Catalytic Decomposition of Ammonia over Nitrided MoNx/α-Al_2O_3 and NiMoNy/α-Al_2O_3 Catalysts

Changhai Liang, Wenzhen Li, Zhaobin Wei,* Qin Xin, and Can Li*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

Ammonia decomposition over nitrided MoNx/α-Al_2O_3 and NiMoNy/α-Al_2O_3 catalysts was investigated at temperatures 600−750 °C, GHSV = 1800−3600 h^{-1}. The conversions of ammonia decomposition over nitrided MoNx/α-Al_2O_3 and NiMoNy/α-Al_2O_3 catalysts at 650 °C are as high as 98.7% and 99.8%, respectively. The catalytic activity of ammonia decomposition varies significantly with the Ni/(Ni + Mo) atomic ratio, and reaches the maximum when the Ni/(Ni + Mo) atomic ratio is near 0.60. XRD characterization shows that the catalyst phases are in nitrided forms, such as Mo_2N and Ni_3Mo_3N. The high activity of the nitrided MoNx/α-Al_2O_3 and NiMoNy/α-Al_2O_3 catalysts is attributed to the nitride phases formed from the preparation and the reaction in the presence of ammonia.

Introduction

The catalytic synthesis and decomposition of ammonia have been studied extensively in both aspects of the fundamental understanding and industrial applications, and the studies on these reactions have had important impact on the development of catalytic sciences and technology.[1−5] The ammonia synthesis provides the world with an essential feedstock for the production of fertilizers and nitric acid derivatives, while the decomposition reaction involves mainly producing controlled atmospheres for heat treatment in the metallurgical industry[6−8] and eliminating the ammonia pollution from the ammonia-containing waste gases.[9−14]

Earlier studies on ammonia decomposition are summarized in a number of reviews.[5,15,16] Among metal catalysts, ruthenium and iridium are the most active catalysts for ammonia decomposition under mild conditions.[17−20] Alloy catalysts, such as Fe−Al−K, Fe−Cr, La−Ni (−Pt) and La−Co (−Pt),[21−23] have been also investigated and show high activity for ammonia decomposition. But noble metals are generally not used in the commercial processes because of the high cost. The supported Ni catalyst has been widely used in industry,[6,10] but the reaction temperature of ammonia decomposition over supported Ni catalysts is usually required to be as high as 1000 °C.[10,11]

Transition metal nitrides and carbides, such as Mo_2N, VN, and VCx, have also been tested for ammonia decomposition. It has been shown that the catalytic properties of nitrides and carbides resemble those of noble metals in the involved-hydrogen reactions.[24−26] However, ammonia decomposition on nitrided NiMo catalyst has not been reported for ammonia decomposition though NiMo alloy catalysts have been examined for ammonia synthesis.[27] It is of interest and of practical importance to study the catalytic decomposition of ammonia over transition metal nitrides. Generally, the ammonia decomposition reaction is carried out at high temperatures, so α-Al_2O_3 was used as the catalyst support. In this paper, it is found that the nitrided MoNx/α-Al_2O_3 and NiMoNx/α-Al_2O_3 are very active for ammonia decomposition and the conversion for NiMoNx/α-Al_2O_3 can be as high as 99.8% even at 650 °C, which is far below the temperature for the commercial process, such as the process producing controlled atmospheres for the heat treatment in metallurgical industry[6] and the process of ammonia from coke-oven gas and citizen gas.[10,11]

Experimental Section

α-Al_2O_3-supported NiMo catalysts were prepared by the incipient wetness technique; namely, the support α-Al_2O_3 (with specific surface area 5 m^2/g from Tianjin Institute of Chemical Engineering) was impregnated with an aqueous solution of ammonium heptamolybdate and/or nickel nitrate. The prepared wet sample was dried in air at room-temperature overnight and then at 120 °C for 5 h and finally calcined in air at 500 °C for 5 h.

