Interaction of Solvent and the Nature of Adducts on the Chemical Synthesis of Molybdenum Nitride Powders

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Transition-metal halides are known to react with hydrazine to form hydrazide complexes. The formation of these complexes, however, is affected by the nature of the solvent used for conducting the reaction. While the existence of these complexes is known, there is a need to explore their subsequent decomposition reactions to form the corresponding metal nitrides. In this work we have studied the reaction of $MoCl_5$ with hydrazine using nonhydroxylic polar solvents such as acetonitrile (CH_3CN) and tetrahydrofuran (C_4H_8O). The interaction of the solvents with $MoCl_5$ have been first examined in order to identify the formation of adducts. The adducts have then been reacted with hydrazine to obtain a precipitate which results in the formation of the nitride on decomposition at higher temperatures. The influence of the solvent on the formation of the nitride phase and its morphology (of the precipitate and the decomposed product) have also been investigated.

Introduction

Transition-metal nitrides have been researched quite extensively in recent years. This is mainly because of several interesting properties exhibited by them due to the nature of their chemical bonds.[1] They are known to be hard refractory solids (e.g., TiN, WN) which make them suitable for cutting tool and high-temperature applications. At the same time, nitrides of molybdenum, for example, are well-known as superconductors, with superconducting properties retained over a wide range of nitrogen composition (30–50 atomic %).[2] In recent years, molybdenum and tungsten nitrides (as well as carbides) have also been investigated for their application as heterogeneous catalysts. Choi et al.[3] have shown the exceptional catalytic activity and selectivity of molybdenum nitrides toward hydrodenitrogenation (HDN) of pyridine, while Volpe and Boudart[4] have demonstrated their use as active catalysts in the synthesis of NH_3.

Identification of γ-Mo_2N as a catalytic material has led to considerable research efforts directed towards its synthesis. Most of the work reported has involved synthesizing the material by reacting the oxide with NH_3 at elevated temperatures. A process that has received much attention is the temperature programmed reaction of MoO_3 with NH_3 (Volpe and Boudart[5]). In this reaction the transformation of MoO_3 to γ-Mo_2N is believed to occur mainly by a topotactic reaction mechanism which involves an increase in the molar density leading to a high surface area nitride.

While solid-state reactions have been considerably successful, a number of nonconventional techniques have been researched over the years for the synthesis of non-oxide materials. One such approach that has received considerable attention is the low-temperature chemical precipitation route wherein the chemical reactions are conducted in solution. In this approach, the formation of the metal–anion bonds at an early stage of the reaction itself helps in accelerating the kinetics of formation of the desired material on further heat treatment. The process is simple, and moreover the possibility exists, of synthesizing either amorphous or nanocrystalline materials at moderately low temperatures. In addition, the precipitation reaction can intrinsically provide powders with uniquely different morphologies and microstructures. With these attributes in mind, in this paper we shall report a chemical process for the synthesis of Mo_2N. As a first step, we shall present interesting results on the study of the influence of solvent on the morphology and phase evolution of the nitride. While the process demonstrates the flexibility for synthesizing molybdenum nitride with a unique morphology, it also forms a basis for the synthesis of other transition-metal nitrides.

The approach utilizes a simple reaction of the metal salt ($MoCl_5$) in solution, with hydrazine (N_2H_4). The preliminary results of this process have already been published elsewhere.[6] It is known that $MoCl_5$ reacts with most hydroxylic solvents and forms adducts in

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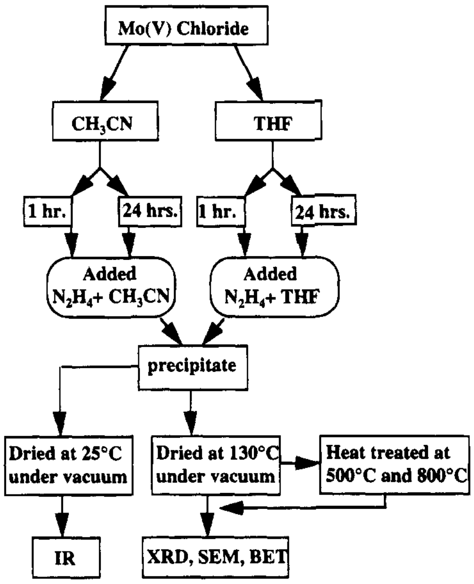


Figure 1. Flow chart showing the experimental procedures followed to synthesize molybdenum nitride.

solution with polar nonhydroxylic solvents. Therefore, initial experiments were conducted to study the formation of adducts using acetonitrile (CH_3CN) and tetrahydrofuran (C_4H_8O, THF) as solvents. The adducts have then been reacted with hydrazine to form a precipitate at room temperature. The precipitate is later decomposed in an inert atmosphere at a moderately elevated temperature to form the single-phase nitride.

