Rapid Solid-State Synthesis of Tantalum, Chromium, and Molybdenum Nitrides

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Solid-state metathesis (exchange) reactions can be used to synthesize many different transition-metal nitrides under ambient conditions including TiN, ZrN, and NbN. Typical metathesis reactions reach temperatures of greater than 1300 °C in a fraction of a second to produce these refractory materials in highly crystalline form. Likely due to the large amount of heat produced in these solid-state reactions, some transition-metal nitrides such as TaN, CrN, and γ-Mo_2N cannot easily be synthesized under ambient conditions. Here metathesis reactions are demonstrated to produce the cubic nitrides TaN, CrN, and γ-Mo_2N when sufficient pressure is applied before the reaction is initiated. By pressing a pellet of $TaCl_5$ and Li_3N with an embedded iron wire, crystalline cubic TaN forms under 45 kbar of pressure after a small current is used to initiate the chemical reaction. Crystalline cubic CrN is synthesized from $CrCl_3$ and Li_3N initiated under 49 kbar of pressure. Crystalline γ-Mo_2N is produced from $MoCl_5$ and Ca_3N_2 (since $MoCl_5$ and Li_3N self-detonate) initiated under 57 kbar of pressure. The addition of ammonium chloride to these metathesis reactions drastically lowers the pressure requirements for the synthesis of these cubic nitrides. For example, when 3 mol of NH_4Cl is added to $CrCl_3$ and Li_3N, crystalline CrN forms when the reaction is initiated with a resistively heated wire under ambient conditions. Cubic γ-Mo_2N also forms at ambient pressure when 3 mol of NH_4Cl is added to the reactants $MoCl_5$ and Ca_3N_2 and ignited with a resistively heated wire. A potential advantage of synthesizing γ-Mo_2N under ambient conditions is the possibility of forming high-surface-area materials, which could prove useful for catalysis. Nitrogen adsorption (BET) indicates a surface area of up to 30 m^2/g using a Langmuir model for γ-Mo_2N produced by a metathesis reaction at ambient pressure. The enhanced surface area is confirmed using scanning electron microscopy.

Introduction

Cubic-phase transition-metal nitrides are of interest due to their hardness (8−9 on Moh's scale) and high melting points (2000−4000 °C).[1] These nitrides are resistant to chemical attack even at elevated temperatures.[2] Potential applications include protective coatings for cutting tools[3,4] and ultra-high-vacuum system components.[5] Recently, molybdenum nitrides have been found to be useful as heterogeneous catalysts in the synthesis of ammonia[6] and for hydrodenitrogenation[7−9] and hydrodesulfurization[10−13] reactions. In addition, chromium nitride coated steels for corrosion protection are now commercially available.[14]

The cubic group 4 (Ti, Zr, Hf) and group 5 (V, Nb) transition-metal mononitrides ($MN_{1.0}$) are generally synthesized by heating the metal in the presence of nitrogen or ammonia at elevated temperatures.[1,15−17] An alternate method is self-propagating high-temperature synthesis (SHS).[18−21] The SHS method involves the ignition of high-surface-area metal powders under high nitrogen pressure or in the presence of sodium azide. Although this method produces nitrides rapidly, unreacted or undernitrided metals can be a problem. Another rapid method for synthesizing transition-metal nitrides uses metal halides and alkali-metal or alkaline-earth-metal nitrides in metathesis (exchange) reactions.[22−24] These solid-state metathesis (SSM) reactions are self-propagating and driven by the formation of stable salt byproducts.[22−26] After initiation at room temperature, these reactions often reach temperatures of >1300 °C in less than 1 s and cool rapidly. This method is especially effective at synthesizing the mononitrides of groups 4 (Ti, Zr, Hf) and 5

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(V, Nb), most likely because they are thermodynamically stable in this temperature range, as indicated in the appropriate phase diagrams.[27,28]

The other cubic transition-metal nitride of group 5 (i.e., TaN) and group 6 cubic nitrides (e.g., CrN and γ-Mo_2N) are not as easy to synthesize by solid-state metathesis reactions because the temperature that the metathesis reactions reach is higher than the decomposition temperatures of these nitrides.[27,28] Attempts to use metathesis reactions to synthesize group 6 nitrides have been reported recently in the literature.[29,30] A new phase of Mo_2N with the Mo_2C structure type was synthesized by a metathesis reaction between $MoCl_5$ and Ca_3N_2 performed in a $CaCl_2$ melt.[29] Solid-state metathesis reactions between $CrCl_2$ and Mg_3N_2, with the addition of $MgCl_2$ as a diluent, can produce CrN when heated at 350−500 °C.[30]