The nitrided MoNx/α-Al_2O_3 and NiMoNy/α-Al_2O_3 catalysts were prepared by temperature-programmed reaction of above oxidic precursor with ammonia using a fixed-bed microreactor, a quartz tube with an inner diameter of 8 mm. Typically, about 700 mg (1 mL) of catalyst particles with 20−40 mesh was used. The temperature was increased from room temperature to 450 °C in 90 min and from 450 to 700 °C in 250 min; finally, the temperature was maintained at 700 °C for 120 min. The nitrided NiMoNy/α-Al_2O_3 sample was cooled to temperature in flowing ammonia and then passivated in a stream of 1% O_2/N_2. The as-prepared sample is called passivated NiMoNy/α-Al_2O_3 catalyst. The nitrided samples without meeting oxygen are called fresh nitrides catalysts.

The oxidic, used, and passivated samples were examined by X-ray diffraction (XRD) on a Rigaku Rotaflex (Ru-500) diffractometer equipped with a Cu target and Ni grating monochromatic system.

The catalytic activities of as-prepared fresh catalyst were tested in situ at 600−750 °C with GHSV 1800 h^{-1}. The ammonia decomposition reaction was performed with pure ammonia (purity >99.9%) under atmospheric

* To whom correspondence should be addressed. Tel: 86-411-4671991 (ext. 728 or 720). Fax: 86-411-4694447. E-mail: canli@ms.dicp.ac.cn.

10.1021/ie990931n CCC: $19.00
Published on Web 09/15/2000

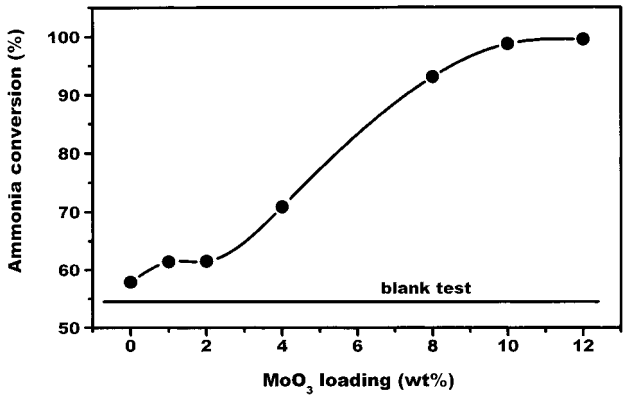

Figure 1. Activity of ammonia decomposition over MoNx/α-Al_2O_3 catalysts with different MoO_3 loading (reaction temperature, 650 °C; GHSV, 1800 h^{-1}).

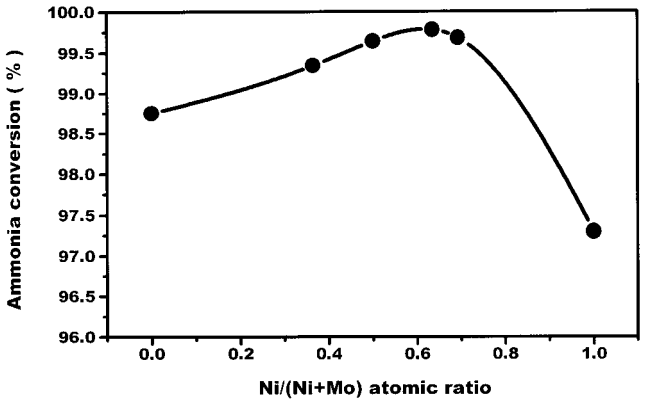

Figure 2. Ammonia decomposition activity as a function of Ni/(Ni + Mo) atomic ratio for the nitrided NiMoNy/α-Al_2O_3catalysts at 650 °C with GHSV of 1800 h^{-1}.

