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A comparison of bulk metal nitride catalysts for pyridine hydrodenitrogenation

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A comparison of various group IV–VIII bulk metal nitride catalysts identified Co_4N and Fe_3N as having higher pyridine hydrodenitrogenation activity per unit area than Mo_2N. Formation of the metal nitrides was confirmed by X-ray diffraction and X-ray photoelectron spectroscopy, and all the nitrides were prepared from metal oxide precursors using the same temperature-programmed reaction technique. In general, the specific activity of the metal nitrides decreased with increased heat of formation of the metal nitride.

Keywords: hydrodenitrogenation, metal nitride, catalyst, pyridine

1. Introduction

Hydrodenitrogenation (HDN) is an important catalytic process used for the removal of organo-nitrogen compounds from petroleum feedstocks. Current HDN technology is based on sulfided catalysts consisting of either Mo or W, promoted with Co or Ni and supported on activated alumina. These catalysts were originally developed for hydrodesulfurization (HDS), and although they meet current requirements for HDN of conventional feedstocks, they lack selectivity, consume a large amount of hydrogen and must be operated at high severity. These limitations, together with the growing need to process heavier petroleum feedstocks that contain high levels of N, has led to the study of new active phases for HDN and HDS catalysis [1,2].

Mo_2N prepared with high surface area ($>100\ m^2/g$) from MoO_3 using temperature-programmed reaction (TPR) in NH_3 [3] is one such phase that has shown promise as an HDN [4–9] and HDS [10–12] catalyst. Schlatter et al. [5] reported that the activity of Mo_2N was similar to that of sulfided Ni–Mo/Al_2O_3 catalyst for quinoline HDN. Colling and Thompson [9] observed that the pyridine HDN activity of alumina-supported Mo_2N catalyst was superior to that of a commercial Ni–Mo/Al_2O_3 sulfided catalyst and similar to that of unsupported Mo_2N. On the basis of active sites determined by O_2 and CO chemisorption, Sajkowski and Oyama [8] reported that the activity of Mo_2N was 3–5 times higher than a commercial Ni–Mo sulfide catalyst. Both HDN and HDS activities followed the order $Mo_2N > Mo_2C/Al_2O_3 > NiMoS/Al_2O_3$. Similar observations were made by Nagai and coworkers [6,11] who reported that MoO_3/Al_2O_3 catalyst, nitrided with NH_3, exhibited high activity per unit surface area for both HDS and HDN. Higher dibenzothiophene HDS activity of supported metal nitrides of Mo, NiMo and CoMo compared to the sulfides has also been reported [13] and a bimetallic CoMo nitride catalyst has been shown to have higher activity than Mo_2N for thiophene HDS [14]. In neither of the latter two studies was the catalyst activity for HDN reported. Mo_2N catalysts reportedly have higher selectivities for C–N bond hydrogenolysis and lower selectivity for aromatic ring saturation compared to the corresponding metal sulfide catalysts. Hence the hydrogen consumption on metal nitride catalysts is lower than with metal sulfides for the same level of HDN [5,7].

Few studies of HDN using metal nitrides other than Mo_2N have been reported in the literature, partly because most bulk metal nitrides have low surface area (SA). For example, Schlatter et al. [5] compared the activity of NbN ($SA = 3.6\ m^2/g$) with Mo_2N ($SA = 88\ m^2/g$) for quinoline HDN and found that the activity of the former was not appreciably different from zero. More recently, Yu et al. [15] demonstrated that V–Mo oxynitride catalyst ($SA = 74\ m^2/g$) had higher activity for quinoline HDN than pure V or Mo nitrides, or a commercial Ni–Mo sulfide catalyst, operated at high pressure.

The present report focuses on the HDN activity of a series of bulk metal nitrides and compares them to a medium surface area Mo_2N using pyridine HDN as a model reaction. The study was motivated by the need to identify new active phases for HDN. Most previous studies have considered Mo_2N and Mo_2C. The objective of the present study was to identify phases that have high specific activity (i.e., activity per unit area) and hence may be good candidates as HDN catalysts when dispersed on high surface area supports. The selection of metal nitrides was restricted to group IV–VIII metals that had favorable thermodynamics for the formation of a metal nitride from the corresponding metal oxide [16].