The cubic transition-metal nitride systems appear to require higher nitrogen pressures than the reactant nitrides (i.e., Li_3N, Ca_3N_2, and/or NaN_3) typically used in metathesis reactions can provide on decomposition.[31] The metathesis reaction between tantalum pentachloride and lithium nitride to produce cubic TaN illustrates this principle. In conventional methods, the synthesis of cubic TaN requires temperatures $>$1700 °C and $\geq$160 bar of nitrogen.[32] The metathesis reaction between tantalum pentachloride and lithium nitride

$$\mathrm{TaCl_5 + {}^5/_3Li_3N \rightarrow TaN + 5LiCl + {}^1/_3N_2} \qquad (1)$$

under ambient conditions produces only the subnitride, Ta_2N, rather than the cubic mononitride, TaN. However, by adding 12 mol of sodium azide (NaN_3) to the above reaction, a significant nitrogen overpressure is created, which enables the cubic phase (TaN) to form along with hexagonal Ta_2N.[23] Although the formation of high-pressure phases has been observed in the products of ambient-pressure metathesis reactions, these products have always been contaminated with a significant fraction of subnitrides (i.e., Ta_2N, Cr_2N) and/or metal (Cr, Mo). This is observed for tantalum nitride (TaN with Ta_2N impurities), chromium nitride (CrN with Cr_2N and Cr impurities), and molybdenum nitride (γ-Mo_2N with Mo impurities).

To synthesize the high-pressure and/or high-temperature phases of chromium, molybdenum, and tantalum nitride directly, at least one of two parameters must be altered to favor the cubic phases. Specifically, either sufficient pressure needs to be applied to the reactions or the temperature of the reaction needs to be lowered to a regime where these compounds become thermodynamically favorable. In this paper, we report the successful synthesis of the cubic nitrides TaN, CrN, and γ-Mo_2N either using high pressures or by adding ammonium salts which decrease the maximum temperature of the reaction and increase the amount of active nitrogen species in the reaction. Solid-state metathesis reactions under pressures of up to 50 kbar have been reported recently using a modified Bridgman anvil cell for the successful synthesis of GaN.[33] This method is now shown to have wider applicability, enabling the synthesis of the group 5 nitride TaN and the group 6 nitrides CrN and γ-Mo_2N.

Experimental Section

Caution! Most solid-state metathesis reactions are highly exothermic, and in some cases the precursors may spontaneously detonate when mixed or ground together. Care should be taken to do reactions of this type on a small scale first (less than 1 g of total reactant mixture) with adequate safety precautions. These reactions may ignite when exposed to small amounts (one drop) of a solvent such as water or methanol. It is also important to calculate the pressure of the nitrogen gas byproduct before performing any reactions in closed vessels, since high gas pressures can lead to explosions.

Reagents. The metal halides $TaCl_5$ (Aldrich, 99.9%) and $MoCl_5$ (Strem, 99.5%) were purified prior to use by vapor transport in sealed, evacuated (10^{-4} Torr) Pyrex tubes across a temperature gradient from 190 °C (for $TaCl_5$) or 200 °C (for $MoCl_5$) to room temperature. This purification enabled separation of the pentachloride from lower halides and oxyhalides as described by Schäffer.[34] The compounds $CrCl_3$ (Aldrich, 99.9%), Li_3N (Cerac, 99.5%), and Ca_3N_2 (Cerac, 99.5%) were used as received. Chromium iodide (CrI_3) was synthesized by heating Cr metal (Cerac, −325 mesh, 99.2%) and solid I_2 (Strem) for 12 h in a sealed, evacuated Pyrex tube across a temperature gradient from 170 to 450 °C. Ammonium chloride (NH_4Cl) (Baker Chemical Co.) was heated to 200 °C under dynamic vacuum with an inline cold trap to remove any adsorbed water.

Synthesis. All reactions were performed in a helium-filled drybox. The finely divided reactants were ground together (see specific reactions below for the order of mixing) in an agate mortar and pestle. The reactants were then transferred to a 45 mL stainless steel reaction vessel (non-air-tight) modeled after a bomb calorimeter.[35] Reactions were restricted to small scales (approximately 1 g of total reactants) since high temperatures and high pressures are often generated. In the γ-Mo_2N synthesis, 4 mmol (~1 g) of $MoCl_5$ was used with a stoichiometric amount of Ca_3N_2 and 3 mol of NH_4Cl (referred to as the ambient-pressure reaction). $MoCl_5$ was initially ground together with NH_4Cl before the addition of Ca_3N_2. *Caution!* Never grind freshly transported $MoCl_5$ with Ca_3N_2 or Li_3N directly, as this mixture will spontaneously detonate. The ambient-pressure reactions that produce TaN and CrN were performed using the same procedure except that the metal halide ($TaCl_5$, $CrCl_3$, or CrI_3) was ground together with both Li_3N and NH_4Cl. These reactions were initiated by a resistively heated Nichrome wire (~850 °C applied for $<$1 s) placed in the reactant powder mixture. The products were removed from the drybox and washed with distilled water to dissolve the salt byproducts and any unreacted starting materials. The products were then isolated using vacuum filtration.