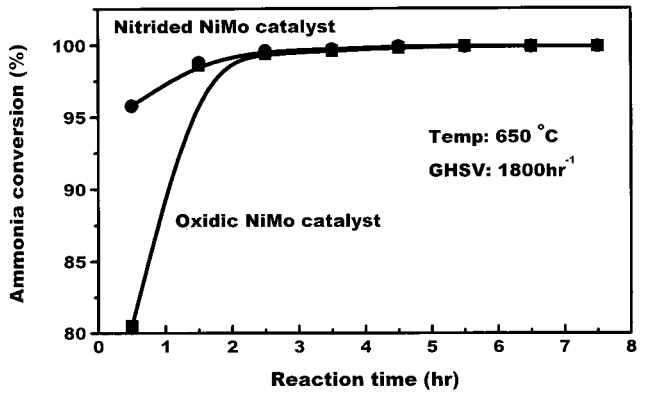

Figure 3. Ammonia conversion vs time on stream for the oxidic NiMo/α-Al_2O_3 and passivated NiMoNy/α-Al_2O_3 catalysts.

pressure and at the different space velocity of ammonia. The gaseous effluent from the reactor was neutralized by sulfuric acidic solution containing an indicator (methyl red). As soon as the neutralizing reaction is over, the color of the solution is changed from red to orange. The amount of effluent ammonia can be estimated accurately from the consumed amount of sulfuric acidic solution. For comparison, a commercially used Ni/MgO (6.0 wt % NiO) catalyst was also tested under the same reaction conditions.

Ammonia conversion is defined as the following:

$$\text{conversion (\%)} = \frac{(NH_3)_{feed} - (NH_3)_{effluent}}{(NH_3)_{feed}} \times 100\%$$

Here $(NH_3)_{feed}$ and $(NH_3)_{effluent}$ are NH_3 moles per unit time in the feed and effluent, respectively. This is so that the ammonia concentration in the effluent can be calculated from ammonia decomposition equation since the feed is pure ammonia. The results obtained are consistent with the concentrations obtained from measuring the amount of N_2 and H_2 in the effluent using a wet-flow meter and the amount of ammonia in the effluent by sulfuric acid absorption.

Results and Discussion

Effect of Mo Loading on the Catalytic Activity of Ammonia Decomposition. Figure 1 shows the ammonia decomposition activity of nitrided MoNx/α-Al_2O_3 catalysts at 650 °C, with the MoO_3 loading from 0 to 12.0 wt %. The conversion of ammonia is about 54% for the blank test at 650 °C. The α-Al_2O_3 support shows conversion of 57%, slightly higher than that of the blank test, indicating that the catalytic contribution from the support is negligible. The catalytic activity is increased progressively with the increase of MoO_3 loading in the range of 2.0−12.0 wt %. The activity of ammonia decomposition is not obviously increased with MoO_3 loading less than 2.0 wt %. The result may suggest that the catalyst with MoO_3 loading below 2.0 wt % is difficult to be nitrided. A dramatic improvement occurs with a further increase in MoO_3 loading above 2.0 wt %. The ammonia conversion becomes constant at about 98.5% when the Mo loading is higher than 10.0 wt %. Therefore, The molybdenum loading of 10.0 wt % MoO_3 loading is used in the following experiments.

Ammonia Decomposition Activity as a Function of Ni/(Ni + Mo) Atomic Ratio. Nickel catalyst has been employed in the commercial processes of ammonia decomposition. However, the bimetallic NiMo catalysts, particularly in the nitrided form, have not been reported for the ammonia decomposition. Figure 2 shows the ammonia decomposition activity of nitrided NiMoNy/α-Al_2O_3 catalyst with Ni/(Ni + Mo) atomic ratio. Interestingly, it is found that the activities of the nitrided NiMoNy/α-Al_2O_3 catalysts are much higher than MoNx/α-Al_2O_3 and Ni/α-Al_2O_3 alone when the Ni/(Ni + Mo) atomic ratio is below 0.60. The catalyst activity increases with the Ni/(Ni + Mo) atomic ratio from 0 to 0.60 but decreases with further increasing of the amount of Ni. The ammonia conversion reaches a maximum of 99.8% when the atomic ratio of Ni/(Ni + Mo) is near 0.60. The results show that adding Ni into the Mo/Al_2O_3 catalyst can improve the activity of ammonia decomposition.

