

THE ROLE OF NICKEL IN PYRIDINE HYDRODENITROGENATION OVER NiMo/Al₂O₃

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Abstract – Al₂O₃ supported Mo, Ni, and NiMo/Al₂O₃ catalysts with various Ni contents were prepared to investigate the role of Ni as a promoter in a NiMo bimetallic catalyst system. The hydrodenitrogenation (HDN) reaction of pyridine as a catalytic probe was conducted over these catalysts under the same reaction conditions and the catalysts were characterized using BET surface area measurement, infrared spectroscopy, temperature programmed reduction, DRS and ESR. According to the results of reaction experiments, the NiMo/Al₂O₃ catalyst showed higher activity than Mo/Al₂O₃ catalyst in the HDN reaction and particularly the one with atomic ratio [Ni/(Ni+Mo)]=0.3 showed the best activity for the HDN of pyridine. The findings of this study lead us to suggest that the enhancement in the HDN activity with nickel addition could be attributed to the improvement in the reducibility of molybdenum and the formation of Ni-Mo-O phase.

Key words : Nickel, Pyridine HDN, Reducibility, Ni-Mo-O, NiMo/Al₂O₃

INTRODUCTION

As world reserves of crude oil and light oil fraction in the feedstocks decrease, processing of heavier feeds becomes increasingly important. The heavier feeds such as vacuum residue oil and synthetic crudes derived from coal and shale have large amounts of sulfur, nitrogen, oxygen, and organometallic compounds. In particular, the coal derived oil contains approximately 1-3 % nitrogen.

Nitrogen compounds are present in the forms of nonheterocyclic compounds (aniline, amine compound, etc.), nonbasic heterocyclic compounds (pyrrole, indole, cabazole, etc.), and basic heterocyclic compounds (pyridine, quinoline, acridine, etc). Such compounds react with hydrogen to hydrocarbon and ammonia. Because nitrogen compounds are more refractory than sulfur compounds, the hydrodenitrogenation (HDN) reaction has not been studied so extensively as the hydrodesulfurization (HDS) reaction. However, since we expect that the environmental regulations for nitrogen compounds will be gradually reinforced in the coming decades, much more attention needs to be given to the HDN process.

One of the most important subjects on the HDN is to develop an active catalyst. So far, most of the studies on the HDN catalyst have been focused on the bimetallic catalysts based on transition metals. In particular, a sulfided NiMo/Al₂O₃ catalyst has been widely used in commercial HDN plants. Although the HDN reaction over NiMo/Al₂O₃ catalyst has been

extensively studied in recent years, the catalytic features involved in the HDN reaction and the effect of Ni as a promoter have been rarely examined. While some researchers proposed the synergistic effect associated with Ni in Ni-Mo catalytic system [Ledoux and Pjellouli, 1990], others reported no significant change in HDN activity after the addition of Ni as a promoter [Sobczak et al., 1988].

Ledoux and Pjellouli [1990] investigated the role of Ni in pyridine and piperidine HDN reactions over NiMo/Al₂O₃ catalyst. They suggested that the introduction of Ni enhanced the decomposition of hydrogen and the migration of hydrogen to polymolybdates. Stanislaus et al. [1989] reported that the addition of Ni resulted in the formation of different active sites. More recently, Brito and Laine [1993] examined the reducibility of NiMo/Al₂O₃ catalysts by the temperature-programmed reduction (TPR) method and elucidated the role of Ni. Louwers and Prins [1992] confirmed the existence of a Ni-Mo-S surface phase by the EXAFS method. According to Ozkan et al. [1994], the role of Ni is to enhance the Mo dispersion over Al₂O₃ support as well as to promote the pyridine hydrogenation by the formation of the synergistic active sites that are single sulfur vacancies associated with Ni in Ni-Mo-S structure.

The aim of this study is to investigate the role of nickel as a promoter in the pyridine HDN reaction over NiMo/Al₂O₃ catalyst. The catalysts are prepared with different loadings of Ni and characterized by applying various techniques such as TPR, FT-IR, ESR and DRS. Reaction experiments for the pyridine HDN are also conducted to examine the effect of Ni promoter on the HDN activity of catalysts under investigation. Finally, the changes in the catalytic activity are elucidated by using various characteristics of catalysts.