High-pressure reactions were performed in modified Bridgman anvil cells, utilizing a method developed originally for the synthesis of gallium nitride.[33] The reactants (~60 mg for a 0.025 mL cell) were ground to a fine powder and put in a pellet press with a thin (0.15 mm diameter) iron wire placed in the middle of the powder. This assembly was then pressed into a dense pellet (~4.8 mm diameter, ~1.5 mm high). An Inconel gasket was coated with an alumina/magnesia paste (dyed red with ~1% iron oxide, added for identification purposes), affixed to the bottom anvil, and cured. The reactant pellet was then placed in the gasket with the top anvil aligned over it. Leads made of tantalum or copper were next put in contact with the tungsten carbide cores of the anvils and then covered with poly(vinyl chloride) sheets. This apparatus was kept in a helium-filled resealable plastic bag for transport to the high-pressure press. The Bridgman anvils were then placed in a hydraulic press that can generate up to 100 kbar of static pressure. The pressure applied was monitored using a calibrated load cell that measures applied force. After the pressure was increased, the reaction was initiated by passing current through the metal leads, which

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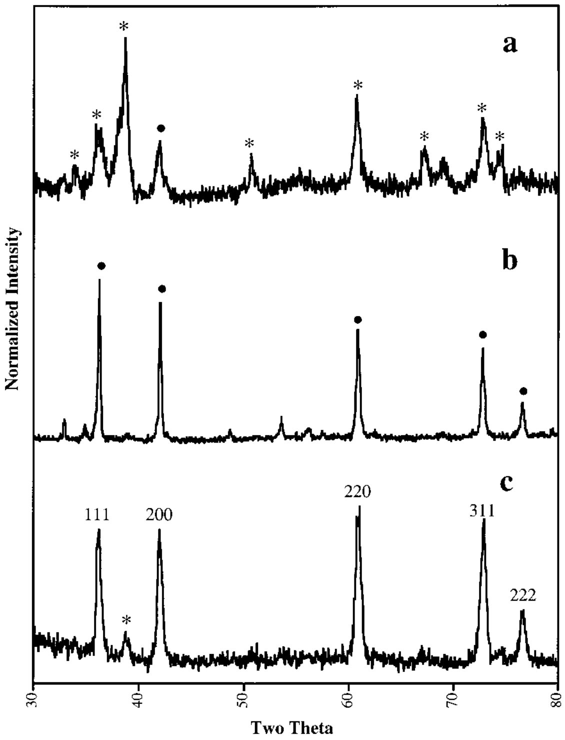

Figure 1. Powder X-ray diffraction patterns of washed products from the SSM reaction of $TaCl_5$ and Li_3N under the following conditions: (a) ignited at ambient pressure in a steel reactor; (b) ignited under 45 kbar of static pressure; (c) combined with NH_4Cl (in a 1:2:3 molar ratio of $TaCl_5$:Li_3N:NH_4Cl) and ignited in a steel reactor under ambient pressure. The Miller indices for cubic TaN are given in (c) and marked with a dot in (a) and (b). The diffraction peaks marked with an asterisk correspond to hexagonal Ta_2N.

