New Approach to the Synthesis of Bulk and Supported Bimetallic Molybdenum Nitrides

Huamin Wang, Wei Li,* and Minghui Zhang

Institute of New Catalytic Materials Science, College of Chemistry, Nankai University, Tianjin 300071, People's Republic of China

A new and facile method for the preparation of bulk and MCM41-supported bimetallic molybdenum nitrides is described. Both Ni_2Mo_3N and Co_3Mo_3N are prepared in a one-step synthesis without ammonolysis. A mixed-salt precursor containing HMT (HMT = hexamethylenetetramine), Ni (Co) nitrate, and $(HMT)_2(NH_4)_4Mo_7O_{24} \cdot 2H_2O$ is directly converted to bimetallic nitride under a flow of argon at 923 K. The formation process shows that Ni (Co) metal and γ-Mo_2N are formed first and that they then transform into the bimetallic nitride phase on remaining at 923 K. The HMT is used as a reducing agent and nitrogen source. The metal salts and HMT are initially contained in the precursor, thus allowing us to obtain bimetallic nitride by a one-step synthesis without ammonolysis. To get high surface catalysts, MCM41-supported bimetallic nitrides have also been successfully prepared with this simple method. The ammonolysis is not a prerequisite here, and the bimetallic molybdenum nitride is facile under mild conditions. The results suggest that this novel method possesses the potential to be a general route for the preparation of bimetallic molybdenum nitrides.

Introduction

Monometallic and bimetallic nitrides of early transition metals have attracted considerable attention in recent years due to a number of interesting properties that they display, which can include hardness, electrical or thermal conductivity, superconductivity, magnetism, and catalytic activity.[1,2] In particular, the Mo-based nitrides have been identified as potential catalysts for many applications.[3−13] In this respect, the bimetallic molybdenum nitrides M_nMo_3N (M = Ni, n = 2; M = Co and Fe, n = 3) showed better activity and have received the most attention.[5,7,9−13] Jacobsen[5] has reported that bimetallic nitrides Ni_2Mo_3N, Co_3Mo_3N, and Fe_3Mo_3N exhibit high catalytic activities in ammonia synthesis and that the promoted catalyst Cs/Co_3Mo_3N is more active than the commercial, multi-promoted, iron-based catalyst. Liang et al.[8] have found that the nickel molybdenum nitride catalyst shows good catalytic activity in ammonia decomposition. On the other hand, several laboratories have investigated the hydrotreating properties of bulk and supported Co_3Mo_3N and Ni_2Mo_3N, as well as supported nitride materials containing Mo with either Co or Ni. These nitrides have proven to be active and selective in hydrodesulfurization (HDS),[9,10] hydrodenitrogenation (HDN),[11,12] and hydrogenation.[13] The results indicate that these materials possess the potential to be used as new industrial catalysts.

The synthesis of bimetallic molybdenum nitrides has been accomplished by several routes. Most of the known bimetallic molybdenum nitrides have been synthesized by the ammonolysis of the bimetallic oxide (e.g., Co_3Mo_3N from $CoMoO_4$) or the mixed-metal oxide (e.g., Ni_2Mo_3N from a mixture of $NiMoO_4$ and MoO_3).[5−20] Other routes that have been utilized include a reaction between from molybdenum nitride and metals,[21] by ammonolysis of metal nitrate supported on molybdenum nitride,[5] and by ammonolysis of a complexed mixed-metal chloride precursor.[22] In addition, to be useful as heterogeneous catalysts, the oxide-supported bimetallic molybdenum nitrides have been prepared to

* Corresponding author. Tel.: +86-22-23508662; fax: +86-22-23508662; e-mail: weili@nankai.edu.cn.

(1) Oyama, S. T. *The Chemstry of Transition Metal Carbides and Nitrides*; Blackie Academic: London, 1996.
(2) Claridge, J. B.; York, A. P. E.; Brungs, A. J.; Green, M. L. H. *Chem. Mater.* **2000,** *12,* 132.
(3) Oyama, S. T. *Catal. Today* **1992,** *15,* 179.
(4) Furimsky, E. *Appl. Catal. A* **2003,** *240,* 1.
(5) Jacobsen, C. J. H. *Chem. Commun.* **2000,** 1057.
(6) Kojima, R.; Aika, K. *Appl. Catal. A* **2001,** *219,* 141.
(7) Kojima, R.; Aika, K. *Appl. Catal. A* **2001,** *215,* 149.
(8) Liang, C.; Li, W.; Wei, Z.; Xin, Q.; Li, C. *Ind. Eng. Chem. Res.* **2000,** *37,* 3694.
(9) Hada, K.; Nagai, M.; Omi, S. *J. Phys. Chem. B* **2001,** *105,* 4084.
(10) Diaz, B.; Sawhill, S. J.; Bale, D. H.; Main, R.; Phillips, D. C.; Korlann, S.; Self, R.; Bussell, M. E. *Catal. Today* **2003,** *86,* 191.
(11) Chu, Y.; Wei, Z.; Yang, S.; Li, C.; Xin, Q.; Min, E. *Appl. Catal. A* **1999,** *176,* 17.
(12) Yuhong, W.; Wei, L.; Minghui, Z.; Naijia, G.; Keyi, T. *Appl. Catal. A* **2001,** *215,* 39.
(13) Wang, H.; Li, W.; Zhang, M.; Tao, K. *Catal. Lett.* **2005,** *100* (1−2), 73.

