

# Transition-metal nitrides for hydrotreating catalyst—Synthesis, surface properties, and reactivities

Masatoshi Nagai

*Graduate School of Bio-applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan*

Available online 4 January 2007

## Abstract

Transition metal and bimetallic nitrides, especially molybdenum nitrides, have been reviewed in the areas of synthesis, structure and composition, surface properties and reactivities. The transition metal nitrides with high surface areas were synthesized by the temperature-programmed reactions of  $\text{MoO}_3$  with  $\text{NH}_3$  and a  $\text{N}_2/\text{H}_2$  mixture for transformation of the  $\text{MoO}_3$  to  $\text{Mo}_2\text{N}$  via  $\text{MoO}_2$  or chemical vapor deposition. The structure and composition of the Mo nitrides are discussed on the basis of the temperature-programmed desorption and reactions, X-ray photoelectron spectroscopy, and high-resolution transition electron microscopy (HR-TEM). The adsorption behavior of  $\text{N}_2$ ,  $\text{H}_2$ , and CO on the nitrides was reported. The transition metal nitrides are effective for the hydrodenitrogenation (HDN), hydrodesulfurization (HDS), hydrogenolysis and hydrogenation. Molybdenum-containing nitrides are very active during HDN, being comparable with sulfided Ni–Mo and Co–Mo catalysts. The nitride catalysts were found to be significantly active during HDS in the initial stage, but rapidly deactivated, from which an equation for the deactivation has been developed. The active sites on the Mo nitrides for the HDN and HDS are discussed.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Transition metal; HDN; HDS; Nitrides

## 1. Introduction

The transition metal nitrides possess characteristics of a high-performance hydrotreating catalysis as well as superconductive properties, and wear-resistant machine part properties [1–8]. Transition metal nitrides have been extensively studied as catalysts, and their surface structure and properties govern their catalytic performance. The high surface area of the material makes it a particularly promising compound for heterogeneous catalysis using a temperature-programmed method of synthesis [9–14]. To compensate for the small surface area of the active Mo nitrides, these catalysts were also developed for dispersion on a high surface area oxide support [15–17]. The oxynitride, as an intermediate of the synthesis of bulk nitrides, is expected to be a useful catalyst for hydrotreating [18–22], since it has a high surface area and bifunctional properties. Furthermore, the synthesis of transition bimetallic nitrides is likely to produce metal nitrides with a high selectivity and performance for hydroprocessing. The transition metal nitride is an interstitial compound, which can release

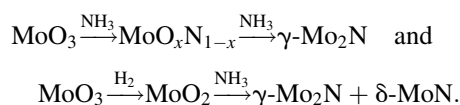
nitrogen from the bulk lattice and creates active sites for adsorption and catalytic reactions.

Mo-containing nitrides in the transition-metal nitrides have been extensively studied as useful and active catalysts for hydroprocessing [7,23,24], hydrogenolysis [10], hydrogenation [10,25–31], and the  $\text{H}_2$ – $\text{D}_2$  exchange reaction [32] that competes with the catalytic properties of noble metals, as well as the activities for HDN [13,15,23,33–51] and HDS [17,52–74]. The surface properties of nitrated molybdena-alumina were studied using temperature-programmed desorption (TPD) [50], temperature-programmed reduction (TPR) [75–77], adsorption/desorption of CO [33,44,63,73,78], and  $\text{O}_2$  [13,16,63], XRD [13,35,44,49,52,75,78,79], IR [63,73,76,80–85], NMR [86], X-ray photoelectron spectroscopy (XPS) [76,87,88], TEM [54,55,77] and (N)EXAFS [6,85,89]. The Mo/ $\text{Al}_2\text{O}_3$  nitrated with ammonia contains numerous  $\text{NH}_x$  ( $x = 0$ –3) species, which were analyzed by TPD and TPR [50,79,90,91]. In this paper, the author reviews the preparation, structure and composition, surface and catalytic properties, particularly for the HDN and HDS reactions, of the transition metal nitrides. The author also discusses the active sites on the surface of the nitrides for HDN and HDS.