Experimental Procedure

Acetonitrile Solvent. As infrared spectroscopic study of the interaction of $MoCl_5$ (Aldrich 98%) with CH_3CN (distilled with CaH_2 under UHP N_2) was conducted using the following procedure. $MoCl_5$ was added to excess amounts of acetonitrile in a flask (in an inert-atmosphere glovebox, ≤ 5 ppm $O_2 + H_2O$). The contents of the flask were continuously stirred to obtain a clear brown solution. The flask was then sealed. Liquid was extracted from the sealed vessel using a syringe after periods of 1 min, 1 h, and 1 day. At each stage, a few drops of the liquid were placed on a NaCl plate and the excess solvent was evaporated. The plate was covered with another NaCl plate and sealed, and an IR spectrum was collected under vacuum (113V, Brucker Instruments, Billerica, MA) using a liquid N_2 cooled mercury cadmium telluride detector.

To study the influence of the solvent on the reaction of $MoCl_5$ with hydrazine, two syntheses conditions were employed:

(a) Experiment 1: $MoCl_5$ was dissolved in acetonitrile, stirred for 5 min, and left sealed for 1 h (in a glovebox) until a clear brown solution resulted (see Figure 1). The solution was transferred to a glovebag purged with N_2, and excess anhydrous hydrazine (Aldrich) dissolved in acetonitrile was slowly added to the mixture. This resulted in the immediate precipitation of a dark brown solid through an exothermic reaction, causing the temperature of the contents of the reaction vessel to increase by 10–20 °C. The precipitate was then filtered (the filtrate was clear and colorless), washed with acetonitrile, and dried in vacuum at room temperature for 2–3 h. Infrared (IR) transmission spectra were collected on the powders, using a KBr pellet, in the wavenumber range 4000–600 cm^{-1}. The precursor was found to be very air sensitive, therefore it was further heated under vaccum at 130 °C for 2 h, leading to a less air-sensitive product (the exclusion of the drying treatment at 130 °C under vacuum would make the powder very susceptible to oxidation in air and consistently cause the formation of MoO_3 upon heating to higher temperatures). Further heat treatments were conducted under flowing ultrahigh-purity (UHP) N_2 at 500 °C for 10 h and at 800 °C for 3 h to obtain jet-black powders. The powders were subjected to X-ray diffractometry (XRD) using Cu Kα radiation (λ = 1.5418 Å) (Rigaku θ/θ diffractometer, Tokyo, Japan, equipped with a diffracted beam graphite monochromator), while their morphology was examined using a scanning electron microscope (SEM, Series 4, CamScan, Cambridge, England). The powders which were dried at 130 °C and heat treated at 800 °C were subjected to surface area analysis using the Brunauer–Emmett–Teller (BET) method (Autosorb 1, Quantachrome Instruments, Syosset NY).

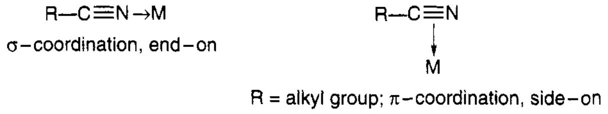
(b) Experiment 2: $MoCl_5$ was dissolved in CH_3CN, the solution was stirred for 5 min and left sealed for 24 h. Excess hydrazine, dissolved in acetonitrile, was then added to the solution to cause the formation of a dark brown precipitate which was filtered to yield the powder and a clear colorless filtrate. An IR spectrum was collected on the precipitate. The precipitate was then heated in vacuum at 130 °C for 2 h and further heat treated in flowing UHP N_2 at 800 °C for 3 h. An X-ray diffractogram was collected on the heat treated powder.

Tetrahydrofuran Solvent. The coordination of $MoCl_5$ by THF was studied by IR spectroscopy using an identical procedure adopted for acetonitrile, described in the first paragraph of the experimental section.

