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Nano-Scale Materials

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Abstract

This is the final report of a three-year, Laboratory Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). Highly selective, alumina-supported molybdenum carbonitrides were prepared by solution impregnation using the metal amide $\text{Mo}_2(\text{N}(\text{CH}_3)_2)_6$ as a molecular precursor. On the basis of relative weight percents, these materials demonstrate a 5- to 8-fold increase in catalytic activity over similar materials prepared by traditional solid-state approaches. The catalytic activities of these materials are very dependent upon the type of alumina support used. Impregnation of $\text{Mo}_m\text{C}_x\text{N}_y$ into preformed alumina pellets resulted in a material that specifically isomerized n-heptane into equal amounts of 2- and 3-methylhexanes, as well as iso-butane. No evidence of aromatic products was observed at operating temperatures below 420 °C. The product selectivity of the isomers was 56% at a n-heptane conversion efficiency of 57%. Impregnating $\text{Mo}_m\text{C}_x\text{N}_y$ into an alumina powder resulted in an extremely selective aromatized and dehydrogenated material. The products from this material consist only of aromatics and n-heptenes with less than 2% isomerization or cracking products.

Background and Research Objectives

When interstitially dissolved in a lattice of early transition metals, the elements carbon, nitrogen, and oxygen produce a class of materials with unique physical and chemical properties.¹ The present interest in these materials originates from the ability of these alloys to catalyze significant industrial processes presently dominated by the rare and expensive Group VIII noble metals: platinum, palladium, and rhodium. For example, an oxygen-modified molybdenum-carbide material catalytically isomerizes and reforms n-heptane. The conversion efficiencies were approximately 30%, with an 85% selectivity to C7 isomers.² Such a process is extremely important for producing high-octane fuels; that is, converting naphtha to lighter, branched hydrocarbons for the refining industry. In addition, molybdenum nitrides are known to exhibit other very attractive catalytic properties, such as ammonia synthesis,³ hydrodenitrogenation,⁴ hydrodesulfurization,⁵ and hydrogenation.⁶ For many of the processes the catalytic activity of these materials is comparable to the Group VIII metal catalysts.

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Originally, these alloyed materials were prepared from corresponding metal oxides by way of a high-temperature, solid-state process. The resulting materials had very low surface areas, in the range of 1-5 m²/g. As a result, the catalytic efficiencies of these early materials were severely limited. Several years later, the introduction of a modified solid-state process, temperature-programmed reaction, overcame this problem.⁷ In the case of nitrides, the reaction temperature of the metal oxide is *slowly* increased in a flow of ammonia. Materials with surface areas greater than 200 m²/g have been prepared with this technique. As expected, many of these materials exhibit catalytic activities comparable to that of platinum-based materials. However, on alumina supports, metal contents of at least 15 wt% are usually required to achieve these catalytic activities. This suggests that the majority of the metal species at the surface are not catalytically active. Other synthetic attempts were made to improve the inherent catalytic nature of these materials. These included self-propagating, high-temperature synthesis⁸ and metal-vapor impregnation of high-surface-area carbon.⁹

A second disadvantage to the solid-state synthesis is the significant oxygen content in the materials. This is caused by the greater thermodynamic stability of the initial oxide relative to both the nitride and carbide. Although in some instances this may be a fortuitous advantage due to the Bronsted acid properties of the oxygen sites, the amount of oxygen in the material cannot be strictly controlled.

This report describes a new route to higher-surface-area molybdenum carbonitride catalysts. The materials show a 5- to 8-fold increase in catalytic activity over materials prepared by traditional solid-state approaches. Our approach takes advantage of the known reactivity of homoleptic metal amide complexes with ammonia to yield metal amido/imido intermediates. These intermediates thermalize at low temperatures, 200 to 500 °C, to yield high-quality metal nitride and carbonitrides.

Importance to LANL's Science and Technology Base and National R&D Needs

This effort involves both basic and applied research in the areas of advanced materials synthesis, characterization, and processing.