Effect of Prenitridation on the Activity of Ammonia Decomposition. It is well-known that nitrides of early transition metals possess excellent catalytic properties in some reaction.[25] Under the reaction condition of ammonia decomposition, the catalyst could be nitrided or partially nitrided. The ammonia conversion versus time on a stream over oxidic catalyst and passivated NiMoNy/α-Al_2O_3 (freshly nitrided sample was passivated in a stream of 1% O_2/N_2 at room temperature) is given in Figure 3. It is found that the ammonia conversion over oxidic catalyst increases with reaction time during the first 2 h and then becomes stable. This can be explained by a slow nitridation of the catalysts under the reaction conditions. The ammonia conversion over passivated NiMoNy/α-Al_2O_3 catalyst shows the higher initial activity, and its activity is

Table 1. Conversion of Ammonia Decomposition over $MoNx/\alpha\text{-}Al_2O_3$ and $NiMoNy/\alpha\text{-}Al_2O_3$ and Commercially Used NiO/MgO Catalysts[a]

catalyst	GHSV (h^{-1})	conversion (%) 600 °C	650 °C	700 °C	750 °C
$MoNx/\alpha\text{-}Al_2O_3$	1800	n	98.75	n	n
	3600	75.2	97.3	99.7	n
$NiMoNy/\alpha\text{-}Al_2O_3$	1800	n	99.3	n	n
	3600	78.9	90.4	99.8	>99.9
NiO (6 wt %)/MgO	1800	69.9	87.5	98.8	99.9
	3600	n	n	89.2	96.8

[a] n = not tested.

further increased slowly with stream on time because some oxidic layer on the passivated $NiMoNy/\alpha\text{-}Al_2O_3$ was renitrided during the ammonia decomposition. The passivated $NiMoNy/\alpha\text{-}Al_2O_3$ catalyst shows higher initial activities than that of oxidic $NiMo/\alpha\text{-}Al_2O_3$ catalyst, and then the activities of both catalysts reach the same level after a reaction for 2 h. The higher activity of the passivated $NiMoNy/\alpha\text{-}Al_2O_3$ catalysts can be attributed to the nitride phases already formed, and the passivated oxidic layer on the nitrided surface is relatively easily renitrided during the reaction with ammonia. The passivated $NiMoNy/\alpha\text{-}Al_2O_3$ catalyst and the oxidic $NiMo/\alpha\text{-}Al_2O_3$ catalyst after ammonia decomposition reaction show the same XRD pattern. This indicates that the oxidic $NiMo/\alpha\text{-}Al_2O_3$ is gradually transformed into the nitrided form under the reaction conditions of ammonia decomposition.

Effects of Temperature and GHSV on the Catalytic Activity of Ammonia Decomposition. The effects of temperature and GHSV on the catalytic activity of ammonia decomposition for the nitrided $MoNx/\alpha\text{-}Al_2O_3$ and $NiMoNy/\alpha\text{-}Al_2O_3$ catalysts have been also investigated. From Table 1, it can be seen when reaction temperature is raised from 600 to 700 °C with the GHSV of 3600 h^{-1} the catalytic activities of ammonia decomposition over the nitrided $MoNx/\alpha\text{-}Al_2O_3$ and $NiMoNy/\alpha\text{-}Al_2O_3$ catalysts are increased from 75.2% and 78.9% to 99.7% and 99.9%, respectively. The catalytic activities over the nitrided $MoNx/\alpha\text{-}Al_2O_3$ and $NiMoNy/\alpha\text{-}Al_2O_3$ catalysts at 650 °C are 99.4% and 99.9%, respectively, when the GHSV is lowered to 900 h^{-1}, indicating that the nitrided $MoNx/\alpha\text{-}Al_2O_3$ and $NiMoNy/\alpha\text{-}Al_2O_3$ catalysts are very active for ammonia decomposition.