(14) Bem, D. S.; Gibson, C. P.; zur Loye, H. C. *Chem. Mater.* **1993,** *5,* 397.
(15) Herle, P. S.; Hegde, M. S.; Sooryanarayana, K.; Guru Row, T. N.; Subbanna, G. N. *Inorg. Chem.* **1998,** *37,* 4128.
(16) Alconchel, S.; Saphiña, F.; Beltrán D.; Beltrán, A. *J. Mater. Chem.* **1998,** *8* (8), 1901.
(17) Alconchel, S.; Saphiña, F.; Beltrán, D.; Beltrán, A. *J. Mater. Chem.* **1999,** *9,* 749.
(18) Alconchel, S.; Saphiña, F.; Ibañez, R.; Beltrán, A. *J. Mater. Chem.* **2001,** *11,* 2311.
(19) Korlann, S.; Diaz, B.; Bussell, M. E. *Chem. Mater.* **2002,** *14,* 4049.
(20) Prior T. J.; Battle, P. D. *J. Solid State Chem.* **2003,** *172,* 138.
(21) Jacobsen, C. J. H.; Zhu, J. J.; Lindløv, H.; Jiang, J. Z. *J. Mater. Chem.* **2002,** *12,* 3113.
(22) Weil, K. S.; Kumta, P. N.; Grins, J. *J. Solid State Chem.* **1999,** *146,* 22.

produce a high surface area and good dispersion of the nitride phase. In this respect, a temperature-programmed reduction (TPR) synthesis method has been shown to be particularly successful and was utilized in almost all research.[5–13,19] In this method, the metal oxide precursor was nitrided at a slow rate (0.1∼5 K/min) to a high temperature (973∼1173 K) under a high flow rate of ammonia. It can be concluded that the ammonolysis has been a necessary procedure in the synthesis of both the bulk and the supported bimetallic molybdenum nitrides up to now. The synthesis conditions were quite rigid and have a strong influence on the catalytic activity of molybdenum nitride.[23] It is worthwhile to find simple and generally applicable methods for the preparation of bimetallic molybdenum nitride catalysts.

Recently, Afanasiev[24] reported that γ-Mo_2N could be obtained from the decomposition of a molybdate HMT (HMT = hexamethylenetetramine) complex. In this method, both carbon and nitrogen were initially contained in the complex precursor, thus providing nitride without ammonolysis. It has also been observed that Ni and Co HMT complexes decomposed with the formation of the corresponding metals. In accordance with the formation of Co_3Mo_3N via Co and Mo_2N reported by Jacobsen,[21] it was natural to attempt the preparation of bimetallic molybdenum nitride by combination of the metal (Ni or Co) reduced by HMT and the Mo_2N obtained by decomposition of the Mo HMT complex. In the current study, such an idea is realized. Both Ni_2Mo_3N and Co_3Mo_3N were prepared in a one-step synthesis, in which a mixed-salt precursor containing $(HMT)_2(NH_4)_4Mo_7O_{24}\cdot 2H_2O$, $Ni(NO_3)_2\cdot 6H_2O$ $(Co(NO_3)_2\cdot 6H_2O)$, and HMT was directly converted to nitride under a flow of argon at 923 K. The investigation of the formation process showed that the bimetallic molybdenum nitride phase was formed via metal (Ni or Co) and γ-Mo_2N. To obtain a high surface catalyst, MCM41-supported bimetallic nitride has also been successfully prepared with this simple method. The MCM41 zeolite was employed as a steady support in this work, due to its good thermal stability, high surface area, and large adsorption capacity for organic molecules. This material has been used as a support in place of alumina by many research groups.[25,26]

Experimental Procedures

Synthesis. Synthesis of Ni_2Mo_3N and Ni_2Mo_3N/MCM41. All reagents used were of analytical purity. A precursor to Ni_2Mo_3N was prepared by dissolving $Ni(NO_3)_2\cdot 6H_2O$, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and HMT with a fixed mole ratio of 14:3:34 in 15% $NH_3\cdot H_2O$ solution. The content of HMT in the precursor had an influence on the products and was carefully optimized. The solution was then evaporated slowly to dryness, and a light green solid was obtained. After drying at 313 K for 6 h, the solid was heated in a stainless steel boat under a flow of argon (99.99%) at a mass rate of 1.5 h^{-1}. The temperature was increased linearly at a rate of 10 K min^{-1} and then kept at 923 K for 4 h. The product was cooled to room temperature (ca. 5 K/min) under argon and passivated for 6 h in a

flow of 1% (v/v) O_2/N_2. To investigate the formation process, some intermediate samples were prepared. The precursor was heated to the desired temperature and then cooled rapidly (ca. 100 K/min) to room temperature. After cooling, the products were passivated as described previously.