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2. Experimental

2.1. Catalyst preparation

The metal nitrides were prepared from metal oxide precursors using temperature-programmed reaction (TPR) in NH_3, following the procedures described in the literature [3,17]. The following metal oxide catalyst precursors were used in the present study: TiO_2 (Aldrich, 99.9%), V_2O_5 (Aldrich, 99.96%), Nb_2O_5 (Aldrich, 99.99%), MoO_3 (Fisher, 99.99%), WO_3 (Aldrich, 99.995%), Fe_2O_3 (Aldrich, 99.98%), Cr_2O_3 (Aldrich, 99.995%), Co_3O_4 (Aldrich, 99.995%), Re_2O_7 (Alfa product, 99.99%), NiO (Aldrich, 99.99%) and ZrO_2 (Aldrich, 99.99%), and these materials were used without further purification.

In a typical experiment, 0.2 g of the metal oxide precursor (particle size 0.7–1.2 mm) was placed in the reactor supported on a quartz wool plug. The down-flow quartz tube reactor (i.d. = 0.8 cm and length = 30 cm) was heated with an electric furnace (Lindberg, model 55031), and the reactor temperature was controlled using a programmable temperature controller (Omega, CN-2010). Anhydrous NH_3 (Linde) was passed through a bed of BaO (Fisher) to remove residual H_2O and then fed to the reactor at a rate of 500 ml(STP) NH_3/min using a Brooks Instruments 5850E mass-flow controller. A high NH_3 flow rate was used to ensure removal of water from the catalyst and increase the purity of the resulting nitride phase. Once the NH_3 flow had stabilized, the reactor temperature was increased from ambient to 350 °C within 30 min, followed by an increase from 350 to 450 °C at rate of 0.67 °C/min and a further increase from 450 to 707 °C at rate of 1.67 °C/min. The temperature was then maintained at 707 °C for an additional hour before cooling to room temperature in flowing NH_3. The resulting material was passivated in 1% O_2/He (UHP grade, Linde) at a flow rate of 100 ml(STP)/min for 1 h, to prevent possible rapid oxidation when exposed to air during subsequent sample handling.

2.2. Catalyst characterization

X-ray photoelectron spectroscopy (XPS). XPS spectra were measured in a Leybold MAX200 spectrometer using an unmonochromatized Mg $K\alpha$ (energy = 1253.6 eV) source which was operated at 10 kV and 20 mA. The spectrometer energies were calibrated using the Au $4f_{7/2}$ peak at 84.0 eV. Charging effects were corrected by referencing the binding energies to that of the adventitious C 1s at 285.0 eV.

X-ray diffraction (XRD). XRD was performed using a Siemens D-5000 diffractometer with monochromatized Cu $K\alpha$ radiation ($\lambda = 1.5404$ Å). Data acquisition and