Comparison between the Supported NiMo Catalyst and a Commercially Used NiO/MgO Catalyst. The reaction activities of ammonia decomposition for the nitrided $NiMoNy/\alpha\text{-}Al_2O_3$ catalyst and a commercially used Ni/MgO catalyst are compared in Table 1. The conversion of ammonia at 750 °C is only 96.8% for Ni/MgO catalyst, while the conversion of ammonia at 700 °C is as high as 99.8% for nitrided $NiMoNy/\alpha\text{-}Al_2O_3$ catalyst with a GHSV of 3600 h^{-1}. It turns out that the nitrided $NiMoNy/\alpha\text{-}Al_2O_3$ catalyst is more active than the Ni/MgO catalyst, so the reaction temperature of ammonia decomposition over nitrided $NiMoNy/\alpha\text{-}Al_2O_3$ can be relatively lower than that for Ni/MgO to get the same conversion.

XRD of Oxidic, Used NiMo Catalysts, and Passivated $NiMoNx/\alpha\text{-}Al_2O_3$ Catalyst. XRD patterns of oxidic and used $NiMo/\alpha\text{-}Al_2O_3$ catalysts were recorded to identify the phases formed in the reaction and to understand the interaction between Ni and Mo on the $\alpha\text{-}Al_2O_3$ support. However, it is difficult to identify the Ni and Mo phases of the $NiMo/\alpha\text{-}Al_2O_3$ catalyst with

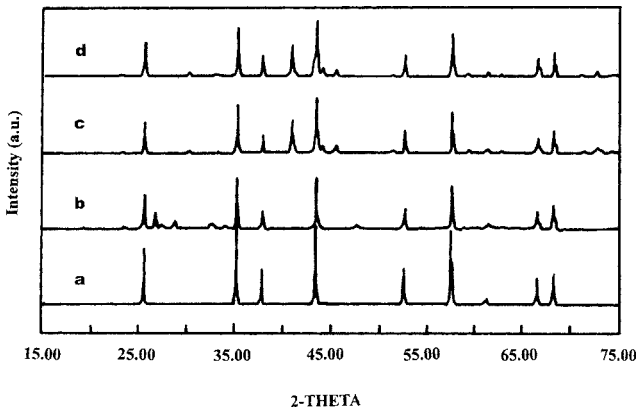

Figure 4. XRD patterns of $NiMo/\alpha\text{-}Al_2O_3$ catalysts and $\alpha\text{-}Al_2O_3$: (a) $\alpha\text{-}Al_2O_3$; (b) oxidic $NiMo/\alpha\text{-}Al_2O_3$ catalyst; (c) passivated $NiMoNy/\alpha\text{-}Al_2O_3$ catalyst; (d) $NiMo/\alpha\text{-}Al_2O_3$ catalyst after a reaction with ammonia at 650 °C.

6.0 wt % NiO and 10.0 wt % MoO_3 for above reaction because of the interference of $\alpha\text{-}Al_2O_3$ patterns and too low Ni−Mo loading. So a $NiMo/\alpha\text{-}Al_2O_3$ catalyst with 12.0 wt % NiO and 20.0 wt % MoO_3 loading was specially prepared for the XRD experiment. As shown in Figure 4, the crystalline phases of the oxidic $NiMo/\alpha\text{-}Al_2O_3$ catalyst are mainly composed of MoO_3 and $NiMoO_4$, and their typical diffraction peaks are at $2\theta =$ 26.8, 28.82, 32.64, 43.8, and 47.5°. The fact that there are no diffraction peaks of crystalline NiO ($2\theta =$ 37.5, 43.2, and 63.0°) in the catalyst precursor suggests that the NiO is dispersed in the oxidic $NiMo/\alpha\text{-}Al_2O_3$ catalyst.