The supported mixed-salt precursor for the Ni_2Mo_3N/MCM41 catalyst with theoretical loadings of 25 wt % Ni_2Mo_3N was prepared by impregnation of MCM41 with an aqueous solution of $Ni(NO_3)_2\cdot 6H_2O$, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and HMT with a mole ratio of 14:3:20, which was made by dissolving the reagents in 15% $NH_3\cdot H_2O$ solution. The sample was then dried naturally for 24 h and dried at 313 K for 6 h. The precursor was then heated at a rate of 10 K min^{-1} and kept at 923 K for 2 h under a flow of argon at a mass rate of 1.5 h^{-1}. The sample was cooled and passivated as described previously to obtain the supported nitride.

Synthesis of Co_3Mo_3N and Co_3Mo_3N/MCM41. A mixed-salt precursor to Co_3Mo_3N was prepared by dissolving $Co(NO_3)_2\cdot 6H_2O$, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and HMT with a fixed mole ratio of 14:2:25 in 15% $NH_3\cdot H_2O$ solution, then evaporating to dryness. A purple solid was obtained. After drying at 313 K for 6 h, the solid was heated under a flow of argon according to the procedure for the preparation of Ni_2Mo_3N described previously. The product was cooled and passivated. The intermediate samples were also prepared as described previously.

The supported mixed-salt precursor for the Co_3Mo_3N/MCM41 catalyst with theoretical loadings of 25 wt % Co_3Mo_3N was prepared by impregnation of MCM41 with an aqueous solution of $Co(NO_3)_2\cdot 6H_2O$, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and HMT with a mole ratio of 14:2:25, which was made by dissolving the reagents in 15% $NH_3\cdot H_2O$ solution. The sample was then aired for 24 h and dried at 313 K for 6 h. The precursor was then heated and passivated according to the procedure for the preparation of Ni_2Mo_3N/MCM41 to produce the supported nitride.

Characterization. X-ray diffraction (XRD) characterization was conducted using a Rigaku D/max-2500 powder diffractometer employing CuKα radiation (40 kV, 40 mA). Transmission electron microscopy (TEM) images were acquired using a TECNAI G2 T20 high-resolution transmission electron microscope equipped with an EDX system (EDAX) operating at 200 kV. The samples were dispersed in ethanol and treated with ultrasound for 5 min. The EDX signals of the nitride particles were obtained by focusing the electron beam on the particles and accumulating the spectra. When it was no longer possible to detect a clear increase in the Ni and Mo peaks, the EDX counting was stopped and the spectrum was stored. Scanning electron microscopy (SEM) images were obtained using a Hitachi S-3500N scanning electron microscope. The samples were covered by a thin film of gold for better image definition. Single-point BET surface area measurements employing nitrogen adsorption were acquired using a Micromeritics ASAP 2010 apparatus. Measurements of CO chemisorption were performed with a standard volumetric adsorption method using a Micromeritics ASAP 2020 apparatus. Prior to measurement, the sample was pretreated under flowing H_2 at 673 K for 3 h. The irreversible CO chemisorption at 343 K was determined by double isotherms. The nickel and molybdenum analyses of the samples were carried out using an IRIS Advantage inductively coupled plasma atomic emission spectrometer (ICP−AES), and the nitrogen and carbon analyses of the samples were carried out with an Elementar Vario EL elemental analyzer.

Results and Discussion

Ni_2Mo_3N and Ni_2Mo_3N/MCM41. As shown in Figure 1, the bulk and MCM41-supported Ni_2Mo_3N were successfully

(23) Trawczyski, J. *Catal. Today* **2001**, *65*, 343.
(24) Afanasiev, P. *Inorg. Chem.* **2002**, *41*, 5317.
(25) Corma, A.; Martínez, A.; Martínez-Soria, V.; Montón J. B. *J. Catal.* **1995**, *153*, 25.
(26) Wang, A.; Wang, Y.; Kabe, T.; Chen, Y.; Ishihara, A.; Qian W.; Yao, P. *J. Catalysis* **2002**, *210*, 319.

Table 1. Chemical Composition and BET Surface Area of Bulk and Supported Bimetallic Nitrides

sample	M (at. %)/Mo (at. %)^a	nitrogen (wt %)^b	carbon (wt %)	elemental composition	S_{BET} (m^2 g^{-1})
Ni$_2$Mo$_3$N	0.65	3.25 (3.34)	0.42	Ni$_2$Mo$_{3.08}$N$_{1.01}$C$_{0.15}$	10.7
Ni$_2$Mo$_3$N/MCM41	0.71 (0.65)	0.89 (0.84)	0.05	Ni$_2$Mo$_{2.82}$N$_{1.03}$C$_{0.07}$	403.4
Co$_3$Mo$_3$N	1.00	3.02 (2.93)	0.16	Co$_3$Mo$_{3.01}$N$_{1.04}$C$_{0.06}$	23.9
Co$_3$Mo$_3$N/MCM41	0.92 (1.04)	0.81 (0.74)	0.08	Co$_3$Mo$_{3.26}$N$_{1.08}$C$_{0.13}$	503.0