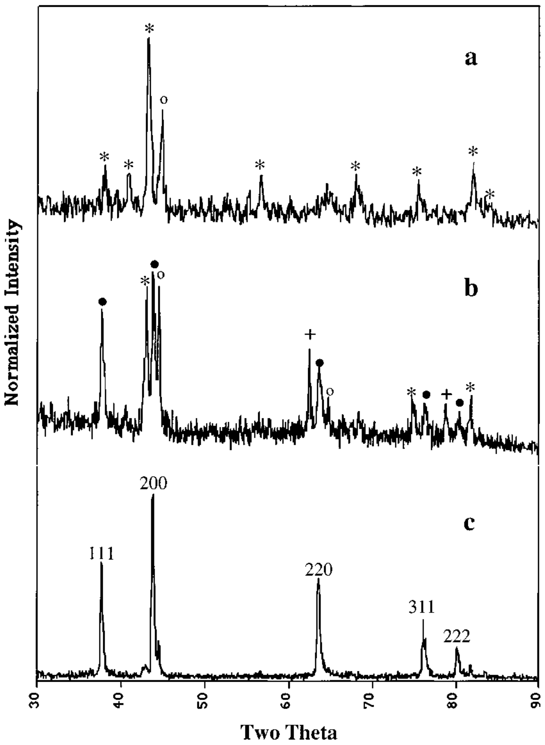

Figure 2. Powder X-ray diffraction patterns of washed products from the SSM reaction between $CrCl_3$ and Li_3N: (a) ignited at ambient pressure in a steel reactor; (b) ignited under 39 kbar of static pressure in a modified Bridgman anvil cell; (c) ignited under 49 kbar of pressure. The Miller indices for cubic CrN are given in (c) and indicated by a dot in (b). The other phases are identified as follows: Cr_2N, asterisk; Cr, open dot; alumina/magnesia paste used in high-pressure cell, plus sign.

resistively heats the wire in the reactant pellet. After the reaction was complete, the products were collected and washed with distilled water to remove the salt byproducts. These reactions can be scaled up using larger volume cells such as those found in a modified-belt-type apparatus.[36,37]

Powder X-ray Diffraction. The washed products were examined by powder X-ray diffraction (XRD) using a $\theta-2\theta$ diffractometer (Crystal Logic) with Cu Kα radiation. Scans were taken in the range of 2θ, 10−100° at 0.10 or 0.05 deg intervals, and with 3 s count times. The lattice parameters were computed using least-squares refinement.

Electron Microscopy. Loose powders were affixed to graphite disks with colloidal graphite paste, and particle morphologies and sizes were analyzed by scanning electron microscopy (SEM; Cambridge Stereoscan 250).

Surface Area Analysis. A 0.5−1 g sample of loose powder was placed in a glass tube with a frit seal cap and heated under dynamic vacuum to 150 °C to remove any adsorbed gases and water. The tube was then moved to a Micrometrics ASAP 2010 BET surface area analyzer. The data were worked up using specialized software (Micrometrics ASAP 2010). Surface areas were measured by the pressure difference between the amount of nitrogen gas adsorbed and desorbed from the powder surface utilizing both the BET and Langmuir methods of analysis.[38]

Results

Tantalum Nitride. The synthesis of tantalum nitrides has been explored at ambient pressure by solid-state metathesis[23] and at high pressure by self-propagating high-temperature synthesis.[31] The ambient-pressure reaction between $TaCl_5$ and $^5/_3Li_3N$ results in the synthesis of hexagonal Ta_2N (Figure 1a). Diffraction peaks of hexagonal Ta_2N are marked with an asterisk in Figure 1a. By applying 45 kbar of static pressure to the reaction of $TaCl_5$ and Li_3N, the only crystalline product produced is cubic TaN (Figure 1b). The diffraction peaks marked with a dot in Figure 1b correspond to face-centered cubic TaN (JCPDS no. 32-1283). The reaction of $TaCl_5$, Li_3N, and NH_4Cl (in a 1:2:3 molar ratio) results in the formation of crystalline cubic TaN along with a trace of hexagonal Ta_2N (Figure 1c).

Chromium Nitride. The reaction of $CrCl_3$ and Li_3N at ambient pressure produces the mixed products Cr and Cr_2N (Figure 2a). The major diffraction peaks of Cr_2N are marked with an asterisk, while the remaining peaks belonging to Cr metal are marked with an open dot. The peaks for Cr_2N are shifted to slightly higher 2θ values likely due to nitrogen vacancies, as compared to a standard pattern (JCPDS no. 11-65). By applying 39 kbar of pressure to the reaction of $CrCl_3$ and Li_3N, some cubic CrN (denoted with a dot in Figure 2b) is formed in addition to the ambient-pressure products Cr and Cr_2N. The peak at 63.55 2θ (denoted by a plus sign) is due to the magnesia/alumina paste used to affix the gasket to the Bridgman anvil cell. Applying 49 kbar of pressure, followed by ignition of the reactants, produces cubic CrN as the only crystalline nitride product (Figure 2c). The ambient-pressure reaction of $CrCl_3$, Li_3N, and NH_4Cl (in a 1:1:3 molar ratio) results in the formation of Cr, Cr_2N, and CrN. Reactants using molar ratios of 1:1:y where y ranges from 0.5 to 5 as well as