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Table 1. Physical properties of the alumina support and the catalysts

	Surface area (m ² /g)	Pore volume (cc/g)	Pore diameter (Å)
γ-alumina	244	0.62	101.6
Mo/Al ₂ O ₃	174.35	0.418	95.82
NiMo/Al ₂ O ₃ (r=0.2)	170.74	0.409	95.82
NiMo/Al ₂ O ₃ (r=0.3)	169.42	0.391	92.24
NiMo/Al ₂ O ₃ (r=0.4)	166.69	0.394	94.54
NiMo/Al ₂ O ₃ (r=0.6)	164.36	0.389	94.67
NiMo/Al ₂ O ₃ (r=0.8)	159.87	0.381	95.33

r: Ni/(Ni+Mo) atomic ratio

EXPERIMENTAL

1. Catalysts Preparation

NiMo/Al₂O₃ catalysts were prepared by successive incipient wetness impregnation of alumina supports with aqueous solutions of (NH₄)₆Mo₇O₂₄·4H₂O and Ni(NO₃)₂·6H₂O to obtain Mo content of 14 wt% and Ni/(Ni+Mo) atomic ratios in the range of 0-1. The catalysts were dried at 120°C overnight and then calcined at 450°C for 5 hr. The physical properties of the alumina support and the catalysts are presented in Table 1.

2. Characterization

The temperature-programmed reduction (TPR) profile was obtained by raising the temperature from room temperature to 900°C at the constant rate of 20°C/min. The apparatus consisted of a flow system connected to a thermal conductivity cell to detect changes in the composition of the reducing gas (6 ml/min H₂ plus 34 ml/min N₂). The sample of 0.1 g was placed into a quartz reactor tube.

IR measurements were conducted by using the FT-IR spectrometer (Midac Co.) equipped with *in situ* high vacuum IR cell. The electron spin resonance (ESR) spectra of the sulfided catalysts were obtained by using the Bruker ER 200E-SRC spectrometer with a single capacity at room temperature in the 2,000-4,000 G range. The working frequency was 9.76 GHz. A Varian strong pitch sample (*g*=2.0028), which was used to calibrate the magnetic field, functioned as a standard for the quality factor of the ESR cavity. Diffuse reflectance spectroscopy (DRS) was done in the range of 230-870 nm, using a Varian CARY 2200 spectrometer.

3. HDN Activity Test

The activation of catalyst and the HDN reaction experiment were conducted in a fixed-bed, high pressure, flow reactor system. The reactor was made of 1/2 in.-o.d. 316 stainless tube (i. d.=0.40 in., thickness=0.05 in., length=320 mm). The reactor was charged with 1 g of catalyst in 35-45 mesh size. The catalytic bed was diluted with glass beads to make the volume of the catalyst bed 4 ml.

In addition, glass beads of 10 to 20 mesh were placed just above the catalytic bed to mix hydrogen with reactants in advance and to maintain the uniformity of flow. The reactor temperature was maintained constant by an electric furnace equipped with a PID temperature controller. The reaction was carried out at 400 °C and 500 psig for 12 hours. The HDN reaction reached the steady state condition after 8 hr. There-

fore, the HDN activities of the catalysts were determined after 12 hours from the start of a run and there was a good reproducibility within 1 % variation in the conversion data. The liquid feed composition was 10 mol% pyridine/n-heptane in all experiments.

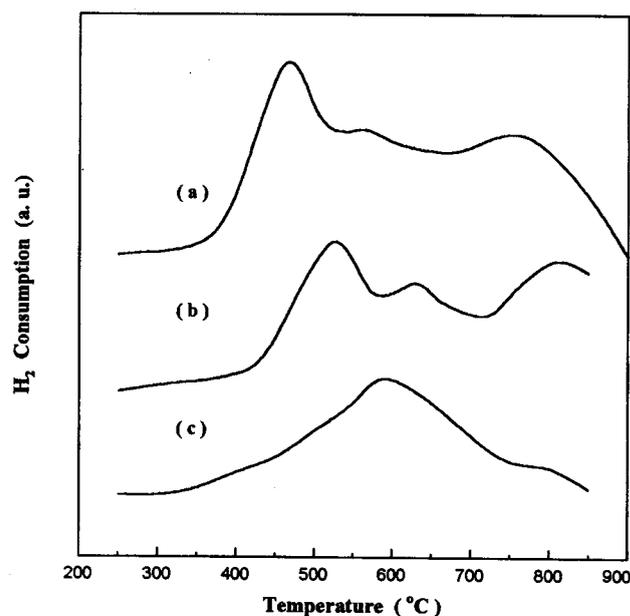
For activation, the catalyst was presulfided by passing a 15 vol % H₂S/H₂ mixture at a flow rate of 50 ml/min, while the temperature was raised from room temperature to 400°C at a constant rate of 10°C/min. The final temperature was maintained for 4 hr, and then the reactor was cooled down to room temperature in a flow of N₂. Reactants and products were analyzed by using Gas Chromatography (Hewlett Packard 5890 series II, FID) equipped with HP-1 capillary column.