^{a} ICP−AES (EDX). ^{b} The value in parentheses is the calculated value.
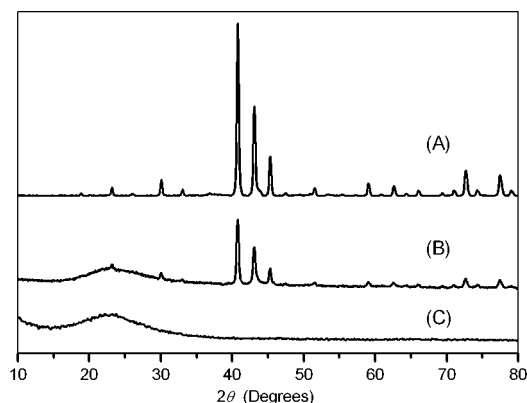
Figure 1. XRD patterns of (A) Ni$_2$Mo$_3$N, (B) Ni$_2$Mo$_3$N/MCM41, and (C) MCM41 supports.
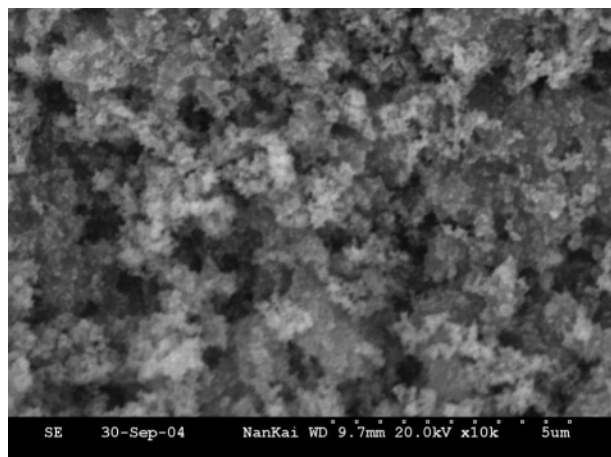
Figure 2. SEM image of the bulk Ni$_2$Mo$_3$N.

prepared by a one-step synthesis from unsupported and MCM41-supported mixed-salt precursor. The XRD pattern for the bulk sample, shown in Figure 1A, is similar to those reported by others[16,19] for nearly single-phase Ni$_2$Mo$_3$N. As listed in Table 1, quantitative chemical analyses of the sample show that the Ni/Mo atom mole ratio, the nitrogen content, and the elemental composition of the bulk sample are in agreement with the theoretical values. Unlike the phase pure Ni$_2$Mo$_3$N prepared by the TPR method, the as-prepared bulk sample contains 0.42 wt % carbon as an impurity, which is due to the decomposition residue of HMT and can probably be eliminated by increasing the reaction temperature.

The SEM image of the as-prepared bulk Ni$_2$Mo$_3$N is shown in Figure 2. The morphology of the bulk Ni$_2$Mo$_3$N is comprised of a few homogeneously nucleated spherical particles embedded in a matrix that primarily consists of large agglomerates of irregularly shaped particles.

The XRD pattern for the MCM41-supported Ni$_2$Mo$_3$N is given in Figure 1B. As compared with the MCM41 support (Figure 1C), additional peaks in the XRD pattern of Ni$_2$-Mo$_3$N/MCM41 all are in accord with those of pure Ni$_2$Mo$_3$N.

Using the Scherrer equation and the full-width at half-maximum (fwhm) of the peak at 40.8°, an average crystallite size of 42.6 nm was calculated and is smaller than the 67.8 nm for the unsupported Ni$_2$Mo$_3$N.

The TEM image of the Ni$_2$Mo$_3$N/MCM41 catalyst is shown in Figure 3 A. The Ni$_2$Mo$_3$N on the support has an oval-shaped morphology with a particle size in the range of 30−50 nm and is well-dispersed over the support. Figure 3B shows an HRTEM micrograph of an oval-shaped Ni$_2$-Mo$_3$N particle on the MCM41 support having dimensions of 30 × 40 nm. Examination of the image as well as others reveals d spacing values of 0.38 and 0.22 nm for the {111} and {221} crystallographic planes of cubic Ni$_2$Mo$_3$N, respectively, which are identical with the calculated value. The EDX results for the particles are shown in Figure 3C and give a Ni/Mo ratio of 0.65, which is in agreement with the theoretical value (0.667). The compositions of the supported Ni$_2$Mo$_3$N have also been analyzed by chemical analysis. As shown in Table 1, the Ni/Mo atom mole ratio, the nitrogen content, and the elemental composition are approximately consistent with the calculated values. The carbon content is 0.05 wt % and obviously lower than that of the bulk Ni$_2$Mo$_3$N, which is due to the low content of Ni$_2$Mo$_3$N in the supported sample. The BET surface areas of both bulk and MCM41-supported bimetallic nitrides have been measured and are listed in Table 1. The bulk Ni$_2$Mo$_3$N has a BET surface area of 10.7 m^2 g^{-1}, and the MCM41-supported Ni$_2$Mo$_3$N has a BET surface area of 403.4 m^2 g^{-1}.