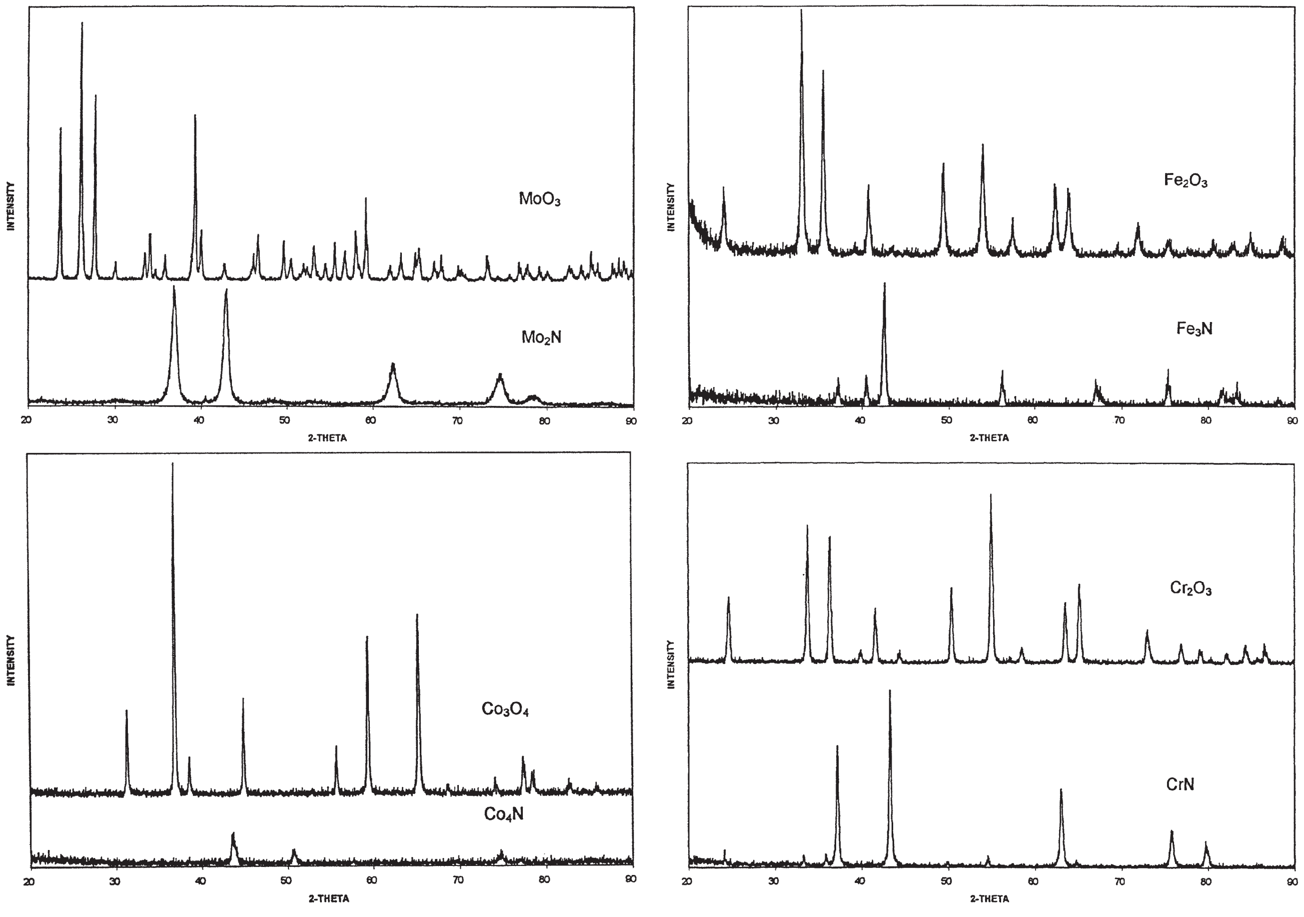

Figure 1. XRD patterns of metal oxide precursors and metal nitrides synthesized by TPR in NH_3.

data plotting were carried out using a computer interfaced to the diffractometer.

BET surface area. BET surface area of the passivated samples was measured using a Micromeretics model ASAP 2010 instrument. Nitrogen gas was used for the standard five-point BET surface area measurements.

2.3. Catalytic activity

Catalyst activities were measured using the same reactor as was used for the catalyst preparation. H_2 gas (UHP grade 99.995%, Linde) was delivered to the reactor using a mass-flow controller (Brooks Instruments, 5850E series). Liquid pyridine (Aldrich, HPLC grade +99.9%) was delivered to the gas feed line upstream of the reactor using a microsyringe pump (Harvard Apparatus, model 44). To ensure complete vaporization of the liquid feed prior to entering the reactor, the feed line located down stream of the point of liquid introduction was maintained above 150 °C using a heating tape.

The reactor effluent was analyzed using a Shimadzu gas chromatograph (model 14A, Mandel Scientific) equipped with an FID detector and auto-sampling valve. Products were separated using a 30 m long, 0.53 mm i.d. Carbowax capillary column with film thickness 1.2 μm.

For a typical activity measurement, 0.15–0.2 g of passivated metal nitride catalyst was placed in the reactor on top of a glass wool plug. The oxide passivation layer was removed from the catalyst by pretreatment in H_2 gas, flowing at a rate of 150 ml(STP)/min. The catalyst was heated in the H_2 flow from ambient to 415 °C over a 6 h period, followed by an additional 2 h at 415 °C. Immediately following H_2 pretreatment, the catalyst was cooled to the reaction temperature (350 °C) in flowing H_2 within 30 min. Pyridine was then introduced to the system. The flow rate of H_2 gas was maintained at 150 ml(STP)/min, and the liquid pyridine flow was held at 0.001 ml/min (1 μl/min). After a 30 min stabilization period, the reaction products were analyzed every 30 min over a 12 h period.