After an ammonia decomposition reaction, the diffraction peaks of MoO_3 and $NiMoO_4$ disappeared. For the used catalyst (Figure 4d), the XRD peak due to Mo_2N is detected at $2\theta =$ 43.9° and the peak at $2\theta =$ 37.8° may be superimposed with the peak of $\alpha\text{-}Al_2O_3$; the diffraction peaks at $2\theta =$ 40.9, 45.4, 51.2, and 72.8° could be ascribed to Ni_3Mo_3N.[28] No diffraction peaks of Ni at $2\theta =$ 44.4 and 51.7° are observed. The passivated nitride sample from temperature-programmed reaction with ammonia at 700 °C also gives the same XRD pattern as those of the used catalyst (see Figure 4c). This indicates that the oxidic $NiMo/\alpha\text{-}Al_2O_3$ catalyst is gradually transformed into the nitrided form $NiMoNy/\alpha\text{-}Al_2O_3$ under the reaction conditions of ammonia decomposition. It is suggested that the nitrided phases, such as Mo_2N and Ni_3Mo_3N, are active phases for the ammonia decomposition because their formation is in parallel with the increase of the activity. Besides, some activity contribution from metal Ni cannot be ruled out.

Conclusion

In summary, the nitrided $MoNx/\alpha\text{-}Al_2O_3$ and $NiMoNy/\alpha\text{-}Al_2O_3$ catalysts show high activities for ammonia decomposition. The conversion of ammonia decomposition over the nitrided $NiMoNy/\alpha\text{-}Al_2O_3$ catalysts is higher than 99% even at 650 °C, and the ammonia conversion reaches a maximum of 99.8% when the atomic ratio of Ni/(Ni + Mo) is near 0.60. XRD characterization of NiMo catalysts indicates whenever the $NiMo/\alpha\text{-}Al_2O_3$ catalyst is in an oxidic or nitrided form, it eventually becomes the nitrided forms under the conditions of the ammonia decomposition reaction. The high activity of the nitrided $MoNx/\alpha\text{-}Al_2O_3$ and $NiMoNy/\alpha\text{-}Al_2O_3$ catalyst is mainly attributed to the nitrided phases, such as Mo_2N and Ni_3Mo_3N.

Acknowledgment

This work was partly supported by the National Natural Science Foundation of China (NNSFC) for Distinguished Young Scholars (Grant No. 29625305).

Literature Cited

(1) Nielsen, A. Ammonia Synthesis: Exploratory and Applied Research. *Catal. Rev.—Sci. Eng.* **1981**, *17*, 23.

(2) Jennings, J. R.; Ward, S. A. Ammonia Synthesis. In *Catalyst Handbook*; Twigg, M. V., Ed.; Wolfe Publishing Ltd.: 1989; Chapter 8.

(3) Boudart, M. Kinetics and Mechanism of Ammonia Synthesis. *Catal. Rev.— Sci. Eng.* **1981**, *17*, 1.

(4) Axelord, L. The Technology of Ammonia Plants. *Catal. Rev.—Sci. Eng.* **1981**, *17*, 53.

(5) Topsoe, H.; Boudart, M.; Norskov, J. K. Frontiers in Catalysis: Ammonia Synthesis and Beyond. *Top.Catal*. **1994**, 1 (3&4).

(6) Nemnyi, R. *Controlled Atmospheres for Heat Treatment*; Pergamon Press: London, 1984.

(7) Qiu, F.; Lu, S. Study on the Decomposition and Partial Oxidation of Ammonia on Porous Ni/Al_2O_3 Catalyst Plate. *Chin. J. Appl. Chem*. **1988**, *5*, 39.

(8) Kiyoshi, N.; Hiroyuki, F.; Akio, N. Highly Purity Hydrogen. JP79, 126,689, 1979.

