Structural, Surface, and Catalytic Properties of a New Bimetallic V–Mo Oxynitride Catalyst for Hydrodenitrogenation

C. Charles Yu,[†] S. Ramanathan,[‡] Fawzy Sherif,[§] and S. Ted Oyama^{*,†,‡}

Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Virginia 24061, Department of Chemical Engineering, Clarkson University, Potsdam, New York 13699, and Akzo Nobel Central Research, Dobbs Ferry, New York 10522

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A new bimetallic V-Mo oxynitride has been synthesized by temperature-programmed reaction of a bimetallic oxide precursor with ammonia gas. The surface properties of this new catalyst are investigated with temperature-programmed reduction (TPR), CO chemisorption, and N₂ physisorption. The catalytic activity of the material is measured in a three-phase trickle-bed reactor at 3.1 MPa and 643 K with model liquid reactants. The bulk characteristics of the oxynitride are studied by X-ray diffraction analysis, Raman spectroscopy, and inductively coupled plasma (ICP) analysis. The new compound, of composition $V_{2.0}Mo_{1.0}O_{1.7}N_{2.4}$, has a face-centered cubic (fcc) metallic structure arrangement, a surface area of 74 m² g⁻¹, and a CO uptake of 167 μ mol g⁻¹. Its catalytic activity in hydrodenitrogenation is higher than that of the pure compounds VN and Mo₂N and a commercial Ni-Mo/Al₂O₃ catalyst (Shell 324). TPR in hydrogen of the passivated oxynitride shows the formation of H₂O, N₂, and NH₃ during activation and thermal stability to 830 K. The reactivity and TPR results indicate that the catalytic properties of the V-Mo oxynitride alloy are enhanced over those of the individual V and Mo nitrides, possibly due to a decrease in the binding strength of reactive intermediates at the surface.

Introduction

Many studies of monometallic transition metal carbides and nitrides have demonstrated their potential to replace platinum group catalysts.¹ One possible way of further improving their catalytic performance is to induce positive interactions among metal and nonmetal atoms by introducing other elements into the material. One critical issue in new catalyst design is to understand the relationship among structural, surface, and catalytic properties of the material. A thorough investigation of surface properties, catalytic activities, and the effect of structural and chemical modifications can help provide insights into the development of new catalysts.

Transition metal nitrides are interesting materials that combine the physical properties of refractory ceramics with the electronic and magnetic properties of metals.² They have found applications in cutting tools, wear-resistant parts, and hard coatings and as electronic and magnetic components and superconductors. Transition metal nitrides have also attracted attention as catalysts in ammonia synthesis,^{3,4} Fischer–Tropsch reaction,^{5,6} hydrogenation,⁷ oxidation,⁸ hydrodenitrogenation (HDN), and hydrodesulfurization (HDS).^{9,10} They have activities resembling those of the noble group VIII metals (Pt, Pd, Rh, etc.) and in some cases have superior selectivity, stability, and resistance to poisoning.¹

Although monometallic transition metal nitrides have been investigated extensively since the 1950s and 60s,² relatively few bimetallic compounds have been synthesized and fully characterized.¹¹⁻¹³ It is known that oxygen atoms can substitute nitrogen atoms in monometallic nitrides due to the similarity in their radii.^{14,15} However, the literature on the subject is scarce, and only limited information on the synthesis and

characterization of bimetallic oxynitrides composed of only transition metals is available.¹⁶

Nitride formation is very common among transition elements of the first row and the early members of the second and third series. Their phases can exist over broad composition ranges with appreciable vacancy concentrations, and their physical properties are quite sensitive to composition. Changes in valence electron density are probably a major cause of the sensitivity to composition. We anticipate that partial exchange of nitrogen by oxygen and, at the same time, partial substitution of one transition metal by another could substantially alter the properties of the compounds.