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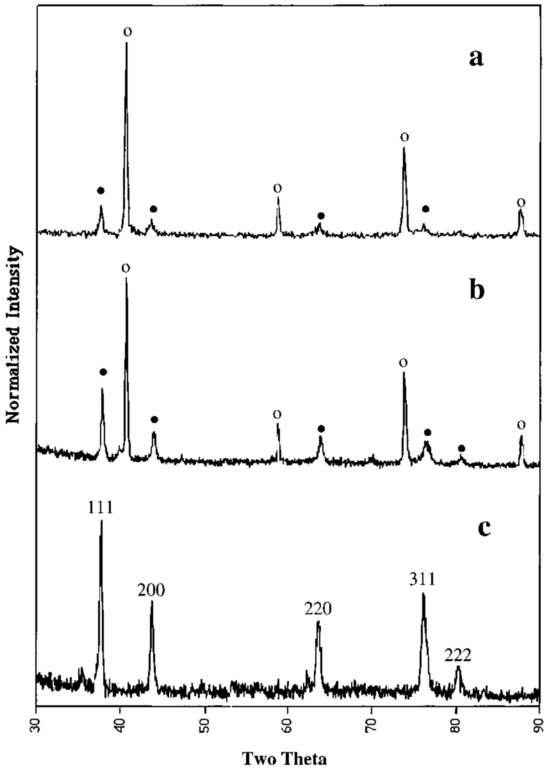

Figure 3. Powder X-ray diffraction patterns of washed products from the SSM reaction between $MoCl_5$ and Ca_3N_2 under the following conditions: (a) reactants ignited as a dense pellet; (b) reactants held under constant-volume conditions; (c) reactants put under 57 kbar of static pressure. The Miller indices for γ-Mo_2N are given in (c), and the diffraction peaks are indicated by a dot in (a) and (b). The peaks marked with an open dot correspond to Mo metal.

1:0.5:0.5 and 1:0.75:0.25 have been carried out. All of these ratios result in similar product mixtures (Cr, Cr_2N, CrN).

The ambient-pressure reaction of CrI_3 and Li_3N results in highly crytalline Cr_2N without any Cr metal impurity. The peaks corresponding to Cr_2N are again shifted to slightly higher angles compared to the standard pattern. By adding 3 mol of NH_4Cl to the ambient pressure reaction of CrI_3 and Li_3N, highly crystalline CrN with some Cr_2N results.

Molybdenum Nitride. The reaction between $MoCl_5$ and Li_3N is self-detonating; i.e., it goes off spontaneously upon grinding the two powders together in a mortar and pestle. An alternative nitrogen source, Ca_3N_2, was therefore used to react with $MoCl_5$. The ambient-pressure reaction of $MoCl_5$ and Ca_3N_2

$$ {}^{6}/_{5}MoCl_5 + Ca_3N_2 \rightarrow {}^{3}/_{5}\gamma\text{-}Mo_2N + 3CaCl_2 + {}^{7}/_{10}N_2 \quad (2) $$

produces highly crystalline Mo metal and no crystalline nitride products. By pressing the reactant mixture into a pellet before detonation, the reaction produces an only slightly crystalline product indexed to γ-Mo_2N (JCPDS no. 25-1366) along with crystalline Mo metal (Figure 3a). The γ-Mo_2N product is denoted with an asterisk in the XRD pattern, while Mo metal is denoted with an open dot. By performing the same reaction in a piston cylinder cell,[39] which provides pseudo-constant-volume conditions, the crystallinity of the γ-Mo_2N produced is improved, but is still far less crystalline than that of the Mo metal contaminant (Figure 3b). When 57 kbar of pressure is applied to these reactants using a Bridgman anvil cell, crystalline cubic γ-Mo_2N forms (Figure 3c). The addition of 3 mol of NH_4Cl to the reaction between $MoCl_5$ and Ca_3N_2 (eq 2) at ambient pressure also produces highly crystalline γ-Mo_2N with a small amount of Mo metal and $CaMoO_4$ (Figure 4a). These impurities can readily be removed by washing with 0.2 M hydrochloric acid (Figure 4b).