In our previous work, the bulk and MCM41-supported Ni$_2$-Mo$_3$N catalysts were also prepared using the typical TPR method (Figure S1). The details are described elsewhere.[13] In the TPR method, the mixed-salt precursor is first calcined at 773 K for 5 h and then nitrided at a slow rate (1 K min^{-1}) to 923 K in flowing ammonia with a volume hourly space velocity (VHSV) of 6500 h^{-1}, whereas in this new method, the precursor is directly heated at a rate of 10 K min^{-1} to 923 K under a flow of argon at a mass rate of 1.5 h^{-1}. In addition, the MCM41-supported oxide (NiMoO$_x$/MCM41) precursor was also nitrided at a rate of 10 K min^{-1} to 923 K that was held for 2 h in flowing ammonia. The result (Figure S1) shows that Ni and γ-Mo$_2$N obviously exist on the supported material except the major phase Ni$_2$Mo$_3$N. It means that the formation of bimetallic molybdenum nitride is easier in this new method than in TPR method under mild conditions for the supported material. Comparison of the two syntheses clearly indicates that the new method described here is simpler and more straightforward.

Furthermore, the bulk Ni$_2$Mo$_3$N obtained by both methods possesses equal BET surface areas, whereas the BET surface area of 403.4 m^2 g^{-1} for the material prepared by this new method is significantly larger than the value of 179.1 m^2 g^{-1} for that prepared by the TPR method. It demonstrates
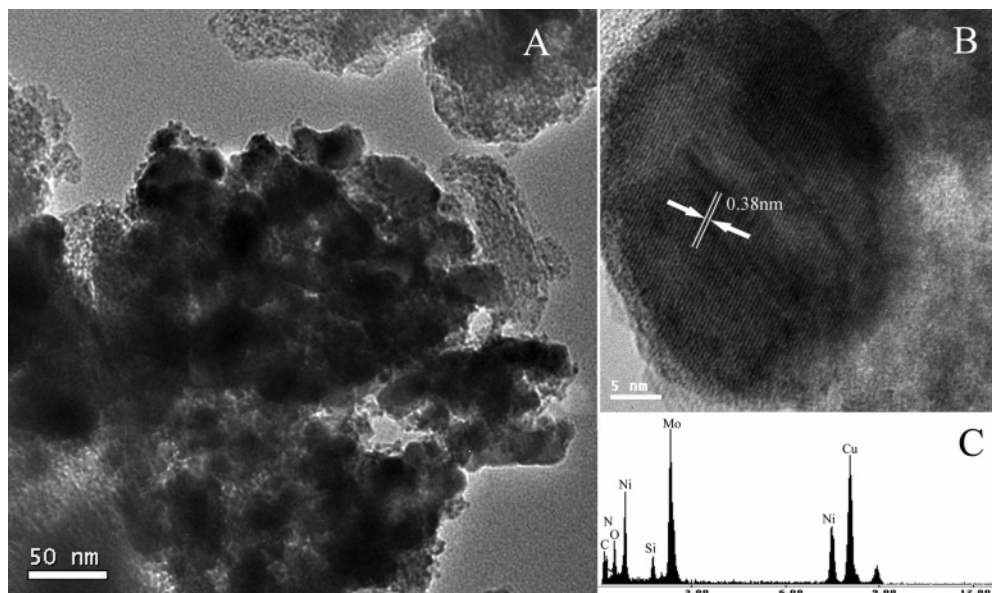
Figure 3. As-prepared Ni$_2$Mo$_3$N/MCM41 material. (A) TEM micrograph, (B) HRTEM micrograph of a Ni$_2$Mo$_3$N particle, and (C) EDX result for the particle.

that the destruction of the MCM41 in this new method is not as severe as that in the TPR method, which is probably due to the shorter time of heat treatment in this method as compared with the TPR method.

Our new synthesis of Ni$_2$Mo$_3$N/MCM41 yields an average crystallite size of 42.6 nm, which is larger than the average crystallite size of 26 nm for the Ni$_2$Mo$_3$N/MCM41 catalyst prepared by the TPR method.[13] The same results can also be concluded from the TEM measurements. Furthermore, the CO chemisorption capacity of the Ni$_2$Mo$_3$N/MCM41 catalyst prepared by the new method (11.2 μmol g^{-1}) is lower than that of the sample prepared by the TPR method (19.6 μmol g^{-1}), mainly owing to the low dispersion of Ni$_2$Mo$_3$N. In addition, it is impossible that the small amounts of carbon impurities exist as surface carbon that is blocking metal sites in the sample prepared by the new method. All the results clearly indicate that this new method yields a lower dispersion of Ni$_2$Mo$_3$N than the TPR method. It is probably due to the stronger interaction between metal oxides and support in the precursor used in the TPR method than between metal salts and support in the precursor used in our new method. During heat treatment of the precursor, the supported metals in our new method tend to conglomerate more easily than in the TPR method. At the same time, the average crystallite size of Ni$_2$Mo$_3$N/MCM41 prepared by this new method (42.6 nm) is considerably larger than that for the Ni$_2$Mo$_3$N/Al$_2$O$_3$ catalyst prepared by the TPR method (16 nm),[19] which could be due to both synthesis method and difference in the support.

Co$_3$Mo$_3$N and Co$_3$Mo$_3$N/MCM41. The success of this synthesis method for Ni$_2$Mo$_3$N led us to consider its applicability for the preparation of other bimetallic molybdenum nitrides. Cobalt nitrate replaced the nickel nitrate in the mixed-salt precursor, and then this precursor was treated similarly to obtain cobalt molybdenum nitride.