High specific surface area (S_g) is essential to a catalyst. Conventional powder metallurgy methods such as direct nitridation of metal powders do not yield high surface area products because of the elevated temperatures necessary for reaction. Temperature-programmed reaction, a new synthesis method developed in the early 1980s, has been successful in producing carbides and nitrides with high specific surface areas.^{17,18} In nitride synthesis, the method involves placing an oxide precursor in a flowing ammonia stream while raising the temperature in a controlled manner.

In the current investigation, a new material, $V_{2.0}Mo_{1.0}O_{1.7}N_{2.4}$, was synthesized by a similar temperature-programmed reaction using a bimetallic oxide (V_2MoO_8) as the precursor. The surface characteristics of this new bimetallic oxynitride, including CO chemisorption, active sites, and reactivity in hydrodenitrogenation (HDN), were carefully studied. The results were compared with those of the corresponding monometallic nitrides, Mo_2N and VN, as well as a commercial sulfided Ni-Mo/Al₂O₃ catalyst (Shell 324).

Experimental Section

Synthesis of Catalysts. For the preparation of the nitrides, V_2O_5 (Johnson Matthey, 99.9%) and MoO_3 (Johnson Matthey, 99.95%) were used as received while V_2MoO_8 was prepared

^{*} To whom correspondence should be addressed.

⁺ Virginia Polytechnic Institute.

[‡] Clarkson University.

[§] Akzo Nobel Central Research.

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by a solid state synthesis consisting of thoroughly grinding V_2O_5 and MoO_3 at a V/Mo ratio of 2:1, pressing the mixture into pellets, and then firing at 948 K for 6 h. After being cooled to room temperature, the pellets were pulverized into a fine powder of dark green color.

For the V-Mo oxynitride synthesis, 1 g (3070 μ mol) of the V-Mo bimetallic oxide powder, placed inside a tubular quartz reactor, was heated linearly at 8.3×10^{-2} K s⁻¹ (5 K/min) in a flow of ammonia gas ($6.82 \times 10^2 \mu$ mol s⁻¹, 1000 cm³/min) to a final temperature ($T_f = 1037$ K) which was held for a period of 0.5 h. At the end of the temperature-programmed reaction, the flow of ammonia gas was switched to helium and the sample was quenched to room temperature and passivated in a 0.5% O₂-99.5% He gas mixture at a flow rate of 24 μ mol s⁻¹ (35 cm³/min). Vanadium nitride and molybdenum nitride were prepared in a similar way following procedures described by Kapoor and Oyama¹⁹ and Volpe et al.¹⁸

Characterization. XRD analysis of both bimetallic oxides and bimetallic oxynitrides was carried out using a powder diffractometer (Siemens, Model D 500 with a CuK α monochromatized radiation source), operated at 40 kV and 30 mA. The surfaces of the V-Mo oxynitride, passivated as well as reduced (in H₂ at 775 K for 2 h), were studied by laser Raman spectroscopy. The laser Raman system was equipped with a Lexel Ar ion laser (1.7 W), a 0.5 m monochromator (Spex 500M), a CCD detector (EG&G), and a controlled-atmosphere rotatable cell. The composition of the V-Mo oxynitride was determined by inductively coupled plasma (ICP) analysis.

The samples were also studied by sequential temperatureprogrammed reduction (TPR) in hydrogen to 738 K, CO chemisorption, N₂ physisorption, and a final TPR to 1373 K. The measurements were carried out in a flowing mode using a mass spectrometer (Ametek/Dycor Model MA100) for analysis. The purpose of the initial TPR process was to study the activation of the passivated samples. In these experiments, a 10% H₂-90% He gas mixture was passed through the sample (0.2 g) at 4.5 μ mol H₂/s, while the temperature was raised linearly at 0.17 K s⁻¹ (10 K/min) to 738 K where it was held for 2 h.

After the initial TPR the samples were then quenched to room temperature in He, and CO uptakes and single point BET surface areas were determined by a pulse method. Finally, a second TPR to 1373 K was carried out to determine stability and to confirm bulk composition. In the mass spectrometer analysis of the final TPR, CO was monitored through mass 12, and N₂ through mass 14 to permit assignment of the peaks. The TPR traces were generally simple, and the signal at 28 (CO or N₂) confirmed that the mass 12 and 14 signals tracked the proper species. Since the mass 28 signal did not provide any additional information, it was not included in Figure 4.