*E-mail address:* [mnagai@cc.tuat.ac.jp](mailto:mnagai@cc.tuat.ac.jp).

## 2. Synthesis

The synthesis of Mo<sub>2</sub>N with a high surface area was extensively developed by Boudart and co-workers [9–12]. They developed the temperature-programmed reaction of MoO<sub>3</sub> with NH<sub>3</sub> (NH<sub>3</sub>-TPR) in the temperature range from 573 to 973 K. Alternatively, a mixture of N<sub>2</sub> and H<sub>2</sub> was used instead of NH<sub>3</sub> to eliminate the heat transfer problems associated with the endothermic decomposition of NH<sub>3</sub> [92]. The surface area of the Mo nitrides appears to be strongly dependent on the employed synthesis conditions. Reduced space velocities (depletion of NH<sub>3</sub> in the MoO<sub>3</sub> bed), increased reactant particle sizes, and increased rates resulted in increased water concentrations during the flow reaction, leading to lower surface areas. Ranhotra et al. [78] also synthesized fcc Mo<sub>2</sub>N, which has a high degree of crystallization, a BET surface area of about 180 m<sup>2</sup>/g, and pores of about 1.7 nm in diameter, according to the procedures of Volpe and Boudart [11]. Jagers et al. [93] and Li et al. [94] stressed the importance of the reaction intermediates in determining the surface areas and phase constituents. They suggested that the solid-state reaction of MoO<sub>3</sub> with NH<sub>3</sub> proceeds through two parallel reaction pathways:



The formation of the oxynitride, MoO<sub>x</sub>N<sub>1-x</sub>, resulted in a large increase in surface area, which was due to the pseudo morphological nature of the reaction, while the formation of MoO<sub>2</sub> and Mo metal led to lower surface area materials. Choi et al. [14] also reported that the key to produce Mo nitrides having high surface areas was channeling the reaction through the H<sub>x</sub>MoO<sub>3</sub> ( $x \leq 0.34$ ) and  $\gamma\text{-Mo}_2\text{O}_y\text{N}_{1-y}$  intermediates. In an earlier study, Hillis et al. [95] reported the reduction of molybdenum dioxide to molybdenum nitride in the temperature range of 723–823 K, and calculated the free energy of the conversion according to the following reaction:  $4\text{MoO}_2 + \text{N}_2 (\text{g}) = 2\text{Mo}_2\text{N} + 4\text{O}_2 (\text{g})$ .

At 398 K, the value of  $\Delta G^\circ$  is 2025 kJ/mol, and at 773 K, the corresponding value is about 1757 kJ/mol, therefore, this reaction is virtually impossible [95]. Thus, based on thermodynamics alone, hydrogen must play an essential part in bringing about the reduction of the oxide as an intermediate stage during the formation of the nitride.

Molybdenum nitrides ( $\gamma\text{-Mo}_2\text{N}$  and  $\delta\text{-MoN}$ ) have been synthesized by the chemical vapor deposition (CVD) of MoCl<sub>5</sub> [72,96,97] and Mo(CO)<sub>6</sub> [67,96] as precursors for the HDS catalyst. Roberson et al. [96] controlled the synthesis of  $\gamma\text{-Mo}_2\text{N}$  and  $\delta\text{-MoN}$  on the polycrystalline Ti substrate by CVD using Mo(CO)<sub>6</sub> between 623 and 723 K and MoCl<sub>5</sub> between 673 and 723 K diluted in NH<sub>3</sub> and either N<sub>2</sub> or Ar, in a cold-wall, vertical pancake-style reactor. Up to 973 K, a reaction-product consisting of two phases,  $\delta\text{-MoN}$  and  $\gamma\text{-MoN}_{1-x}$ , was obtained. A single phase  $\delta\text{-MoN}$  film was deposited at 973 K for Mo(CO)<sub>6</sub>. For the starting material of MoCl<sub>5</sub>, a  $\delta\text{-MoN}$  film