Scientific Approach and Accomplishments

The synthetic preparation and handling of the materials were performed in a Vacuum Atmospheres helium-filled glove box or through utilization of a standard argon Schlenk line (unless specifically stated). The organic solvents used in preparing $\text{Mo}_2(\text{N}(\text{CH}_3)_2)_6$ were dried with appropriate drying agents then degassed with helium or argon before use. Tetradecane and dodecane were used as received and were stored over sodium metal. Combustion analysis was performed by Oneida Research Services. Surface area measurements were collected on a Micrometrics ASAP 2000. Simultaneous thermal analyses were performed on a Rheometric STA 1500, in an argon-filled glove box. X-ray diffraction (XRD) data were collected on a Rigaku RTP 300 rotating-anode diffractometer equipped with an Inel CPS 120 position-sensitive detector. Auger electron spectroscopy (AES) data were obtained with a PHI Model 545 and Model 548 cylindrical mirror system. Typical conditions for AES were 5 KeV energy electrons and less than $1\mu\text{A}$ total beam current in a $5\mu\text{m}$ diameter spot size. Sample sputtering was done using 3.5 KeV argon ions in a 2 mm by 2 mm raster area. Gas analysis was performed with a HP 5890 gas chromatograph (GC) equipped with a Gas Pro GSC 9408-04 capillary column and either a flame ionization detector (FID) or HP 5971 mass selective detector. The 0.3 wt% Pt on alumina, as well as the alumina supports, were supplied by Akzo-Nobel. The platinum catalyst was reduced in a 20 sccm flow of hydrogen at 450°C for 6 h before evaluation. The alumina supports were calcined at 500°C for 24 h before use.

The reactor used for catalytic activity measurements consisted of a 12-mm outer-diameter, vertical quartz-tube furnace. This tube was connected to a gas manifold that supplied the hydrogen and argon gas flows. The flows were controlled by calibrated mass flow controllers. This gas stream had a combined flow of 15 sccm and was introduced through the normal hydrocarbon with a fine glass bubbling frit. The gas mixture was then introduced into the reactor containing the prepared materials at various operating temperatures.

Synthesis of molybdenum carbonitride on alumina powder. In a glove box, $\text{Mo}_2(\text{N}(\text{CH}_3)_2)_6$ (0.21 g) was dissolved in 9 ml of dodecane. This solution was added slowly to the alumina (3.1 g), then the two components were thoroughly mixed. The wetted mixture was placed loosely within a quartz tube and was contained with two plugs of quartz wool. The quartz tube was placed in a stainless-steel tube with a valve at each end. The stainless-steel tube served to seal the air-sensitive mixture from the external environment when removed from the glove box. The system was placed in a tube furnace

and ammonia was introduced at 1 atm. The tube was slowly heated to 80 °C and this temperature was maintained for 4 h. Next, temperature was increased from 80 to 500 °C over a 34 h period. Afterward, the system was cooled to room temperature while maintaining a slight ammonia flow. The tube was reintroduced back into the glove box, and a second 6 ml solution containing 0.12 g of $\text{Mo}_2(\text{N}(\text{CH}_3)_2)_6$ was used to wet the darkened alumina. The heating procedure was repeated. The material was cooled to room temperature, and a 0.5 wt% oxygen in nitrogen gas flow was used to passivate the material for 3 h. The material was removed from the reaction tube and 1.0 g of the material was placed within the quartz reactor tube for catalytic evaluation.

Synthesis of molybdenum carbonitride on alumina pellets. A similar synthetic procedure as described above was used to coat the support; however, three wetting and heating cycles were used because of the decrease in pore volume of this support.

Synthesis of molybdenum carbonitride on alumina pellets with 0.3 wt% Pt. A similar synthetic procedure as described above was used to coat the support. However, the support with platinum was heated initially to 450 °C in hydrogen. Recently, several monometallic nitrides have been prepared by the process outlined in Equation 1.¹⁰⁻¹⁴

Our initial work in this area focused on the addition of ammonia at 1 atm to solutions of $\text{Mo}_2(\text{N}(\text{CH}_3)_2)_6$ in high-boiling-point organic solvents such as tetradecane. The reaction temperature was increased slowly until the characteristic yellow solution containing the precursor resulted in a fine black precipitate and a clear reaction solution. Surprisingly, reaction temperatures of 140 °C and long reaction times (6-8 h) were required to complete the transamination process. Simultaneous thermal analysis and combustion analyses suggest that these materials are composed of approximately 15 to 18 wt% carbon, and 2 to 3 wt% hydrogen. In addition, the infrared spectrum contains a broad band at 3200 cm^{-1} . This feature is tentatively assigned as a combination of several C-H stretches. Heating these materials at 350 °C for 3 h in vacuum results in the disappearance of this infrared feature and a 20 to 30 wt% loss. Combustion analysis indicates a remaining carbon and hydrogen content of 2-3 wt% and 0.3-0.5 wt%, respectively. The XRD data showed no observable features for these materials.

The unspattered Auger spectra did show an asymmetrical resonance for the carbon peak, suggesting that at least some of the carbon present is graphitic. With sputtering, the carbon feature became more carbide-like. Also, nitrogen, oxygen, and molybdenum resonances were observed in the AES spectra. Further heating of these materials to temperatures above 800 °C results in an additional 10% weight loss at approximately 650 °C. In addition, reflections assigned to crystalline α -Mo₂C and molybdenum were present in the XRD data. No evidence of a crystalline, molybdenum nitride material is observed in the XRD pattern following the final high-temperature anneal.