3. Results and discussion

3.1. Catalyst preparation and characterization

The metal nitrides were all prepared using the same TPR profile and NH_3 space velocity, since this study neither intended to quantify the effect of synthesis conditions, nor did it attempt to optimize synthesis conditions to accommodate each metal oxide precursor. Figure 1 compares the XRD spectra of the materials obtained following TPR to those

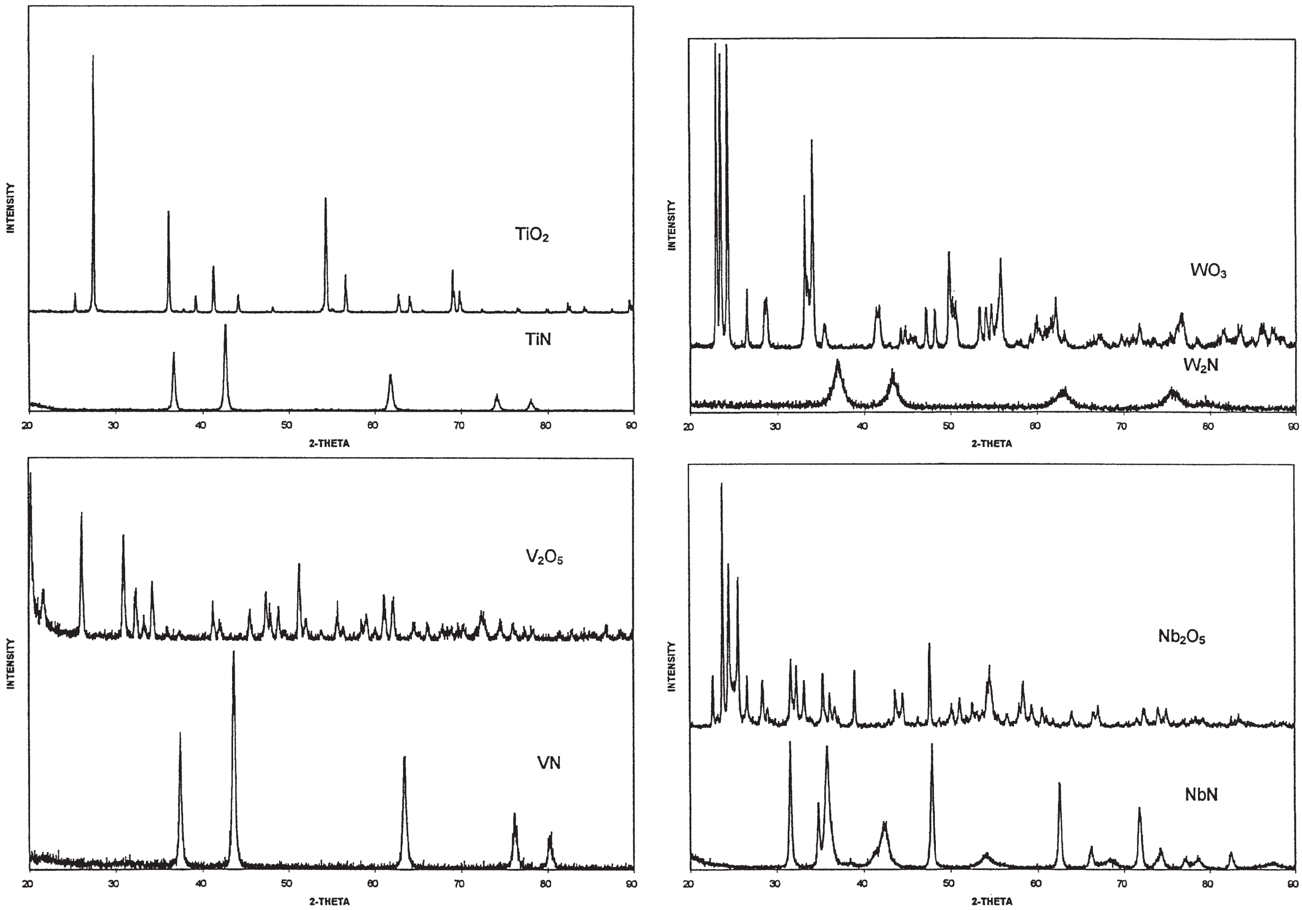

Figure 1. (Continued.)