The reaction of $MoCl_5$ in THF was conducted in the following manner (see Figure 1). $MoCl_5$ was dissolved in THF to obtain a transparent light green solution. Anhydrous hydrazine (diluted in THF) was slowly added to the solution. An exothermic reaction ensued resulting in a dark brown precipitate. The precipitate was then filtered, washed with THF and further dried under vacuum at 130 °C for 2 h. The vacuum dried powders were individually heated in flowing UHP N_2 for 10 h at 500 °C and for 3 h at 800 °C. At each stage XRD patterns were collected on the powders and the surface area was measured using the BET technique. All the powders obtained were examined under the SEM to study and compare their morphology.

Results and Discussions

Acetonitrile Solvent. The interaction of transition-metal halides with nitriles has been well documented and reviewed in the literature.[7–9] It is known that organonitriles can coordinate transition metals in an end-on fashion as well as in a side-on fashion as indicated below:



$$\underset{\sigma\text{-coordination, end-on}}{R{-}C{\equiv}N{\rightarrow}M} \qquad \underset{\displaystyle M}{\overset{R{-}C{\equiv}N}{\downarrow}}$$

R = alkyl group; π-coordination, side-on

In the case of the reaction of $MoCl_5$ with acetonitrile, Allen et al.[10] have reported the formation of the $MoCl_4{\cdot}2CH_3CN$ adduct, which precipitates out only after several days of the reaction of the chloride with excess nitrile. The formation of this adduct has been confirmed by observation of a shift in the C≡N stretching frequency in the IR spectrum of the precipitated solid. Normally this shift is manifested by an increase of 20–30 cm^{-1} in the $\nu_{C\equiv N}$ vibration detected in the spectrum of the solid adduct as compared to the free nitrile, indicating an end-on coordination of the nitrile with the metal.

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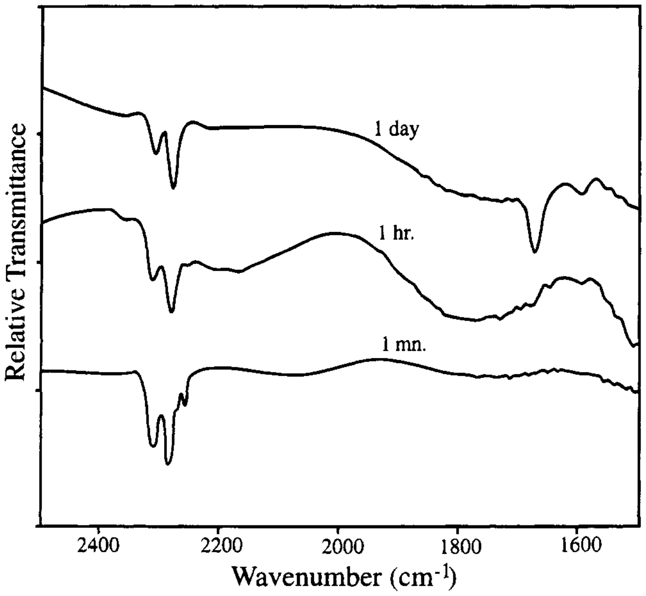
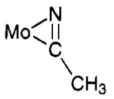


Figure 2. Infrared spectra of dried residue of $MoCl_5$ in acetonitrile (see text for details on sample preparation) collected after periods of 1 min, 1 h, and 1 day. The two absorptions at 2280 and 2315 cm^{-1} correspond to $\nu_{C\equiv N}$ vibrations of end-on coordinated nitrile, while the absorption at 1680 cm^{-1} which appears after reacting for a day corresponds to the side-on coordinated complex with considerable double-bond character (η^2-coordination).

The IR spectra in the wavenumber range 2500–1500 cm^{-1} obtained on samples collected after the three time durations mentioned above in the experimental procedure, are shown in Figure 2. The spectra indicate some interesting results on the interaction of $MoCl_5$ with CH_3CN. The formation of the end-on adduct at an early stage is confirmed by the observation of a shift in $\nu_{C\equiv N}$ to higher values (from 2250 cm^{-1} in acetonitrile to 2280 cm^{-1} in the adduct). This shows that the formation of *an* adduct with CH_3CN is quick, but the precipitation of the adduct: $MoCl_4{\cdot}2CH_3CN$, is kinetically limited (as observed by Allen et al.[10]). However, the formation of the adduct is not detrimental to its reaction with N_2H_4 as demonstrated by our previous results.[6] It has also been adequately demonstrated[11-13] that such end-on coordinated nitriles can easily be replaced by other ligands. The end-on coordinated nitrile is also seen to persist in the IR spectrum of samples prepared after a period of 1 day. The other interesting observation which is pertinent to the discussion in this section is the appearance of an additional absorption band at about 1680 cm^{-1} in the IR spectrum of samples collected after a period of 1 day. This band is attributed to the vibration of the carbon–nitrogen bond of acetonitrile upon side-on coordination with the Mo atom.[14,15] Moreover, there is a significantly large decrease in the stretching frequency of the carbon–nitrogen vibration in comparison to the $\nu_{C\equiv N}$ vibration of free acetonitrile ($\Delta\nu = -570$ cm^{-1}) which indicates an essentially double bond character with a η^2-coordination:



In summary, after a period of up to an hour, CH_3CN coordinates with Mo only in the end-on form ($\nu_{C\equiv N}$ = 2280 cm^{-1}), while after prolonged interaction for a day, it coordinates with Mo in both end-on and side-on fashions ($\nu_{C\equiv N}$ absorptions at 2280 and 1680 cm^{-1}). The influence of both these adducts on the formation of the nitride is discussed in the following subsections.

There is significant information available in the literature regarding formation of hydrazine complexes of transition-metal halides, carbonyls, and cyclopentadienyls,[16] but the study of their decomposition reactions has not been directed toward the synthesis of nitrides. It is well-known that the early transition metals (groups IVB to VIB) have an affinity to form stable metal–nitrogen bonds through exothermic (sometimes explosive) reactions. In the following sections we have discussed the influence of solvent interaction on the formation of the precursor and the nature of the decomposed product.

Reaction of N_2H_4 with $MoCl_5$ in CH_3CN (Dissolved and Mixed for an Hour). The objective of the study, as mentioned earlier, was to show the effect of solvent on the phase formation and microstructure. Hence, no detailed analyses were conducted on the precipitate obtained from the reaction to determine its structure and composition. However, on the basis of information available in the literature it is possible to make judicious hypotheses regarding the mechanism of the chemical reaction. For example, it is known that transition-metal halides form adducts with hydrazine.[16,17] The IR spectrum of the solid obtained from the reaction did not show any evidence of nitrile bonds confirming the expected replacement of the adduct by N_2H_4. In addition, the XRD spectrum of the precipitate (dried at room temperature under vacuum) showed that ammonium chloride was the only crystalline by-product of the reaction (Figure 3a). The formation of ammonium chloride could be attributed to the replacement of Mo–Cl bonds by N_2H_4 resulting in the liberation of HCl and the formation of hydrazide bonds on Mo ($Mo{-}NHNH_2$). The HCl gas released could subsequently react with N_2H_4 to form hydrazine hydrochloride, whose decomposition is known to yield ammonium chloride (Schmidt,[16] p 392).

To eliminate the crystalline NH_4Cl byproduct and to initiate decomposition of the precipitate, the powders were subjected to different heat treatments. Figure 3 shows the XRD patterns collected on the powders after drying at room temperature in vacuum, after heating at 130 °C under vacuum and after the two heat treatments in nitrogen at 500 °C for 10 h and 800 °C for 3 h. The drying treatment at 130 °C causes the decomposition of most of the NH_4Cl, leaving the amorphous hydrazide precursor behind. Heat treatment of the dried precursor at 500 °C in UHP N_2 causes the formation of γ-Mo_2N, although some NH_4Cl is retained (this has been consistently observed for this particular

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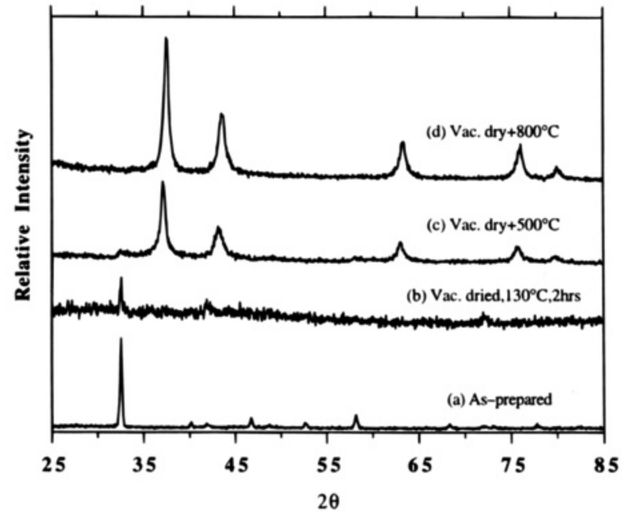