To investigate the catalytic activity of the 350 °C annealed material, 1.0 g was placed in a flow reactor. A hydrogen and heptane gas stream at 20 sccm was flowed through the material at various bed temperatures. The product stream was analyzed by gas chromatography. Ethane was the only significant product observed in the chromatogram at bed temperatures between 250 °C to 475 °C. The conversions were 18% to 20% and were independent of temperature. At a temperature of 135 °C, propane was the only significant product observed at a conversion efficiency of 18%. Although the selectivity of the material is exceptionally high, the observed cracking activity is uninteresting and the conversions efficiency are low compared to other known metal nitride and carbide materials. The surface area of this material, between 8 to 10 m²/g, is surprisingly low for a material prepared by a modified sol-gel process. This may account for the low product conversion efficiency.

Isomerization. Alumina-supported molybdenum nitrides and tungsten carbides are known to isomerize straight chain hydrocarbons (such as n-heptane) to branched hydrocarbons. Products of the isomerization include methylhexanes, dimethylpentanes, and isobutane. The conversion is highly selective and relatively high conversion efficiencies are observed.² Unfortunately, these previously reported materials require relatively high metal-to-alumina weight percentages that suggest that the majority of the material is not catalytically active. For example, such materials require 10 to 20 wt% of metal compared to 0.5 wt% of the platinum materials to achieve similar catalytic activities. Thus, our immediate interest has focused on new synthetic processes that would allow greater kinetic control during the preparation of the Group VI alloys. We envisioned such processes would result in materials with greater overall catalytic properties than those materials prepared by solid-state methods.

The molecular precursor, Mo₂(N(CH₃)₂)₆, was dissolved in tetradecane, then the solution was used to wet the alumina pellets. These pellets had a surface area of

approximately 200 m²/g and a pore volume of approximately 0.7 ml/g. Unfortunately, the rather poor solubility of the precursor, ~20 mg/ml, limited the amount of material that one could place within the alumina to approximately 2 wt%. The transamination chemistry, as well as the thermal anneal, would further reduce the molybdenum to alumina ratio to approximately 0.9 wt%/cycle. To compensate for these relatively low loadings, three wettings and annealing cycles were used to produce the final materials for testing. Catalytic evaluation of these materials demonstrated an enhancement of nearly 5- to 8-fold compared to the previously reported molybdenum nitrides based on a relative weight percentage. The greatly enhanced activity of these materials is most likely due to the unique method of preparation described in this report. This method results in a more catalytically active material. Figure 1 shows a gas chromatograph of the products. Only five significant products are observed. They are 2-methyl and 3-methyl hexane, 2-methylpropane, propane, and butane. The production of equal quantities of the methyl hexanes is consistent with methyl shift reactions of carbenium-ion intermediates.¹⁵ Table 1 summarizes the isomerization activity of the molybdenum carbonitride. Isomerization data obtained for a commercial catalyst, 0.3 wt% Pt on alumina, is provided for comparison.

Fig. 1. Gas chromatograph of the products from Mo_mC_xN_y on alumina pellets. The reaction conditions were 365°C, 15 sccm H₂, heptane and 4 hr. (PP=n-propane, MP=2-methylpropane, NB=n-butane, MH=methylhexanes)

Table 1. Isomerization of n-Heptane by 1.8 wt% Mo_mC_xN_y on Alumina Pellets and a Commercial Catalyst of 0.3 wt% Pt on Alumina.

	conversion efficiency (%)	isomer selectivity (%)	MH ^a	IB ^a	NB/NP ^a	PP ^a	others	tolue
Mo _m C _x N _y - 1.8%								
T = 350 °C	35	91	15	6	4	7	3	—
T = 375 °C	56	93	22	9	8	12	5	—
Pt - 0.3 %								
T = 225 °C	15	73	11	—	—	—	1	3
T = 400 °C	58	72	34	2	3	2	8	9
T = 440 °C	84	50	25	6	7	4	21	21

^a MH - methylhexanes, MP- 2-methylpropane, NB/NP - normal butane and pentane, PP - propane

Aromatization. In 1995, aromatic hydrocarbons accounted for seven of the top thirty chemicals produced in the United States.¹⁶ For example, the production of benzene has grown by 5.5% over the past decade; 16 billion pounds were produced in 1995. In addition, the total production of the other aromatic chemicals, ethylbenzene, styrene, toluene, xylenes, and cumene exceeded 53 billion pounds in 1995. Although these chemicals are inherently found in base crude, the majority are produced in petrochemical refineries from the conversion of saturated hydrocarbons, light naptha, by various catalytic processes. The present catalysts used in this process are based upon platinum, whereas the older technology was usually based upon chromia-alumina.¹⁷