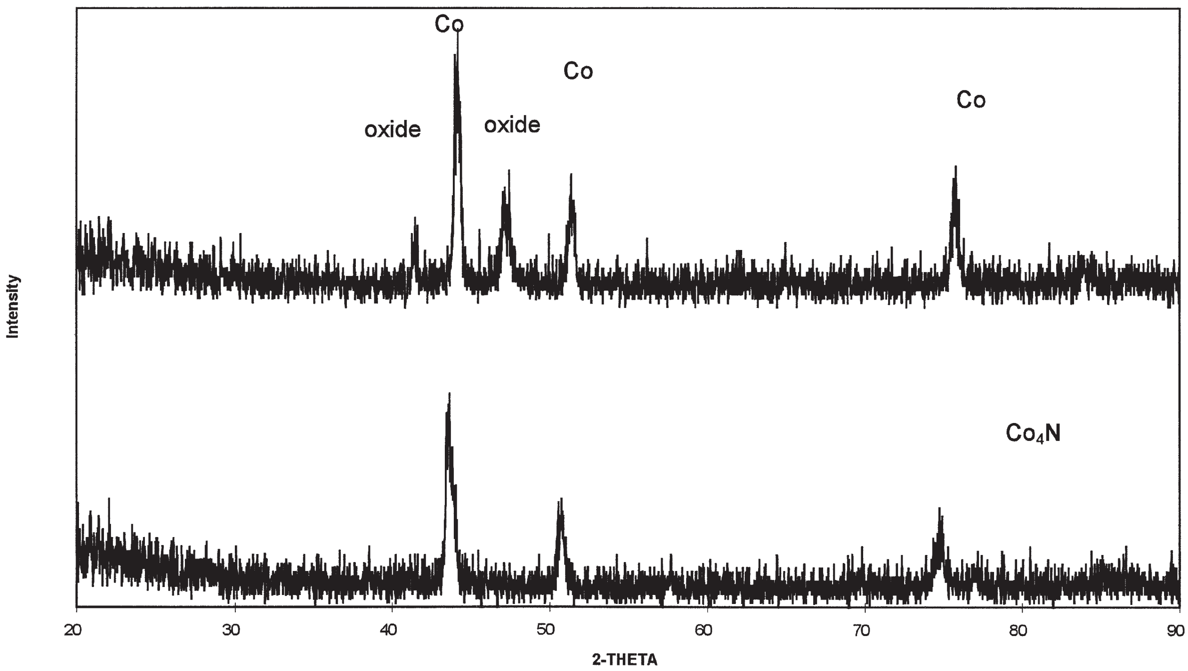

Figure 2. XRD pattern of cobalt and cobalt nitride synthesized from Co_3O_4 by TPR in H_2 and NH_3, respectively.

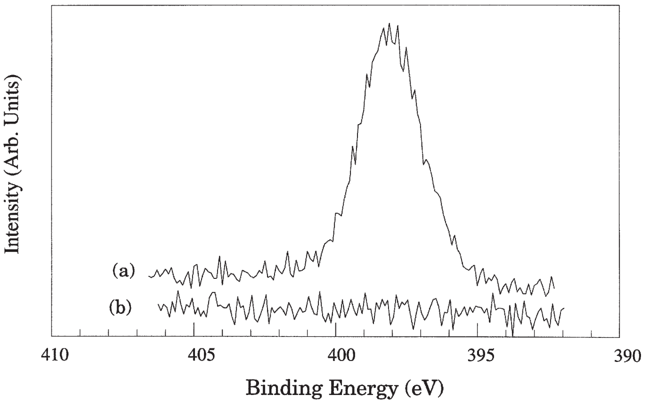

Figure 3. N 1s region of XPS spectra following TPR treatment of Co_3O_4 in NH_3 (a) and H_2 (b).

obtained for the respective oxide precursors. The phases present were identified by comparing the XRD spectra to standard spectra from a powder diffraction data base [18]. The synthesis of bulk rhenium nitride and nickel nitride from their respective oxides by TPR in NH_3 at the conditions of the present study did not occur. Instead, a reduction to zero valent metal took place as confirmed by XRD (not shown). An attempt to prepare zirconium nitride under the same synthesis conditions resulted in the formation of either zirconium oxynitride or a zirconium oxide phase different from the parent oxide (ZrO_2). For all the other metal oxides examined, there was no evidence of unreacted metal oxide and no nitride phase other than the one shown. These results suggest that optimized synthesis conditions may be required to prepare some of the metal nitrides.

The results of figure 1 showed that cobalt oxide was nitrided to Co_4N. This result is contrary to the result reported recently by Kim et al. [14] who concluded that, under similar TPR conditions, Co_3O_4 was converted to Co^0. The characteristic XRD peaks for Co_4N and Co^0 are similar, and these authors ascribed the XRD peaks of their nitrided sample to Co^0. To distinguish between Co_4N and Co^0 in the present study, the Co_3O_4 precursor was also reduced in H_2 at 500 °C for 12 h. The XRD spectra of the NH_3- and H_2-treated samples are shown in figure 2. Both samples were passivated after synthesis with 1% O_2/He. Clearly, the two samples possess similar but different XRD spectra that may lead to misinterpretation. From the present data, it can now be concluded that the peaks at $2\theta = 43.64$, 50.64 and 74.55° can be ascribed to the Co_4N phase and not Co^0, as suggested by Kim et al. [14].