RESULTS AND DISCUSSION

1. Temperature Programmed Reduction (TPR)

The TPR profiles from three different catalysts are presented in Fig. 1. The TPR profile from Ni/Al₂O₃ catalyst is characterized by two broad peaks that indicate the presence of two different kinds of interaction between NiO and Al₂O₃. The peak observed at higher temperature (T_m=761°C) is identified as bulk species like NiAl₂O₄, whereas the more easily reducible phase observed at lower temperature (T_m=590°C) may be considered as Ni species interacting with alumina.

In addition, the peak at lower temperature indicates the existence of a surface phase with stoichiometry similar to NiAl₂O₄. This phase, however, is different from the one observed at higher temperature. Dufresne et al. [1981] reported that there were two different kinds of interaction between NiO and Al₂O₃, depending on the calcination temperature of the catalyst. For the Ni/Al₂O₃ catalyst, the maximum peak temperatures are observed at 590°C and 761°C, which are higher than the reduction temperature (220°C) of bulk NiO. This implies that there exists a strong metal-support interaction between Ni and

**Fig. 1. TPR profiles from various catalysts.**(a) NiMo/Al₂O₃ (r=0.3), (b) Mo/Al₂O₃ and (c) Ni/Al₂O₃.

alumina.

The TPR profile from Mo/Al₂O₃ shows three different peaks. The peak at the lowest temperature ($T_m=523^\circ\text{C}$) represents the partial reduction of well-dispersed polymolybdate, and the peak at the middle temperature ($T_m=630^\circ\text{C}$) is assigned to the further reduced polymolybdate, which exerts stronger interaction with alumina, whereas the peak at the highest temperature ($T_m=805^\circ\text{C}$) is thought to represent the continued reduction of polymolybdate plus reduction of the tetrahedrally coordinated molybdate group. From this result it is obvious that three different kinds of interactions exist between Mo and alumina.

Fig. 1 also shows the TPR profile from NiMo/Al₂O₃, which is similar in shape to that from Mo/Al₂O₃. Although Ni introduced into Mo/Al₂O₃ catalyst has no significant effect on the shape of the TPR pattern, the peak temperatures of TPR profile from NiMo/Al₂O₃ catalyst are all shifted toward the lower temperature ranges compared to those from Mo/Al₂O₃ catalyst. The change in the reducibility of Mo/Al₂O₃ with Ni addition is caused by the surface interaction between Ni and Mo, which was suggested by Dufresne et al. [1981]. This interaction is understood to give the formation of Ni-Mo-O phase that is the precursor of Ni-Mo-S phase known as the active site for HDN reaction.

Presented in Fig. 2 are the TPR profiles from the catalysts with different atomic ratios [Ni/(Ni+Mo)]. The TPR profile of Mo/Al₂O₃ ($r=0$) shows three different peaks as discussed in the above. The TPR spectra of NiMo/Al₂O₃ catalysts are similar in shape to that of Mo/Al₂O₃. However, the maximum peak temperatures of TPR spectra of NiMo/Al₂O₃ catalysts are influenced by the content of nickel. In particular, the reduction peak in the intermediate temperature range ($500\text{--}600^\circ\text{C}$) is closely related to the Ni content. The change in the reducibility of Mo with Ni content is due to the surface interaction between Ni and Mo. This chemical interaction between