Catalytic (HDN) Testing. The catalytic performance of the catalysts was evaluated, after pretreatment in H_2 at 723 K for 3 h, in a three-phase trickle-bed reactor system operated at 450 psig (3.1 MPa) and 643 K. A sulfided commercial catalyst, Ni-Mo/Al₂O₃ (Shell 324), was used as reference for comparison.

Catalysts (quantity loaded = 30 m^2 for all samples) were in the form of coarse powders or pellets sieved to 16/20 mesh (1.00-0.841 mm) and were held between quartz wool plugs in a stainless steel reactor. The liquid feed consisted of 3000 ppm as sulfur (dibenzothiophene, Aldrich, 99%), 2000 ppm as nitrogen (quinoline, Aldrich, 99.5%), 500 ppm as oxygen (benzofuran, Aldrich, 99.5%), 20 wt % aromatics (tetralin, Aldrich, 99.9%), and balance aliphatic (tetradecane, Jansen Chimica, 99.5%). The liquid feed was mixed with hydrogen



Figure 1. XRD patterns of (a) V_2O_5 , (b) MoO_3 , (c) V_2MoO_8 , and (d) $V_{2,0}Mo_{1,0}O_{1,7}N_{2,4}$.

at a gas/liquid ratio corresponding to 9800 SCF/barrel (liquid flow rate at 5 cm³/h and hydrogen flow rate at 150 cm³(NTP)/ min). Analysis was done by gas chromatography (Hewlett Packard Model 5890) using a CPSIL-5CB fused silica capillary column (Chrompack) and a flame ionization detector.

Results and Discussion

Bulk Characteristics. Figure 1 parts a-d shows the XRD patterns of the three oxide precursors, V_2O_5 , MoO_3 , and V_2MoO_8 , and the product V-Mo-O-N. The pattern of the V-Mo oxide did not show any features belonging to the parent oxides, indicating the formation of a true bimetallic oxide. This double oxide was identified as V_2MoO_8 by a pattern search in the JCPDS files (JCPDS card 20-1377).

The V-Mo-O-N pattern (only 4 peaks are visible in the scale presented) can be indexed to a cubic (NaCl type, space group Fm3m) structure, *d*-spacing (pm) = (238, 206, 146, 124, 119); indexing = (111, 200, 220, 311, 222). In the V-Mo-O-N phase the metal atoms are located in a face-centered cubic arrangement, and N and O fill every octahedral interstitial position. The fcc metallic arrangement has also been found in vanadium nitride (VN),¹⁵ molybdenum nitride (Mo₂N), and oxycarbide (MoO_xC_y).²⁰ For bimetallic nitrides and oxynitrides, however, this type of structure is unreported, as indicated in a recent comprehensive review.²¹

Besides the simplicity of the XRD pattern, another distinctive feature is the unusual broadening of the peaks. This indicates that V-Mo oxynitride has very small crystallite size, which in turn suggests high surface area (S_g). The crystallite size (D_c), calculated by the Scherrer equation, indicates a dimension of 11 nm, in good agreement with the particle size of 7.9 nm obtained from the equation $D_p = 6/(S_g \rho)$ where the density, ρ , is taken to be 10.2 g cm⁻³, assuming a perfect rock salt structure for the compound. The agreement between D_p and D_c indicates that the particles are not polycrystalline aggregates. Elemental analysis of the V-Mo oxynitride indicated a chemical formula of V_{2.0}Mo_{1.0}O_{1.7}N_{2.4}. The oxygen content, obtained by difference, is higher than the theoretical value of 0.6 for a perfect NaCl structure. This could be due in part to metal atom vacancies, which are known to occur in binary carbides and nitrides. As discussed below, the passivation oxide layer also probably contributes significantly to the oxygen content of this high surface area material.