(9) Mojtahedi, W.; Abbasian, J. Catalytic Decomposition of Ammonia in a Flue Gas at High Temperature and Pressure. *Fuel* **1995**, *74*, 1698.

(10) Svoboda, K. P.; Diemer, P. E. Catalytic Decomposition of Ammonia from Coke -Oven Gas. *Iron Steel Eng.* **1990**, Dec, 42.

(11) Currey, J. H. Ammonia Destruction at Citizens Gas and Coke Utility. *Iron Steel Eng.* **1991**, July, 43.

(12) Li, Y.; Armor, J. N. Selective NH_3 Oxidation to N_2 in a Wet Stream. *Appl. Catal., B* **1997**, *13*, 131.

(13) De Boer, M.; Huisman, H. M.; Mos, R. J. M.; Leliveld, R. G.; van Dillen, A. J.; Geus, J. W. Selective Oxidation of Ammonia to Nitrogen over SiO_2-Supported MoO_3 Catalysts. *Catal. Today* **1993**, *17*, 189.

(14) Armor, J. N. Environmental Catalysis. *Appl. Catal., B* **1992**, *1*, 221.

(15) Tamaru, K. A New General Mechanism of Ammonia Synthesis and Decomposition on Transition Metals. *Acc. Chem. Res.* **1988**, *21*, 88.

(16) Ozaki, A.; Aika, K. Catalytic Activation of Dinitrogen. *Catalysis-Sciences & Technology;* Anderson, J. R., Boudart, M., Eds.; Springer-Verlag: Berlin, 1981; Vol. *1*, p 88.

(17) Tsutomu, S.; Minuru, A.; Takao, I. Catalysts for Decomposing ammonia. WO 8904210, 1989.

(18) Bradford, M. C. J.; Fanning, P. E.; Vannice, M. A. Kinetics of NH_3 Decomposition over Well Dispersion Ru. *J. Catal.* **1997**, *172*, 479.

(19) Mary, S.; Kappenstein, C.; Balcon, S.; Rossignol, S.; Gengembre, E. Monopropellant Decomposition Catalyst: I Aging of Highly Loaded Ir/Al_2O_3 Catalysts in Oxygen and Stream. *Appl. Catal., A* **1999**, *182*, 317.

(20) Papapolymerou, G.; Bontontozolou, V. Decomposition of NH_3 on Pd and Ir Comparison with Pt and Rh. *J. Mol. Catal. A* **1997**, *120*, 165.

(21) Arabczyk, W.; Zamlynny, J. Study of the Ammonia Decomposition over Iron Catalysts. *Catal. Lett.* **1999**, *60*, 167.

(22) Willey, R. J.; Fox, M. F., II. Ammonia Decomposition over 430-ss Etched Metal Catalysts. *J. Catal.* **1988**, *112*, 590.

(23) Junichi, Y.; Kotato, T.; Tatsuo, S. Decomposition of Ammonia and Manufacture of Hydrogen. JP05,330,802, 1993.

(24) Wise, R. S.; Markel, E. J. Catalytic Ammonia Decomposition by Topotactic Molybdenum Oxides and Nitrides: Effect on Temperature Programmed Mo_2N Synthesis. *J. Catal.* **1994**, *145*, 335.

(25) Oyama, S. T. Kinetics of Ammonia Decomposition on Vanadium Nitride. *J. Catal.* **1992**, *133*, 358.

(26) Choi, J.-G. Ammonia Decomposition over Vanadium Carbide Catalysts. *J. Catal.* **1999**, *182*, 104.

(27) Keunecke, E. *Z. Elektrochem.* **1930**, *36*, 690.

(28) Bem, D. S.; Gibson, C. P.; Zurloye, H. C. Synthesis of Intermetallic Nitrides by Solid-State Precursor Reduction. *Chem. Mater.* **1993**, *5*, 497.

Received for review December 30, 1999
Revised manuscript received April 24, 2000
Accepted June 29, 2000

IE990931N