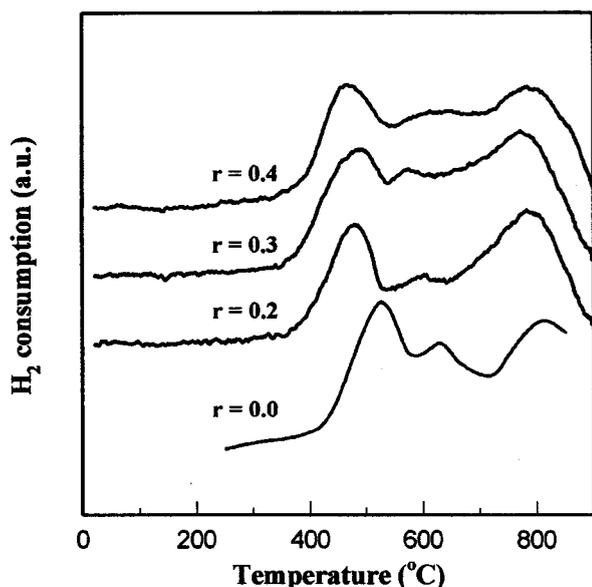


Fig. 2. TPR profiles from the oxidic NiMo/Al₂O₃ catalysts with various Ni contents.

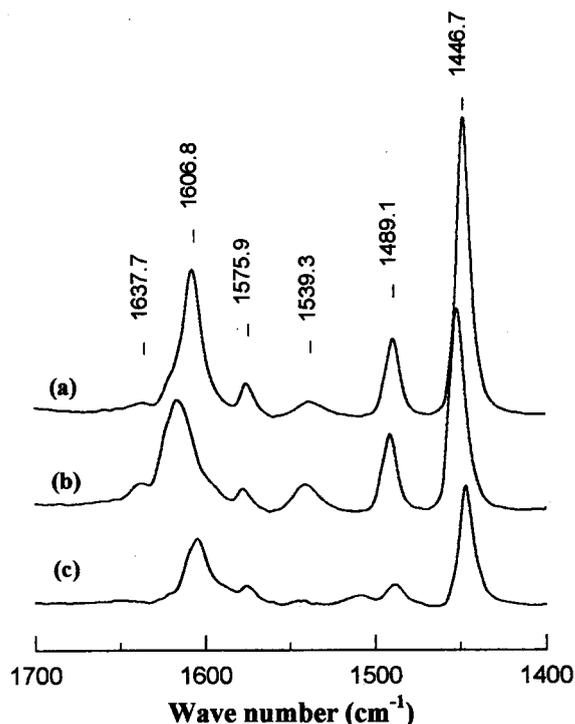


Fig. 3. Infrared spectra of pyridine chemisorbed catalysts of oxide state.

(a) NiMo/Al₂O₃ ($r=0.3$), (b) Mo/Al₂O₃ and (c) Ni/Al₂O₃.

Ni and Mo in the oxidic form of NiMo/Al₂O₃ has been suggested in previous work [Dufresne et al., 1981]. Therefore, it seems evident that the Ni-Mo-O phase formed by this interaction is the precursor of the Ni-Mo-S phase known as the HDN active site and that the reduction peak in the intermediate temperature range is related to the HDN activity.

2. Fourier Transform Infrared Spectroscopy (FT-IR)

The IR spectra of pyridine-adsorbed catalysts (Ni/Al₂O₃, Mo/Al₂O₃, and NiMo/Al₂O₃) of oxide states are shown in Fig. 3. The bands at 1446.7, 1575.9, and 1606.8 cm^{-1} indicate the Lewis acid sites, while the bands at 1539.3 and 1637.7 cm^{-1} represent the Brönsted acid sites. In the case of Ni/Al₂O₃ catalyst, the IR spectrum contains only those bands for the Lewis acid sites. When molybdenum is impregnated into alumina support, the bands for the Brönsted acid sites are distinctly found. When nickel is impregnated into Mo/Al₂O₃, it is clearly seen that the amount of Lewis acid sites increases while that of Brönsted acid sites decreases.