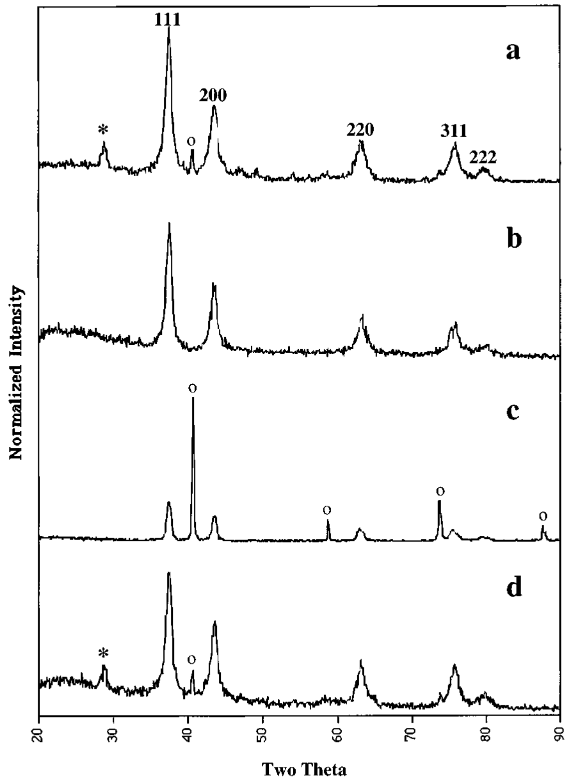

Figure 4. Powder X-ray diffraction patterns of washed products from the ambient pressure reaction between $MoCl_5$ and Ca_3N_2 with (a) 3 mol of NH_4Cl added to ~1 g of total reactants, (b) product of washing (a) in a 0.2 M HCl solution, (c) 3 mol of NH_4Cl aded to ~2 g of total reactants, and (d) 3.5 mol of NH_4Cl added to ~2 g of total reactants. The Miller indices for cubic γ-Mo_2N are given in (a). The diffraction peaks marked by an asterisk correspond to $CaMoO_4$, and those marked by an open dot correspond to Mo metal.

The mixing order of the reactants is important in the synthesis of γ-Mo_2N. If untransported $MoCl_5$, which contains lower oxidation state molybdenum chlorides and oxychlorides, is used in the reaction with Ca_3N_2 and NH_4Cl, the $MoCl_5$ and Ca_3N_2 can be safely ground together. However, if pure, vapor-transported $MoCl_5$ is used, it must first be mixed with NH_4Cl before Ca_3N_2 is added to avoid spontaneous detonation. The above ambient-pressure synthesis is the result of reactions carried out on a small scale (<1 g of total reactants). When the reaction is scaled up (≥1 g of total reactants), the γ-Mo_2N formed is less crystalline compared to that in the small-scale reaction and crystalline Mo metal is found (Figure 4c). Addition of an extra 0.5 mol of NH_4Cl (ratio 1.2:1:3.5) to a ~2 g reaction results in products comparable to those of the small-scale reaction (Figure 4d).

Surface Area. Cubic molybdenum nitride (γ-Mo_2N) powder synthesized from a small-scale ambient-pressure reaction among $MoCl_5$, Ca_3N_2, and 3 mol of NH_4Cl (Figure 3c) has a surface area of 22 m^2/g calculated using the BET modeling system and 30 m^2/g using a Langmuir model. The surface area of the γ-Mo_2N produced by a large-scale reaction (~2 g of reactants, Figure 3d) of $MoCl_5$, Ca_3N_2, and 3.5 mol of NH_4Cl was slightly

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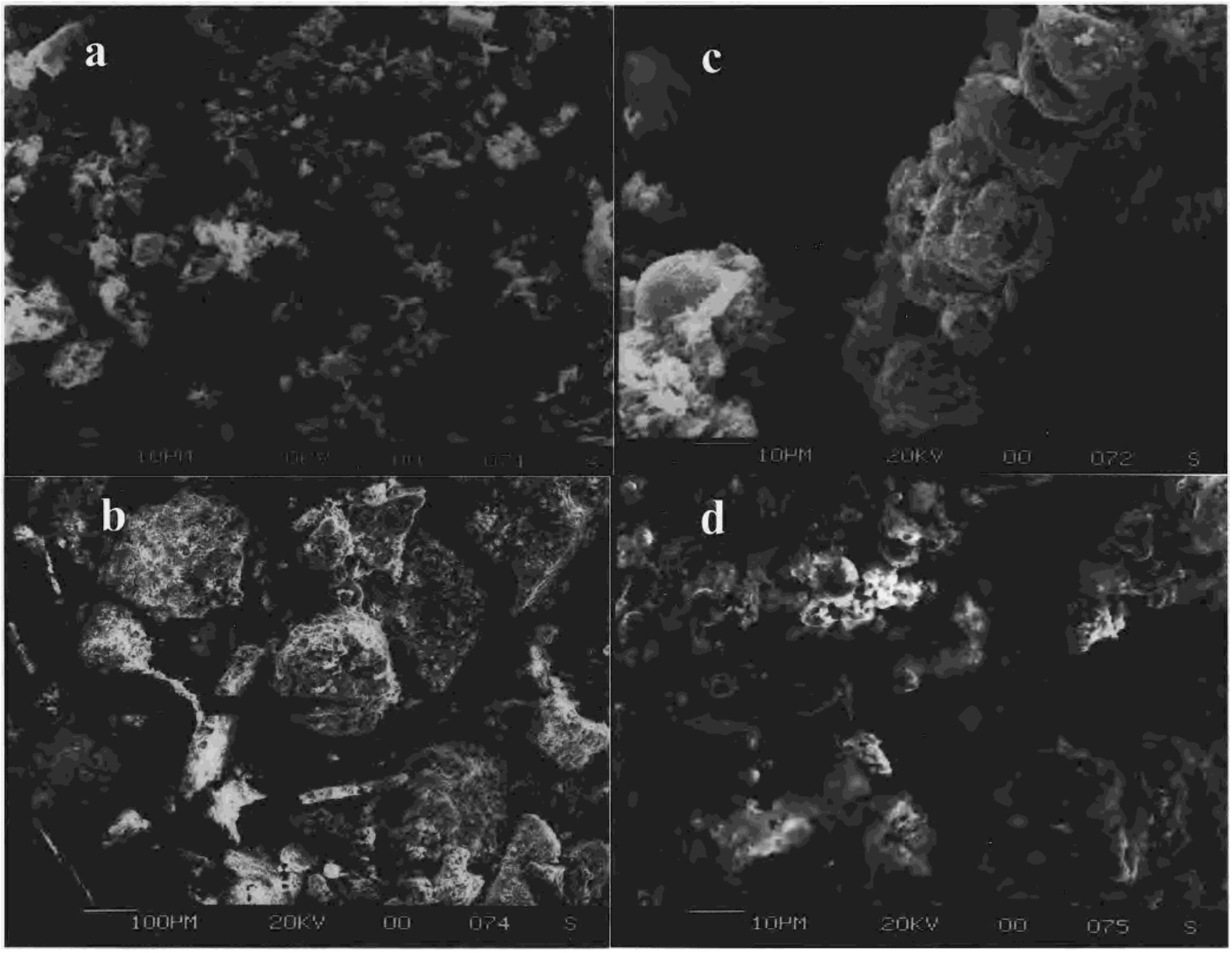