Figure 3. X-ray diffraction patterns collected on the as-precipitated (vacuum dried at room temperature, vacuum dried at 130 °C) and heat treated powders obtained from the reactions conducted in CH_3CN. The as prepared powder shows the presence of NH_4Cl, which is retained after the vacuum-drying treatment. Heat treatment in flowing UHP N_2 results in the formation of γ-Mo_2N at 500 °C itself.

heat treatment of the precipitate, and it could be due to the continued reaction of hydrazine liberated from the adduct or due to the condensation of the hydrazide with unreplaced chloride groups). However, further heat treatment at 800 °C for 3 h results in the formation of single-phase γ-Mo_2N.

The morphology of the dried (under vacuum at 130 °C) and heat-treated powders were observed using a scanning electron microscope. Figure 4 shows the unique microstructures of the powders obtained in the present reaction. Figure 4a shows a cellular porous microstructure of the powder with some small (~0.5 μm) spherical particles. Upon heat treatment at 500 and 800 °C the powders show the original perforated network structure being maintained, as shown in Figure 4b,c. In addition, both heat-treated materials show the spherical particles retained from the precursor stage. Thus, it can be seen that the nature and form of the precursor plays a very important role in the development of the resultant product morphology. BET surface area measurements were performed on the vacuum dried precipitate at 130 °C and on the heat-treated powders. The analyses gave a specific surface area value of 8 m^2/g for the vacuum-dried powder, and 30 m^2/g for the powder heat treated at 800 °C. The surface area data collected on the vacuum dried precipitates and of γ-Mo_2N (obtained at 800 °C) for both the solvent systems (acetonitrile and THF) are shown in Table 1 for comparison.

Reaction of N_2H_4 with $MoCl_5$ in CH_3CN (Dissolved and Mixed for a Day). As mentioned in the previous paragraphs, allowing the $MoCl_5$ to stay in solution in CH_3CN for over a day caused the appearance of an absorption band ($\nu_{C\equiv N} = 1680$ cm^{-1}) in the IR spectrum of the residue extracted from the solution (see experimental section for sample preparation details). The absorption band could be attributed to the η^2-coordination of CH_3CN with Mo. The IR spectrum collected on the dark brown precipitate obtained after the reaction of the $MoCl_5$ solution in CH_3CN with N_2H_4, showed the same absorption (1680 cm^{-1}) present in the solid. This suggests that the relatively stable η^2-coordinated nitrile group is not replaced by hydrazine during the reaction in solution and is still retained in the precipitate. The XRD pattern of the powder heat treated at 800 °C for 3 h in flowing UHP N_2 is shown in Figure 5. In addition to the diffraction peaks corresponding to γ-Mo_2N, peaks indicating the presence of α-Mo_2C can also be observed.