The NH_3- and H_2-treated cobalt catalysts, after passivation with 1%O_2/He, were also examined by XPS. Figure 3 shows N 1s spectra measured for both these samples. The spectrum for the H_2-treated catalyst is unable to detect the presence of N, but that treated with NH_3 shows a single peak corresponding to a binding energy of 398.1 eV. This value is consistent with nitride formation [19,20]; by contrast, physically adsorbed NH_3 is expected to show a binding energy of about 399 eV [21], while species such as NH_4^+ or NO_3^- have higher values (typically around 402 and 404 eV, respectively [22]). Figure 4 reports corresponding Co 2p spectra including the full $j = 3/2$ and $1/2$ doublet structure. For each surface, the dominant peak close to 781 eV ($j = 3/2$) is consistent with the presence of surface $Co(OH)_2$; the accompanying structure at higher binding energy (around 787 eV) is formed via the shake-up mechanism [19]. The general features repeat, although with reduced intensities, for $j = 1/2$ in the higher binding energy range. For both the $j = 3/2$ and $j = 1/2$ main peaks, the lower binding energy side of the NH_3-treated sample is broader (less steep) than is the case for the H_2-treated sample. This is taken to indicate that the NH_3 treatment results in slightly more Co in a low oxidation state than is the case for the sample formed by the H_2 treatment. The former undoubtedly gives metal nitride, but coexistence with hydroxide is indicated in the surface region after the passivation. This observation from XPS is consistent with the conclusion here from XRD insofar as the presence of Co^0 after the NH_3 treatment cannot be more than at a very minor level (any zero oxidation state component would be expected to contribute structure to the Co 2p spectrum for binding energy close to 778 eV [19]).

BET surface areas of the nitrided and passivated catalysts are summarized in table 1. The bulk VN, W_2N and Mo_2N catalysts possess significantly higher surface area (>30 m^2/g) than Fe_3N, Co_4N, CrN, TiN and NbN (<20 m^2/g). Nitriding resulted in increased surface area compared to the metal oxide precursors which had surface areas in the range of 1–3 m^2/g. The increased surface area is a consequence of the lower molar volumes of the metal nitrides compared to the corresponding metal oxides.

The activities of the metal nitrides synthesized in the present work were compared to a medium surface area Mo_2N. The passivated Mo_2N catalyst surface area (table 1) obtained in the present study was lower than the 52 m^2/g, reported by Choi et al. [17], using the same synthesis conditions, but measured after reduction in H_2 at 400 °C to remove the passivated oxide layer. Although the effect of passivation on metal nitride catalysts on surface area was not examined in the present study, passivation has been reported to result in a loss in surface area for Mo_2N [23].

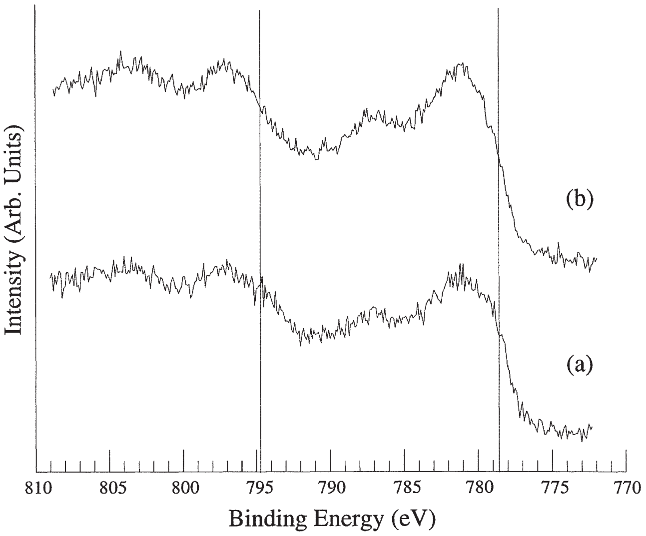

Figure 4. Co 2p region of XPS spectra following TPR treatment of Co_3O_4 in NH_3 (a) and H_2 (b).

Table 1
BET surface area and activity of bulk metal nitrides for pyridine HDN.