As shown in Figure 4, the bulk and MCM41-supported Co$_3$Mo$_3$N were successfully prepared. The XRD pattern for the bulk sample, shown in Figure 3A, is similar to those
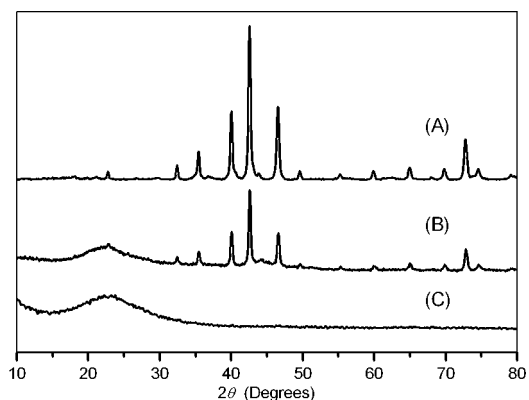

Figure 4. XRD patterns of (A) Co$_3$Mo$_3$N, (B) Co$_3$Mo$_3$N/MCM41, and (C) MCM41 support.

reported by others[13,16] for nearly pure Co$_3$Mo$_3$N. It can be seen that the as-prepared bulk Co$_3$Mo$_3$N contains a minor impurity. The additional impurity peaks can be identified as corresponding to metal cobalt and molybdenum nitride. In this respect, it should be mentioned that phase-pure Co$_3$Mo$_3$N can be prepared by the TPR method.[19] The Co/Mo atom mole ratio, the nitrogen content, and the elemental composition of the as-prepared bulk sample are in agreement with the Co$_3$Mo$_3$N composition for the majority phase. The carbon content is 0.16 wt %. Figure 5 shows an SEM image of the bulk Co$_3$Mo$_3$N. Inspection of the image indicates that the morphology of Co$_3$Mo$_3$N is quite similar to that of Ni$_2$Mo$_3$N.

The XRD pattern for the MCM41-supported Co$_3$Mo$_3$N is given in Figure 4B. In addition to peaks associated with the MCM41 support, the XRD pattern of Co$_3$Mo$_3$N/MCM41 shows peaks that are all in good agreement with those of single phase Co$_3$Mo$_3$N. The average crystallite size of Co$_3$Mo$_3$N can be calculated using the Scherrer equation and the fwhm of the peak at 42.6°. For Co$_3$Mo$_3$N/MCM41, the crystallite size of 27 nm is smaller than that of 47 nm for an unsupported Co$_3$Mo$_3$N and slightly larger than that of 21 nm for a Co$_3$Mo$_3$N/γ-Al$_2$O$_3$ catalyst prepared by the TPR method.[19]
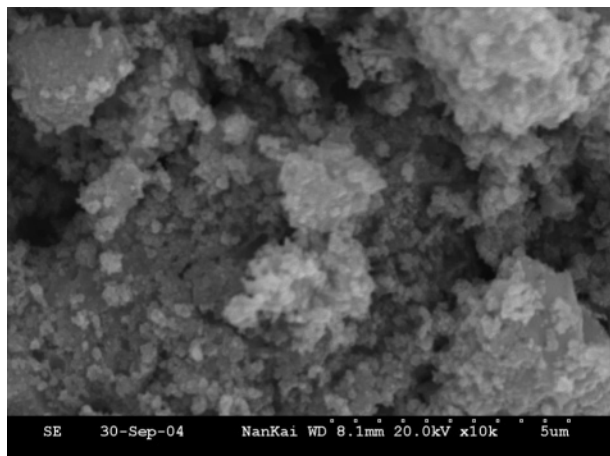
Figure 5. SEM image of the bulk Co₃Mo₃N.

Shown in Figure 6 is the TEM image and EDX result of a supported Co₃Mo₃N sample. Observation of Figure 6A shows that Co₃Mo₃N on the support has an oval-shaped morphology with a particle size in the range of 25−40 nm. Figure 6B shows an HRTEM micrograph of a Co₃Mo₃N particle on the MCM41 support having dimensions of 26 × 30 nm. This image, as well as others, yields *d* spacing values of 0.39 and 0.63 nm for the {220} and {111} crystallographic planes of Co₃Mo₃N, respectively, which are in good agreement with the calculated values. The EDX results for the particles are shown in Figure 6C and give a Co/Mo mole ratio of 1.04, which is approximately consistent with the theoretical value. The chemical compositions of the supported Co₃Mo₃N are given in Table 1. The Co/Mo atom mole ratio, the nitrogen content, and the elemental composition are approximately consistent with the calculated values.

The BET surface areas of both bulk and MCM41-supported Co₃Mo₃N are listed in Table 1. The bulk Co₃Mo₃N has a BET surface area of 23.9 m² g⁻¹, which is obviously larger than that of Ni₂Mo₃N stated previously and the value of 11 m² g⁻¹ reported by Jacobsen[5] for bulk Co₃Mo₃N

prepared by the TPR method. The as-prepared MCM41-supported Co₃Mo₃N has a BET surface area of 503 m² g⁻¹.