Figure 2. Raman spectra of the $V_{2,0}Mo_{1,0}O_{1,7}N_{2,4}$ surface.

Surface Properties. Figure 2 shows the in situ laser Raman spectra of reduced and passivated V-Mo-O-N. The sample reduced at 775 K for 2 h shows features at 100 and 300 cm⁻¹ characteristic of the O + A bulk phonon modes of cubic compounds such as NbC, TaC, and ZrC.²² The spectrum is very weak because first-order Raman scattering does not occur in these cubic compounds and 8 h of spectral acquisition were required to obtain the scattering signal. On the other hand, oxides do scatter strongly and the passivated sample readily shows the presence of orthorhombic vanadium oxide²³ and molybdenum oxide,²⁴ consistent with the high oxygen content of the sample. Although the oxides are formed as thin layers on the surface of the cubic oxynitride, their strong signal completely dominates the Raman spectrum and the faint oxynitride signature is invisible. From the known scattering properties of the pure oxides^{23,24} the relative intensities indicate enrichment in the V component. These measurements indicate that the reduction pretreatment in hydrogen used in the catalytic testing serves to remove the passivation layer so that the oxynitride surface is exposed. However, the true composition of the surface at catalytic conditions is unknown.

Figure 3 shows the initial low temperature TPR traces of masses 15 (NH₃), 18 (H₂O), and 28 (N₂) as well as the temperature profile used for the nitride samples. Nitrogen evolution in the forms of N₂ and NH₃ occurs in the course of the temperature program and is substantially over by the time the isothermal region is reached. Water production begins concurrently with ammonia but persists well into the isothermal region, consistent with the high oxygen content of the surface. Nevertheless, the appearance of both N and O species in the pretreatment suggests that the surface is an oxynitride.

Table 1 lists CO uptake, surface area, and active site density of the samples. Normally for metals and metal alloys the surface site density is $\sim 1 \times 10^{15}$ cm^{-2,25} The site density of the three current samples, VN, Mo₂N, and V_{2.0}Mo_{1.0}O_{1.7}N_{2.4}, is in the range (0.11–0.21) $\times 10^{15}$ cm⁻², indicating that only 10–20% of the metal atoms are chemisorbing CO. These values are consistent with previously reported quantities for carbides and





Figure 3. Low temperature TPR surface activation traces of (a) $V_{2,0}Mo_{1,0}O_{1,7}N_{2,4}$, (b) VN, and (c) Mo_2N .

TABLE 1: Characteristics of VN, Mo_2N , and $V_{2.0}Mo_{1.0}O_{1.7}N_{2.4}$

(a) V-Mo-O-N

738 K

595 K

	CO uptake (µmol g ⁻¹)	surface area S _g (m ² g ⁻¹)	site density $(\times 10^{15}$ cm ⁻²)	crystallite size D _c (nm)	particle size D _p (nm)
VN	36	20	0.11	17	9.8
Mo ₂ N	184	54	0.21	8.4	7.3
V _{2.0} Mo _{1.0} O _{1.7} N _{2.4}	167	74	0.14	11	7.9
Ni-Mo/Al ₂ O ₃	718 ^a	160	0.27		

^a Pulse oxygen chemisorption at room temperature.



Figure 4. High temperature TPR traces after CO adsorption of (a) $V_{2.0}Mo_{1.0}O_{1.7}N_{2.4}$, (b) VN, and (c) Mo_2N .

nitrides.²⁶ It is likely that the current activation process does not remove all the N and O species from the surface, which thus blocks CO chemisorption.^{5,27,28} This may be exacerbated by replenishment of N and/or O from the bulk. These species are known to be mobile in the subsurface at these temperatures.²⁹

Figure 4 shows the high temperature TPR traces of masses 12, 14, 16, 18, and 44 (CO, N₂, NH₃, H₂O, CO₂) for the samples after exposure to CO. The TPR process of the samples after CO adsorption can be roughly divided into two regions: (a) a low temperature desorption region (room temperature up to 800 K) where the adsorbed CO comes off the sample surfaces in the form of CO and CO₂ and (b) a high temperature reduction region (800–1373 K), where the bulk compounds are reduced by hydrogen as indicated by the formation of ammonia and water.