Metal oxide precursor	Phase identifed by XRD after TPR in NH_3	Nitride surface area (m^2/g)	Pyridine consumption at 350 °C and 101 kPa	
			μmol g-cat^{-1} s^{-1}	μmol m^{-2} s^{-1}
Co_3O_4	Co_4N	1.4	0.422	0.301
Fe_2O_3	Fe_3N	1.4	0.300	0.215
MoO_3	Mo_2N	31	0.525	0.017
WO_3	W_2N	49	0.242	0.005
V_2O_5	VN	57	0.047	0.001
Nb_2O_5	NbN	18	0.048	0.003
Cr_2O_3	CrN	10	0.021	0.002
TiO_2	TiN	7	0.016	0.002

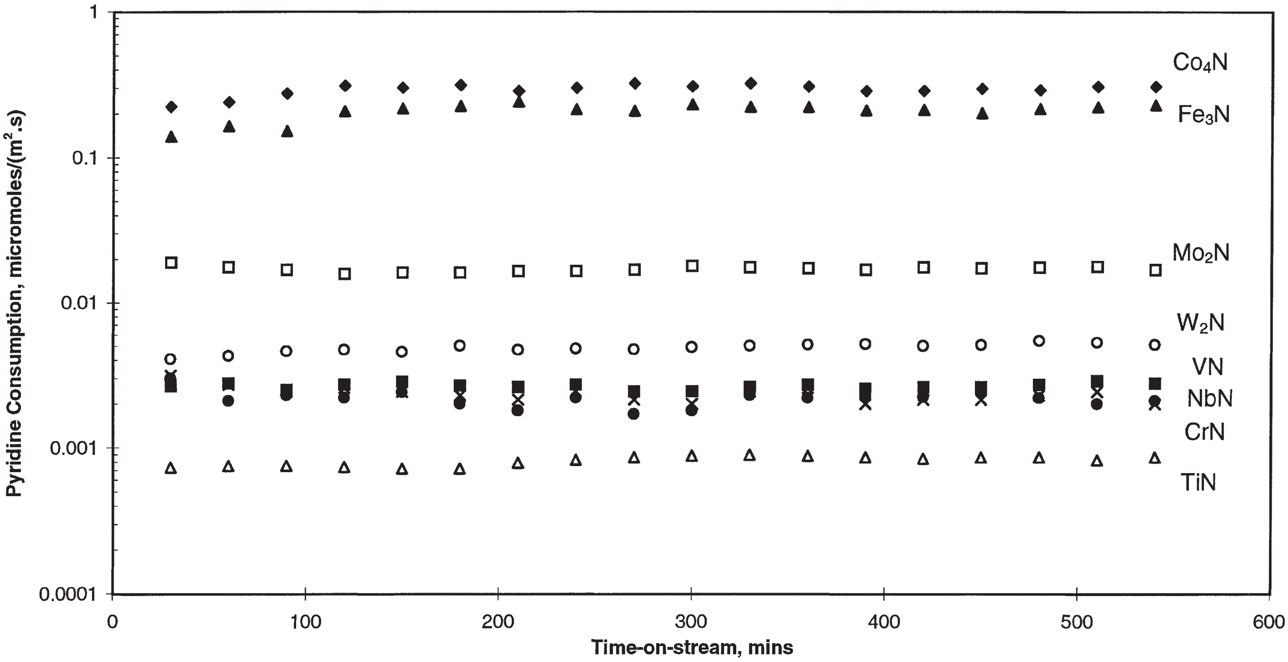

Figure 5. Activity of metal nitrides for pyridine HDN at 350°C and 101 kPa as a function of time-on-stream.