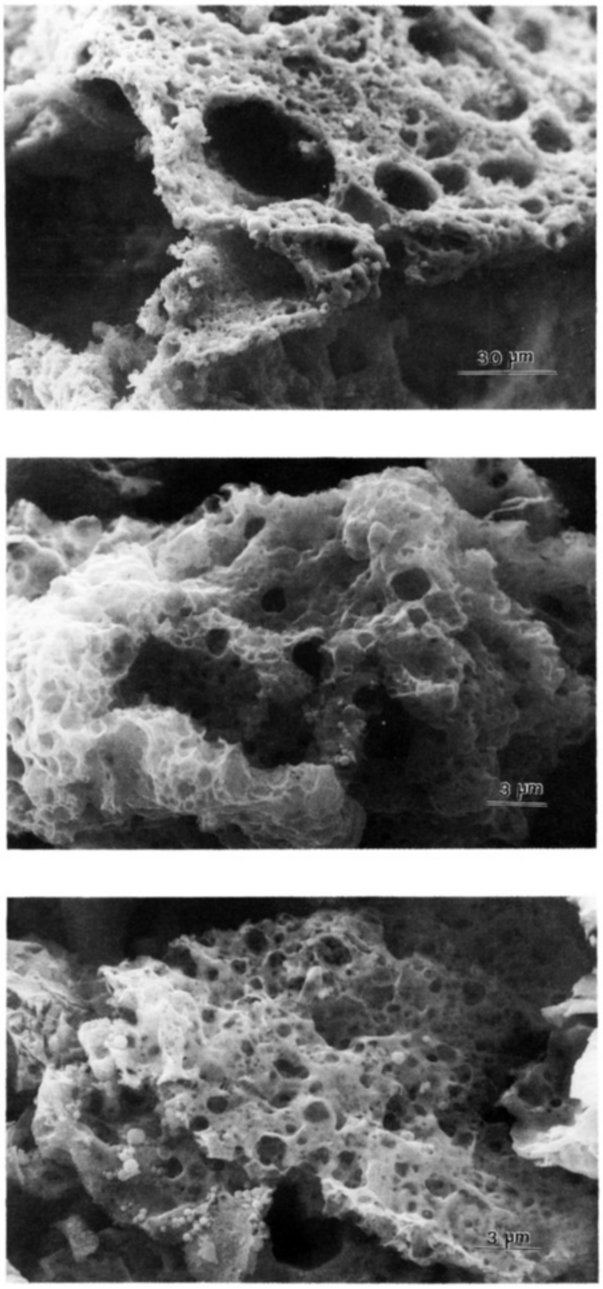

Figure 4. SEM micrographs showing the cellular morphology of the powders obtained from the reaction conducted in acetonitrile solvent. (a, top) The precipitate dried under vacuum at 130 °C, and the vacuum-dried powder heat treated under flowing UHP N_2 at (b, middle) 500 °C for 10 h and (c, bottom) 800 °C for 3 h. Note that the initial morphology of the precursor is largely retained in the final nitride product.

Table 1. BET Specific Surface Area Values (m^2/g) of Precursors (Vacuum Dried at 130 °C) and of γ-Mo_2N Powders (Obtained after Decomposition of the Precursor at 800 °C)

	solvent system	
	CH_3CN	THF
precursor	8	6
γ-Mo_2N	30	25

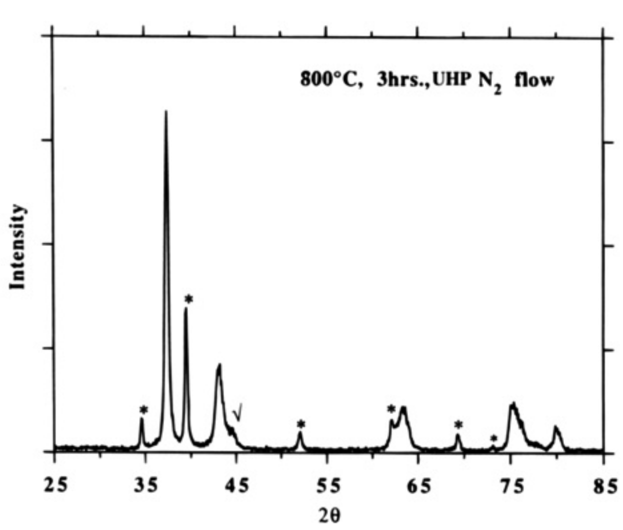

Figure 5. Upon extended interaction of $MoCl_5$ with CH_3CN, the precipitate obtained from the resultant reaction of the adduct in solution with N_2H_4 shows the formation of γ-Mo_2N as well as α-Mo_2C (indicated by asterisks) on heat treatment in UHP N_2 at 800 °C. The shoulder marked by a "√" could not be attributed to any known crystalline phase.

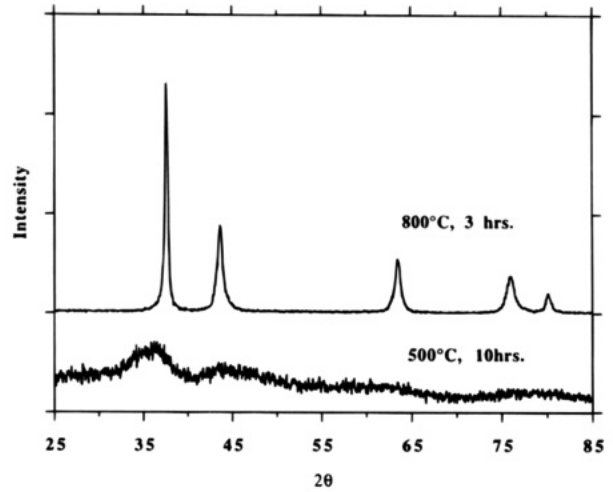

Figure 6. X-ray traces of the powders obtained from the reaction of $MoCl_5$ with N_2H_4 in THF. (a, bottom) After heat treatment in UHP N_2 at 500 °C for 10 h, the powder is nanocrystalline or amorphous in nature. (b, top) Heat treatment of the powder in UHP N_2 at 800 °C for 3 h results in the formation of single-phase γ-Mo_2N.