Figure 5. Scanning electron microscopy images of (a) a small-scale reaction (~1 g) between $MoCl_5$ and Ca_3N_2 with 3 mol of NH_4Cl added, (b) the reaction of $MoCl_5$ and Ca_3N_2 in a piston cylinder cell, (c) a large-scale reaction of $MoCl_5$ and Ca_3N_2 with 3.5 mol of NH_4Cl added, and (d) an expanded view of the center particle in (b).

lower, 16 and 22 m^2/g using the BET and Langmuir models, respectively. SEM images of the washed powders are shown in Figure 5. As can be seen in Figure 5a, these SEM images indicate that the powder synthesized from $MoCl_5$, Ca_3N_2, and 3 mol of NH_4Cl on a small scale (~1 g of total reactants) consists of spherical particles with average diameters of 5−10 μm. Figure 5c shows that the γ-Mo_2N powder synthesized on a larger scale (~2 g of total reactants) consists of much larger, nonspherical particles 30−50 μm in diameter. Parts b and d of Figure 5 are images of the γ-Mo_2N powder synthesized from the reaction between $MoCl_5$ and Ca_3N_2 in a piston cylinder cell under pseudo-constant-volume conditions. The particle size of the γ-Mo_2N in Figure 5b is much larger than that synthesized at ambient pressure. The γ-Mo_2N consists mainly of spherical particles approximately 150 μm in diameter. Figure 5d shows a more detailed view of the particles found in the center of Figure 5b.

Discussion

The nitrides reported here (TaN, CrN, and γ-Mo_2N) have proven to be difficult to synthesize in previous attempts using solid-state metathesis reactions, likely due to the following: (1) tantalum mononitride (TaN) requires higher nitrogen pressures to form in comparison to its subnitride, Ta_2N;[15] (2) both CrN and γ-Mo_2N have a small stability range in comparison to the group 4 and 5 nitrides;[28] (3) since metathesis reactions take place in <1 s, the nitrogen gas produced by reactant decomposition may not be sufficient to form the product nitride. It appears that, to incorporate a stoichiometric amount of nitrogen, a significant nitrogen overpressure must be maintained during the reaction. In the synthesis of TaN, CrN, and γ-Mo_2N, the non-air-tight steel reactor is inadequate to contain the nitrogen gas produced from the solid-state metathesis reactions. As is found in the case of γ-Mo_2N, by pressing the reactant mixture into a fully dense pellet, the amount of nitride formed in the reaction increases. The pellet likely provides a larger barrier to diffusion of gas out of the reactant mixture, thus increasing the amount of nitrogen available for nitride formation. By applying sufficient pressure (e.g., >40 kbar) to an SSM reaction in a Bridgman anvil cell, this diffusion barrier can be greatly enhanced. This is particularly important in the reaction between $CrCl_3$ and Li_3N to produce CrN. From the phase diagram of chromium and nitrogen, it is known that only in a small finite range (49.5−50.0 atom % nitrogen) will cubic CrN form.[28] Thus, experimentally we observe that only at high pressures (≥49 kbar), where the nitrogen produced by Li_3N is maintained in the reactant mixture throughout the reaction, can cubic CrN be synthesized by solid-state metathesis reactions. Similar high pressures are needed for both the tantalum nitride (45 kbar) and molybdenum nitride (57 kbar) systems.