was deposited even at 873 K [72]. At high temperature (1773 K) and high NH<sub>3</sub> pressure (2 MPa), hexagonal MoN was synthesized by the reduction of a mixture of MoO<sub>2</sub> and NH<sub>4</sub>Cl [98]. Tungsten nitride [99–101] and niobium nitride [71] were also prepared and tested for thiophene HDS. Mo nitride clusters were found to be possibly Mo<sub>2</sub>N dimers by Mo K-edge XAFS, encaged in micropores of the NaY zeolite during the NH<sub>3</sub> treatment of Mo(CO)<sub>6</sub> as a precursor at 673 K [67]. It was also reported that MoN<sub>x</sub>/NaY was more resistant to deactivation during thiophene HDS than MoS<sub>x</sub>/NaY which was prepared by sulfiding Mo(CO)<sub>6</sub>/NaY. Liu et al. [89] analyzed Mo nitride, prepared by the temperature-programmed nitridation of the zeolite-supported MoO<sub>3</sub> with NH<sub>3</sub>, using EXAFS. They reported that the supported Mo<sub>2</sub>N has a greater configurational disorder than the unsupported  $\gamma\text{-Mo}_2\text{N}$  sample and the N atoms in  $\gamma\text{-Mo}_2\text{N}$  lengthen the distance between the Mo atoms and weaken the Mo–Mo bond, resulting in a greater activity during some reactions. The HR-TEM image of the Mo nitride is shown in Fig. 1. Based on high-resolution transmission electron microscopy, the structure of Mo<sub>2</sub>N was more likely a body-centered structure, because it was self-consistent with respect to both the (0 0 1) and (1 1 1) zone axes [13]. The body-centered Mo nitride structures, which are already known, are Mo<sub>2</sub>N (bcc) and  $\beta\text{-Mo}_{16}\text{N}_7$  (bct). The derived lattice constants and structures differed from that of the bulk  $\gamma\text{-Mo}_2\text{N}$ , which was the predominant phase identified by the X-ray diffraction analyses. Because the structure-image was taken from regions near the surface of the catalyst within 50 Å of the particle edge, the near surface structure was significantly different from that of the bulk structure.

Transition bimetallic nitrides [2–4,9–17,95] have been recently studied as novel alternative Co–Mo and Ni–Mo sulfide catalysts for the HDS of kerosene and gas oil. Cobalt molybdenum nitrides were prepared from the temperature-programmed nitriding of the CoMoO<sub>4</sub> precursor under

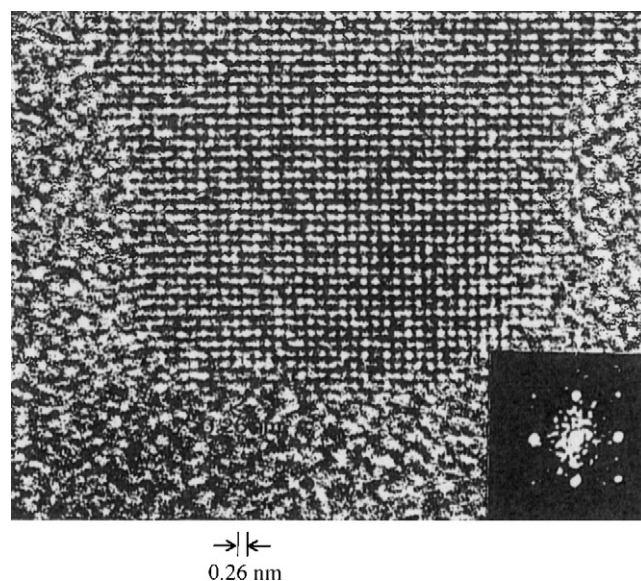


Fig. 1. Atomic TEM image of unsupported molybdenum nitride, looking-down a (1 0 0) zone axis [12].

Download English Version:

<https://daneshyari.com/en/article/43927>

Download Persian Version:

<https://daneshyari.com/article/43927>

[Daneshyari.com](https://daneshyari.com)