The formation of Mo–C bonds (caused by side-on coordination of the nitrile with the Mo center) in the precursor could facilitate crystallization of the carbide phase (α-Mo_2C) upon heat treatment of the precursor to 800 °C.

Tetrahydrofuran Solvent. The IR spectra collected on solutions of $MoCl_5$ in THF after three time durations of 1 min, 1 h, and 1 day (samples were prepared as described in the experimental procedure) showed a shift in the asymmetric C–O–C vibration[11] from 1075 cm^{-1} to about 1000 cm^{-1}. This confirmed the preferred end-on coordination of the Mo atom by THF.

The addition of N_2H_4 to $MoCl_5$ dissolved in THF resulted in the formation of a brown precipitate. XRD analysis of the precipitate also shows the presence of crystalline NH_4Cl similar to the reaction conducted in CH_3CN. IR spectra collected on the precipitate showed no evidence of any unreplaced THF adducts. Therefore, it is possible that the reaction in THF proceeds similar to the reaction in CH_3CN, namely the formation of a hydrazine adduct, as well as partial replacement of the Mo–Cl bonds to form the Mo–hydrazide bonds. Similar to the earlier case, it is also possible that HCl liberated from the substitution reaction further reacts with N_2H_4 to form hydrazine hydrochloride which decomposes to yield NH_4Cl.

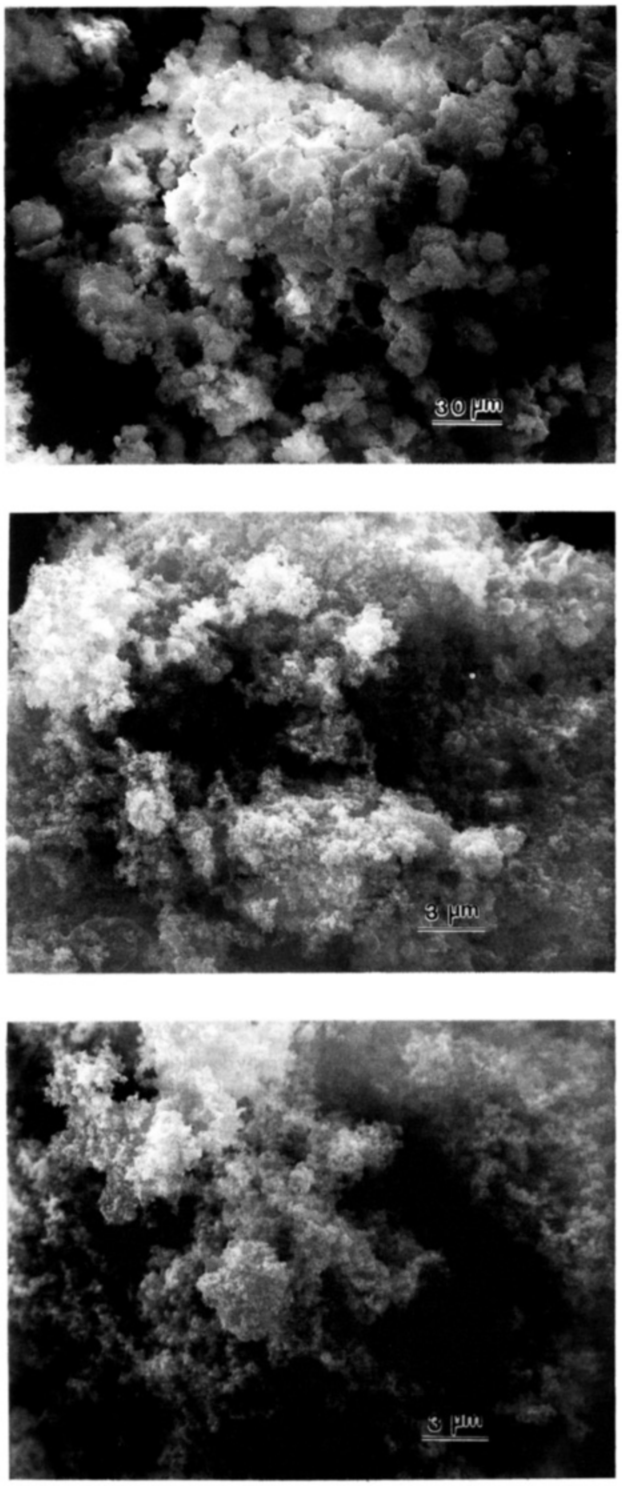

Figure 7. SEM micrographs of powders obtained from the reaction of $MoCl_5$ with N_2H_4 in THF (a, top) vacuum dried at 130 °C, (b, middle) heat treated at 500 °C in UHP N_2 for 10 h, and (c, bottom) heat treated at 800 °C in UHP N_2 for 3 h. The agglomerates contain fine submicron-sized particles and the original morphology of the precursor is by-and-large retained in the nitride.

