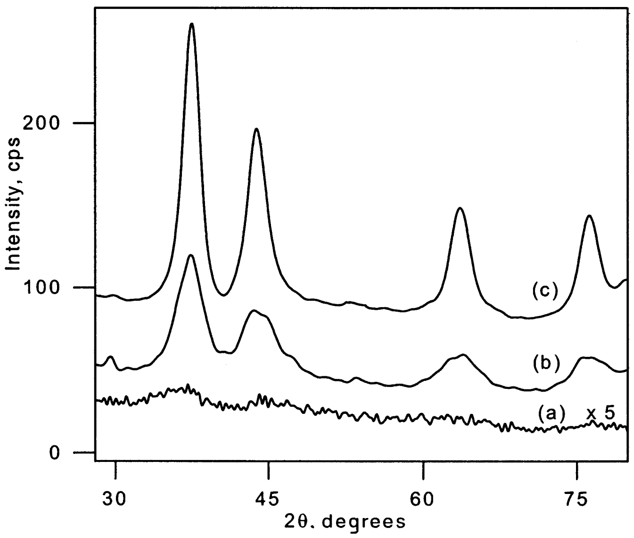

Figure 1. XRD patterns of the products of solid **I** thermal decomposition in Ar flow at 550 °C (a), 650 °C (b), and 800 °C (c). All peaks Mo_2N (JCPDS 25-1366).

Figure 2. SEM image of the **I**-650 solid.

The specific surface area of the samples measured by the BET method is high for **I**-550 and **I**-650 but decreases for **I**-800 (Table 1). The SEM study shows that the solids consist of submicrometer-sized thin sheets (Figure 2). Because Mo_2N has a cubic structure, whereas initial solid **I** contains large rectangular crystals, the observed morphology of **I**-650 suggests that a lamellar intermediate is formed during decomposition, which further decomposes to Mo_2N with a topotactically controlled geometry. Such a highly dispersed nitride material should present considerable interest for the catalytic applications. A question arises whether formation of nitride is a unique property of HMT molybdate complex,

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or might thermal decomposition of other nitrogen containing precursors and/or other transition or main group metals complexes give nitrides upon decomposition? For the time being, the decomposition of **I** remains the sole example of the nitride formation.

Our preliminary results suggest that decomposition of other nitrogen containing compounds, such as tetraalkylammonium molybdates, leads not to the Mo_2N nitride but to the abundant carbonaceous matter containing some MoO_2 within it. It seems that the rather high N/C ratio in precursor **I** and, at the same time, the amount of carbon sufficient to remove the totality of oxygen are the necessary conditions for the formation of Mo_2N. On the other hand, the N/Mo atomic ratio in starting compound **I** does not exactly correspond to that in the target Mo_2N; therefore, the last can probably be obtained from the other precursors.

As concerns other metals, we observed that, in the case of the tungstate HMT complex, the product of decomposition is WO_2, whereas Ni and Co HMT complexes decompose with the formation of the corresponding metals.

In conclusion, a new simple method has been found for the synthesis of Mo_2N. Decomposition of the molecular precursor provides a synthesis route free of diffusion limitations. To obtain crystallized products, high temperature is required, but the amorphous nitride begins to form already at 550 °C.

Supporting Information Available: Chemical analysis data for the decomposition products, mass spectra of gases released during the decomposition, and SEM photo of solid **I**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC025564D