The molybdenum carbonitrides produced by the organometallic solution process become highly selective aromatization catalysts when alumina powder is used as a catalyst support. Figure 2 shows a gas chromatograph from one of our catalytic activity tests. For comparison, Figure 3 shows the product distribution of a commercial platinum system. The molecular precursor, Mo₂(N(CH₃)₂)₆, is dissolved in dodecane and this solution is used to "wet" the catalyst support. In contrast to the pellets, the alumina powder could

absorb more of this solution for a given weight of support. Significant metal loadings could be achieved in a single cycle. A single repetition of the coating procedure results in a

Fig. 2. Gas chromatograph of $\text{Mo}_m\text{C}_x\text{N}_y$ on alumina powder. The reaction conditions were 470 °C, 12 Ar-3 H_2 sccm, octane and 5 hr (B=benzene, NO=n-octane, T=toluene, EB=ethylbenzene, and XYL=xylene).

Fig. 3. Gas chromatograph of 0.3% Pt on alumina powder. The reaction conditions were 470 °C, 15 H_2 sccm, octane and 24 hr (B=benzene, NO=n-octane, T=toluene, EB=ethylbenzene, XYL=xylene, PP=n-propane, NB=n-butane, MB=2-methylbutane, NP=n-pentane).

material composed of approximately 3.4 wt% Mo_mC_xN_y on alumina. One gram of this material was placed in a furnace. A gas stream consisting of 3 sccm of hydrogen and 13 sccm of argon was bubbled through n-heptane or n-octane. The product stream was then analyzed by GC-MS and their relative percentages determined by a GC equipped with a FID. The new molybdenum carbonitride material demonstrated a 30% conversion efficiency of n-heptane to toluene and heptenes with a selectivity greater than 97%. Table 2 shows dehydrocyclization of n-octane. This results in the formation of benzene, toluene, ethylbenzene, styrene, and o-xylene as the principal products. In both instances, isomerization and cracking products contributed to less than 3% of the reformed products. To the best of our knowledge, such high catalytic selectivity to aromatics is unprecedented for any reported material.

Table 2. Aromatization Data for Mo_m C_xN_y on Alumina Powder. ^a

time ^b (hours)	conversion efficiency (%)	isomer selectivity (%)	B ^c	T ^c	EB ^c	STY ^c	XYL ^c	others
2	37	91	2.2	2.2	12.8	0.8	15.8	3.2
5	62	94	2.6	4.6	20.6	1.2	29.1	3.9
24	55	87	3.1	4.4	17.0	2.4	21.0	7.1
102	38	85	1.7	3.0	12.7	1.9	13.0	5.7

^a Operating temperature of 475 °C.

^b Amount of time the catalyst was under operating conditions.

^c B - Benzene, T - toluene, EB - ethylbenzene, S - styrene, XYL - xylenes.

In an attempt to increase the conversion activity of this later material, a bimetallic material was prepared by depositing the molybdenum precursor on alumina previously impregnated with reduced platinum. This bimetallic material exhibited a dramatic decrease in catalytic activity relative to both the previously evaluated molybdenum and platinum materials.

Conclusions

Highly selective, alumina-supported molybdenum carbonitrides have been prepared by solution impregnation using the metal amide, $\text{Mo}_2(\text{N}(\text{CH}_3)_2)_6$, as a molecular precursor. On the basis of relative weight percents, these materials demonstrate a 5- to 8-fold increase in catalytic activity over similar materials prepared by traditional solid-state approaches. The catalytic activity was very dependent upon the type of alumina support. Impregnation of $\text{Mo}_m\text{C}_x\text{N}_y$ into preformed alumina pellets resulted in a material that specifically isomerized n-heptane into equal amounts of 2- and 3-methylhexanes, as well as iso-butane. No evidence of aromatic products was observed at operating temperatures below 420 °C. The product selectivity of the isomers was 56% at a n-heptane conversion efficiency of 57%. In comparison, a commercial platinum based material had a isomerization selectivity of 72% with similar conversions.

Impregnation of $\text{Mo}_m\text{C}_x\text{N}_y$ into an alumina powder resulted in an extremely selective aromatization and dehydrogenation material. The products of this material consist of only aromatics, as well as n-heptenes with less than 2% isomerization or cracking products. Such a high degree of selectivity for n-heptane or n-octane is unprecedented for both commercial platinum systems and the previously reported Group VI nitrides or carbides.

Publication

1. Barrera J. and Smith, D., "Alumina Supported Molybdenum Carbonitrides: An Extremely Selective Material for the Aromatization of n-Octane," *Journal of Catalysis*, submitted.

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