After the precipitate was heated under vacuum at 130 °C for 2 h, the powder was heat treated in flowing UHP

N_2 at 500 °C for 10 h and at 800 °C for 3 h. The X-ray traces of the heat treated powders are displayed in Figure 6. At 500 °C, there is no evidence of any well-crystallized product (compare with the results obtained using acetonitrile solvent shown in Figure 3, where we see the formation of crystalline γ-Mo_2N at 500 °C). The crystallization of γ-Mo_2N is complete at 800 °C.

The micrographs of the vacuum dried, and heat treated powders are shown in Figure 7. The vacuum-dried precipitate (Figure 7a) consists of very fine sub-micron-sized particles, and agglomerates of these with some larger spherical particles to form large clusters in the range of several tens of microns. This structure is essentially maintained up to 500 °C as shown in Figure 7b as well as at a higher temperature (800 °C as shown in Figure 7c). It can be seen that the microstructures of the powders obtained using THF as the solvent system are very different from those obtained using acetonitrile (compare with Figure 4). The BET surface area of the vacuum dried powder is 6 m^2/g which increases to 25 m^2/g on heat treatment to 800 °C (see Table 1).

Although we have not exactly identified the mechanisms involved in the development of the precipitate morphology and the resultant microstructure of the precipitate, the important role played by the solvent on the precipitate morphology has been clearly demonstrated. Such an influence could be due to the reaction kinetics affecting the rate of release of HCl gas combined with the competitive rates of nucleation and growth of the hydrazide precursor. For example, the inhomogeneous nucleation and rapid growth rates combined with an uncontrolled escape of gaseous byproducts of the reaction in CH_3CN could have resulted in the formation of the observed cellular morphology. On the other hand, a more homogeneous nucleation and slower growth combined with an effective separation of the particles in THF could have caused the fine particulate morphology which is retained even after heat treatment of the precursor. Thus it can be seen that by conducting the reaction of $MoCl_5$ in different aprotic polar solvents, the final nitride (γ-Mo_2N) can be synthesized with uniquely different morphologies. The process can also be extended to the synthesis of the nitrides of other transition metals, which forms a part of our ongoing work.

Conclusions

Two nonhydroxylic polar solvents, acetonitrile and THF, were used to conduct the reaction of $MoCl_5$ with N_2H_4. $MoCl_5$ coordinates with both acetonitrile and THF in solution to form adducts. In acetonitrile however, we have seen the formation of two types of adducts, end-on (σ-bonded) and side-on (η^2-coordinated). The end-on coordinated adduct forms upon dissolution of the chloride in acetonitrile, while the side-on adduct is seen to form after a period of about a day. It has also been observed that on reacting the solution with hydrazine, the σ-bonded adduct is replaced by hydrazine, and when no side-on coordinated adducts exist in solution, the precipitate that is formed decomposes in flowing UHP N_2 to form single-phase γ-Mo_2N. On the other hand, when the solution is left for a day in order to form the η^2-coordinated adduct, the precipitate obtained from the reaction with hydrazine decomposes to result in a mixture of γ-Mo_2N and α-Mo_2C. We attribute the formation of the carbide to the nonreplacement of the η^2-coordinated adduct by hydrazine, giving rise to the presence of Mo−C bonds in the initial precipitate, which facilitate the carbide formation upon subsequent decomposition during heat treatment.

THF also forms an end-on adduct in solution with $MoCl_5$ which is easily replaced by hydrazine to yield a brown precipitate. The precipitate formed from the reaction decomposes on heat treatment in UHP-N_2 to form single-phase γ-Mo_2N. The morphology of the precipitates obtained by conducting the reaction in the two solvent systems are very different. In acetonitrile the precipitates have a cellular porous nature, while in THF they consist of agglomerates of fine particles. In either case, the original precipitate morphology is retained in the final nitride even after subsequent heat treatment.

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