Formation Process. To investigate the formation process of the bimetallic molybdenum nitrides, some intermediate samples were characterized. Figure 7 shows a series of XRD patterns of the unsupported precursor for Ni₂Mo₃N treated at different temperatures. At 773 K, the precursor phase was transformed into a mixture of poorly crystalline Ni metal and some amorphous unidentified species. When the temperature increased to 873 K, Ni metal still existed, and γ-Mo₂N was formed. When the sample was heated to 923 K, Ni₂Mo₃N was found with the existence of Ni metal and γ-Mo₂N. After treating at 923 K for 0.5 h, the desired product Ni₂Mo₃N was obtained as the majority phase, and small amounts of Ni and γ-Mo₂N still remained. When the temperature was held at 923 K for 4 h, the intensity of the Ni and γ-Mo₂N peaks detectable in the sample pattern decreased, and Ni₂Mo₃N was obtained as nearly a single phase. Such a process has also been observed in the formation of Co₃Mo₃N. As shown in Figure 8, the precursor phase transformed into a mixture of Co metal, γ-Mo₂N, and an unidentified phase when the sample was heated to 673 K. Then Co₃Mo₃N, Co metal, and γ-Mo₂N phases appeared at 923 K. When the sample was treated at 923 K for 1 h, Co₃Mo₃N was formed as the main phase. After holding at 923 K for 4 h, the intensity of the Co and γ-Mo₂N peaks clearly decreased, and Co₃Mo₃N was obtained as nearly a single phase, except for minor Co and γ-Mo₂N.

From these experiments, it can be noted first that the minimum temperature at which the bimetallic nitride appears as the majority phase is 923 K for both Ni₂Mo₃N and Co₃-Mo₃N. To our knowledge, this temperature is the lowest observed for the preparation of bimetallic nitride up to now. Furthermore, it can be concluded that an elevated temperature (≥923 K) is a necessary condition for the formation of Ni₂-Mo₃N and Co₃Mo₃N. In this respect, other evidence can be found in the literature. Alconchel et al.[16] showed that a
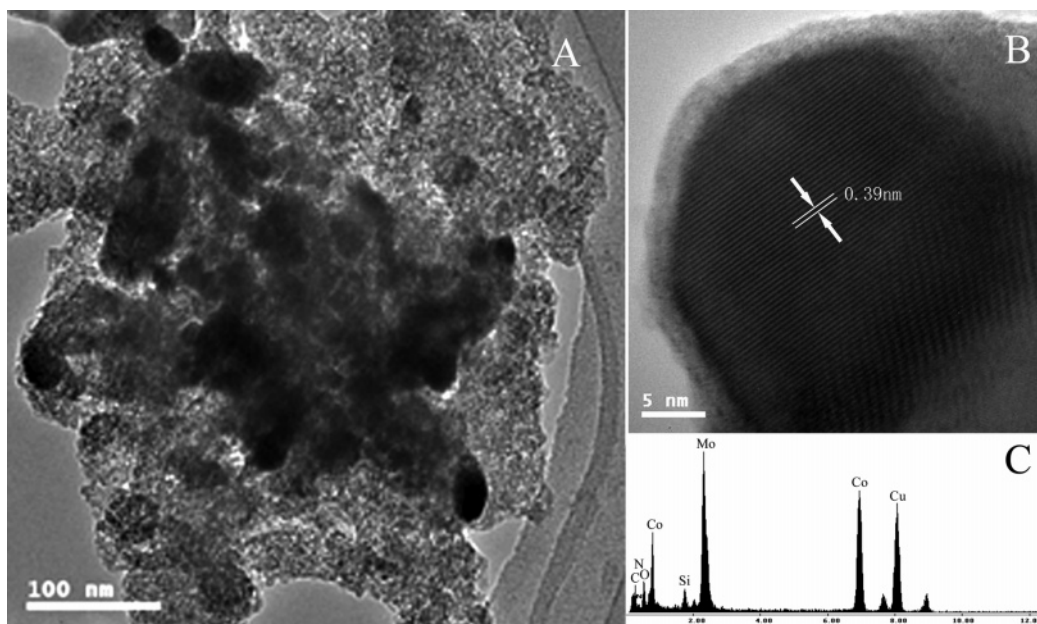
Figure 6. As-prepared Co₃Mo₃N/MCM41 material. (A) TEM micrograph, (B) HRTEM micrograph of a Co₃Mo₃N particle, and (C) EDX result for the particle.