Both V-Mo-O-N and Mo₂N show strong CO desorption signals in the low temperature region. CO₂ formation also occurs, but at a higher temperature than CO desorption, suggesting the existence of strong interactions between chemisorbed CO and surface oxygen. In the case of VN only CO₂ desorption is observed (the small CO signal is due to fragmenta-



Figure 5. Comparison of catalytic activity for HDN (643 K; 3.1 MPa).

 TABLE 2:
 Summary of Catalyst Performance in

 Hydrotreating Process at 643 K and 3.1 MPa

catalyst	HDN (%)	LHSV (h ⁻¹)	space time $(10^{3}/\text{cm}^{3} \text{ g}^{-1} \text{ s}^{-1})$
Shell 324	38	5	3.8
Mo ₂ N	22	5	3.5
VN	8	5	1.5
V-Mo-O-N	44	5	1.8

tion). The strong binding of CO may be related to the low catalytic activity of VN.

Above 800 K, a gradual bulk reduction occurs, but no destructive decomposition was observed until higher temperatures were reached. This indicates that samples are stable to reduction at moderate conditions and that adsorbed species like CO can react before bulk decomposition occurs. For the V-Mo-O-N sample, integration of the desorption traces (with proper calibration factors) yields a N/O ratio of 1.6, consistent with the value of 1.4 obtained by ICP analysis. For VN and Mo₂N the H₂O signals shown are actually very weak and may be a consequence of cross-talk from the adjacent strong mass 17 (NH₃) channel. Both low and high temperature TPR traces show common features among all the compounds, as expected from the similarity in their nature. However, they also show characteristic differences indicating that composition gives rise to subtle chemical interactions.

Catalytic Activity. In quinoline HDN, propylcyclohexane (PCH) was the major product followed by propylbenzene (PBz), ethylcyclohexane (ECH), and ethylbenzene (EBz). Small amounts of benzene and cyclohexane were also detected. The appearance of PCH in the product indicates that decahydroquinoline (DHQ) is probably an intermediate in quinoline HDN. However, only a small amount of DHQ was detected in the product, showing that DHQ readily undergoes C-N bond scission to yield PCH. O-propylaniline was found to be relatively unreactive at the reaction conditions, indicating that the C-N bond scission occurred after complete ring saturation of quinoline. Propylbenzene could be the product of dehydrogenation of PCH, while ECH and EBz could have resulted from dealkylation of PCH and PBz. All the catalysts showed similar HDN product distributions at the conditions tested. However, V-Mo-O-N showed HDN performance superior to the rest of the catalysts (Figure 5, Table 2).

The comparison of activity based on equal surface areas loaded in the reactor is appropriate, since the commercial catalyst is highly optimized and most of its surface area is likely to be active. If the comparison is made based on surface metal atoms titrated by chemisorption (Table 1), the oxynitride is 2.3 times more active than the $Ni-Mo/Al_2O_3$.

The V-Mo-O-N is stable at the high temperature and pressure conditions of reaction. XRD analysis after the 50 h run shows retention of the fcc metallic structure and the absence of any extraneous metal, oxide, nitride, or sulfide peaks.

Conclusions

A new material, $V_{2,0}Mo_{1,0}O_{1,7}N_{2,4}$, has been synthesized by a temperature-programmed reaction process, using a bimetallic oxide precursor.

 $V_{2.0}Mo_{1.0}O_{1.7}N_{2.4}$ has a face-centered cubic metallic arrangement, a surface area of 74 m² g⁻¹, and a CO uptake of 167 μ mol g⁻¹. The material shows superb HDN performance with an activity higher than that of VN and Mo₂N on a surface area basis. The surface study results and the high catalytic activity of this new compound clearly demonstrate that one can substantially alter and optimize the properties of mononitrides by simultaneous partial element exchange (oxygen for nitrogen and one metal for another).

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