The containment of the nitrogen byproduct is essential for obtaining a stoichiometric ratio of transition metal to nitride. This is a major factor influencing the synthesis of group 6 nitrides as well as tantalum nitride. By applying static pressure, the nitrogen gas can be contained and the stoichiometry maintained, making cubic nitride formation favorable.

A result of applying pressure to solid-state metathesis reactions is that the products have the property of well-sintered materials. The SEM image of the product of the pseudo-constant-volume reaction between $MoCl_5$ and Ca_3N_2 (Figure 5d) shows this sintering effect. The material produced is highly crystalline but has a low surface area. Because some of these nitrides, particularly γ-Mo_2N, are potential catalytic materials, low-pressure synthetic methods are desirable.

The addition of ammonium chloride to an SSM reaction has been shown to provide a low-pressure route to other nitrides.[40] Ammonium chloride appears to have two functions, acting first as a heat sink and then as a source of nitrogen. The practice of using inert salts (i.e., LiCl, NaCl, etc.) as heat sinks in solid-state metathesis reactions is well documented in the literature.[41-43] However, ammonium chloride only functions as a heat sink until the reaction temperature exceeds its sublimation point of 340 °C. Upon sublimation, it decomposes to NH_3 and HCl, providing a local ammonia atmosphere for the reactants.[44] Experimental evidence indicates that the ammonia produced can have an active role in the nitridation process. For example, when 2 mol of NH_4Cl is added to an SSM reaction expected to form TaC

$$TaCl_5 + CBr_4 + {}^9/_2Mg \rightarrow TaC + {}^5/_2MgCl_2 + 2MgBr_2 \quad (3)$$

the only nonsalt product formed is partially crystalline TaN. Therefore, as the reaction temperature increases above 340 °C, it reaches a regime where the NH_3 produced from NH_4Cl decomposition is capable of further acting as a nitriding agent. Since the amount of ammonium chloride that is effective in acting as a nitriding agent is unknown and may vary from one reaction to another, this could explain why its use is not effective in producing CrN. Cubic chromium nitride (CrN) has a very small stability range, and if nitrogen is in excess, a mixture of products will result. Therefore, our results appear to be consistent with the phase diagram of CrN.[28]

The use of NH_4Cl in solid-state metathesis reactions enables a rapid, low-temperature route to bulk group 5 (tantalum) and group 6 (chromium and molybdenum) nitrides. The nitride of most interest may be γ-Mo_2N. Since reports of the temperature-programmed reaction of MoO_3 and NH_3 at high temperatures resulting in high surface area (up 170 m^2/g) γ-Mo_2N powders,[45] many efforts have been made to produce bulk, high-surface-area molybdenum nitride powders for catalysis. The molybdenum nitride powders synthesized here have considerably smaller surface areas (up to 30 m^2/g, using BET with a Langmuir model), which is consistent with γ-Mo_2N synthesized by other chemical methods.[46] Recent studies on the catalytic properties of γ-Mo_2N powders indicate that both high- and medium-surface-area powders demonstrate the same activity and selectivity as hydrodesulfurization catalysts.[13] Thus, molybdenum nitrides of medium surface area, such as those synthesized by solid-state metathesis reactions, could be potentially useful as hydrodesulfurization catalysts.

Conclusions

Highly crystalline cubic chromium, molybdenum, and tantalum nitrides have been synthesized by using solid-state metathesis reactions under pressure. The application of static pressures (>40 kbar) to solid-state metathesis reactions favors the formation of nitrides that have small stability ranges and require high nitrogen pressures to form. An alternative route to synthesizing these materials is to add several moles of ammonium chloride to the reactants. Ammonium chloride acts as both a nitriding agent and a heat sink for the reactants. The use of this salt is effective in synthesizing both cubic TaN and γ-Mo_2N. Materials synthesized under ambient conditions have higher surface areas than those synthesized under high pressure, as confirmed by scanning electron microscopy. Molybdenum nitride, γ-Mo_2N, synthesized under ambient conditions, is shown to have a surface area of 30 m^2/g using the Langmuir model. Materials synthesized under ambient conditions could be potentially useful in catalysis.

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