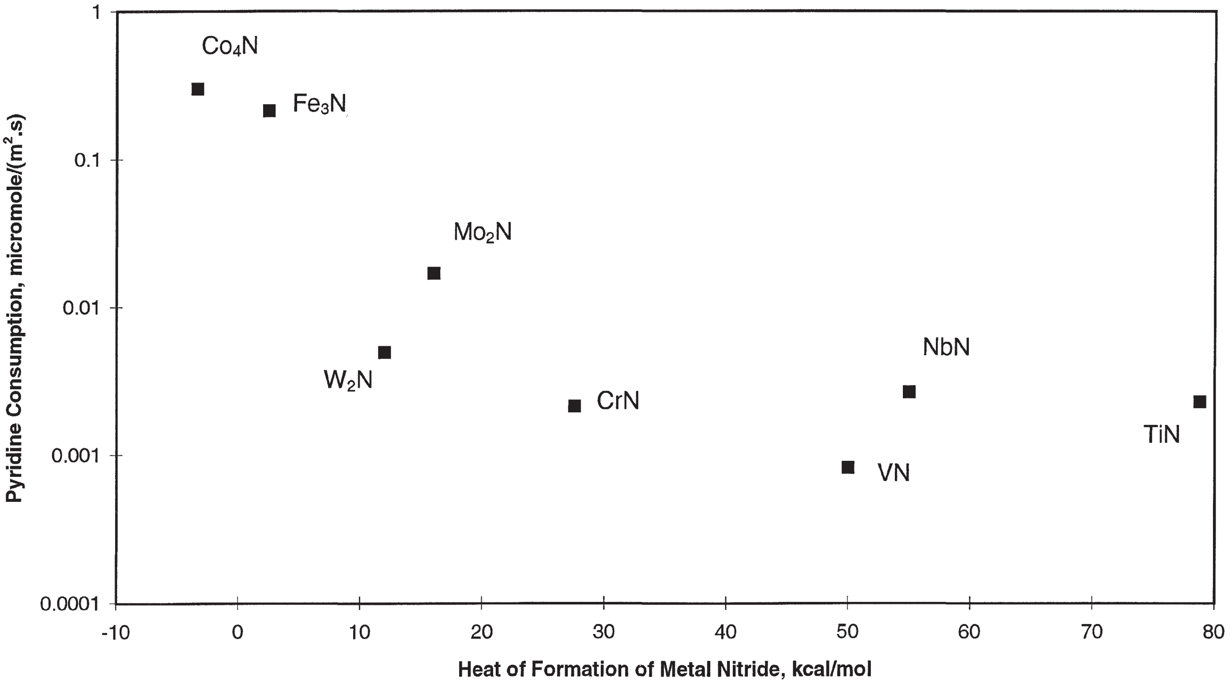

Figure 6. Specific activities of metal nitrides as a function of the metal nitride standard heat of formation.

3.2. Activity measurements

The HDN activity of the catalysts of the present study were evaluated in terms of pyridine consumption. Selectivities are not reported, but most of the product consisted of light hydrocarbons (C_1–C_5). Figure 5 shows the catalyst activity as a function of time-on-stream over a period of approximately 9 h. All the catalysts show a constant activity after an initial period of about 30 min, during which the activity declined slightly for some of the catalysts.

Table 1 compares the average moles of pyridine consumed, as determined in the 0.5–9 h time-on-stream period, for each of the metal nitrides reported per gram of catalyst and per unit area of catalyst. Although the Mo_2N had the highest activity per gram, Co_4N and Fe_3N exhibited the highest activities per unit area of catalyst. These results suggest that, in addition to Mo_2N, high HDN activity per gram may be possible with well dispersed Co_4N- and Fe_3N-supported catalysts.

It is well known that the heats of formation of transition metal sulfides (TMS) correlate with their HDS activity according to the classical volcano plot [24,25]. In an analogous way, figure 6 presents the specific activities of the TMN catalysts, measured in the present study, as a function of their heats of formation. Metal nitrides with lower heats of formation exhibited higher HDN activities. The trend follows one side of a classical volcano plot and is presumably related to increased stability of the adsorbed surface species with increased heats of formation of the TMN nitrides.

The low heats of formation for some of the metal nitrides, shown in figure 6, suggests that they may not be stable under the present reaction conditions. Although the used catalysts were not characterized in detail, XRD analysis confirmed the presence of bulk metal nitride in the case of Mo, Fe and Co. In the latter case, however, there was also evidence for the presence of Co^0. This result is somewhat surprising given the stable activities shown in figure 5 for all the catalysts examined.

4. Conclusions

A series of bulk metal nitrides were prepared by temperature-programmed reaction of NH_3 with Fe_2O_3, Co_3O_4, MoO_3, V_2O_5, TiO_2, Cr_2O_3 and Nb_2O_5, whereas NiO and Re_2O_7 were reduced to zero-valent metal. The formation of Co_4N was confirmed by XPS and XRD analysis. The present study identified Co_4N and Fe_3N as having higher specific activities for pyridine HDN at atmospheric pressure than Mo_2N. The HDN activities were found to correlate with the heats of formation of the bulk nitride, the metal nitrides with lower heat of formation exhibiting higher activity for pyridine HDN.

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