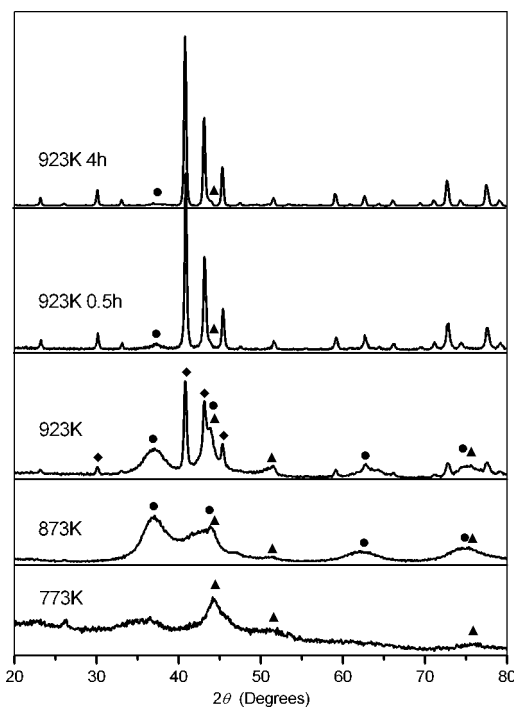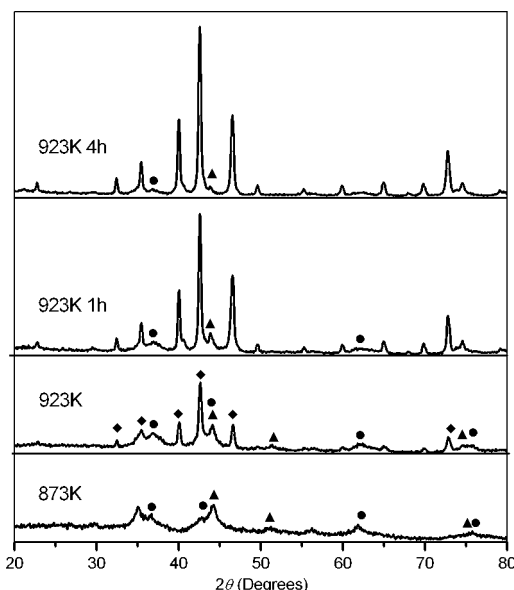**Figure 7.** XRD patterns of the precursor for bulk Ni_2Mo_3N treated at different temperatures. Peaks marked with triangles, circles, and squares represent Ni, γ-Mo_2N, and Ni_2Mo_3N, respectively.

Figure 8. XRD patterns of the precursor for bulk Co_3Mo_3N treated at different temperatures. Peaks marked with triangles, circles, and squares represent Co, γ-Mo_2N, and Co_3Mo_3N, respectively.

mixture of only Ni_2Mo_3N, Ni, and Mo nitrides was obtained after ammonolysis of the nickel molybdate precursor at 873 K for 12 h. Jacobsen et al.[21] prepared Co_3Mo_3N by ball-milling Mo_2N and Co and found that it was necessary to heat the sample to 973 K for 2 h to obtain the bimetallic nitride, although the sample was pretreated by ball-milling for 90 h.

Investigation of the synthesis process clearly shows that Ni (Co) and γ-Mo_2N are formed first and that they are then mixed on the atomic level to form the bimetallic nitride phase

on remaining at 923 K. Such a procedure is very similar to the formation process of bimetallic molybdenum nitride by ammonolysis described by others. Kojima et al.[27] characterized the intermediates during the nitridation of $CoMoO_4$ precursor under NH_3 flow and found that the oxide precursor first transformed into Co and γ-Mo_2N and then that Co and γ-Mo_2N formed Co_3Mo_3N on remaining at 973 K for 6 h. Jacobsen[5] prepared Co_3Mo_3N by ammonolysis of an NH_5-$(CoOHMO_4)_2$ precursor and observed that the precursor initially transformed into Co and Mo_2N and finally that Co_3-Mo_3N was formed from Co and Mo_2N. All the results proved that for both this new method and the traditional ammonolysis method, the formation of the bimetallic molybdenum nitride follows a general procedure: first metals and Mo_2N, then bimetallic nitrides. The difference is that in the ammonolysis method, the Ni metal is reduced by NH_3, and γ-Mo_2N is formed by ammonolysis of molybdate oxide, whereas in this new method, the Ni metal is reduced by HMT, and γ-Mo_2N is formed by decomposition of the molybdate HMT complex. That is, the HMT is used as a reducing agent and nitrogen source instead of NH_3. Metals, the reducing agent, and the nitrogen source are all initially contained in the precursor, thus allowing us to obtain nitrides by a one-step synthesis. It is notable that ammonolysis is not a prerequisite and that the bimetallic molybdenum nitride is facile under mild conditions. Such a simple and straightforward synthesis route is expected to be a general method for preparing the bulk and supported bimetallic molybdenum nitrides.

Conclusion

A mixed-salt precursor containing Mo HMT complex, Ni (Co) nitrate, and HMT was directly converted to bimetallic nitride under a flow of argon at 923 K. Both Ni_2Mo_3N and Co_3Mo_3N were successfully prepared. The investigation of the formation process showed that the bimetallic nitride phase was formed via metal (Ni or Co) and γ-Mo_2N. Furthermore, MCM41-supported bimetallic nitride has also been successfully prepared by this simple method. The supported nitride materials have a high surface area and good dispersion of the nitride phase. The results suggest that these syntheses provide a potential route for the preparation of a wide range of bimetallic molybdenum nitrides.

Supporting Information Available: XRD patterns of the Ni_2-Mo_3N/MCM41 prepared by the TPR method (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

CM047735D

(27) Kojima, R.; Aika, K. *Appl. Catal. A* **2001**, *219*, 157.