3. Electron Spin Resonance (ESR)

Since Mo³⁺ ions are paramagnetic, an ESR analysis can be employed to characterize the NiMo/Al₂O₃ catalyst. It is a highly sensitive probe for defect sites that are likely to be chemically active. The ESR spectra of the sulfided catalysts are shown in Fig. 4. Two different signals are identified from the ESR spectrum of Mo/Al₂O₃ catalyst. Signal I ($g=1.93$) can be assigned to oxo-Mo³⁺ interacting with alumina support, and signal III ($g=2.00$) to Mo species in sulfur environment; *i.e.*, bulk defects in MoS₂-like phase or Mo³⁺ ions connected with an anion vacancy site [Silbermagel et al., 1978; Thakur and Delmon, 1985; Derouane et al., 1986].

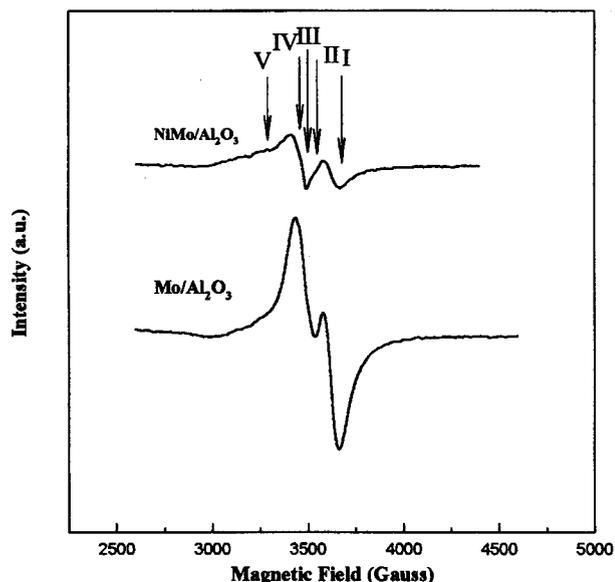


Fig. 4. ESR spectra of the sulfided $\text{Mo}/\text{Al}_2\text{O}_3$ and $\text{NiMo}/\text{Al}_2\text{O}_3$ ($r=0.3$) catalysts.

Introduction of nickel as promoter to $\text{Mo}/\text{Al}_2\text{O}_3$ leads to intensity changes. The intensity of signal I decreases while that of signal III increases more or less with the addition of nickel. This result suggests that the addition of nickel decreases the number of oxo- Mo^{5+} species interacting with alumina support and increases bulk defects in MoS_2 -like phase or Mo^{3+} ions connected with anion vacancies, which are directly related to the catalytic activity. In addition, comparison of ESR spectra between $\text{Mo}/\text{Al}_2\text{O}_3$ and $\text{NiMo}/\text{Al}_2\text{O}_3$ shows that signal II ($g=1.97$), signal IV ($g=2.02$) and signal V ($g=2.11$) are indeed new signals. Signal II and signal IV can be assigned to the surface Mo^{3+} or Mo^{5+} ions with different sulfur ligand symmetries, and signal V to the surface Mo species related to Ni ions [Konings et al., 1978, 1981]. But the intensities of these signals are very small.

4. Diffuse Reflectance Spectroscopy (DRS)

Fig. 5 shows the results of DRS measurement in the visible range for oxidic $\text{Ni}/\text{Al}_2\text{O}_3$, $\text{Mo}/\text{Al}_2\text{O}_3$, and $\text{NiMo}/\text{Al}_2\text{O}_3$ catalysts. For the $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst, three distinct bands appear at 430 nm, 590-630 nm, and 710-720 nm, respectively. According to Jocomo et al. [1971], the band at 430 nm represents octahedrally coordinated Ni^{2+} species and the band in the wavelength range of 590-630 nm corresponds to a Ni-spinel species. The band in the range of 710-720 nm is responsible for the tetrahedrally coordinated Ni^{2+} species.

The $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst shows a broad band in the wavelength range of 250-350 nm and this may be attributed to the presence of the Mo^{6+} species in tetrahedral and octahedral coordinations. Ramirez et al. [1991] and Moon et al. [1988] reported that the band in the lower wavelength range (260-280 nm) is responsible for the tetrahedrally coordinated Mo^{6+} species and the band in the higher wavelength range (300-340 nm) for the octahedrally coordinated Mo^{6+} species.

For the $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst, Mo band tends to shift and broaden toward the band of octahedrally coordinated Mo^{6+} species and a new band is observed at 450 nm besides those

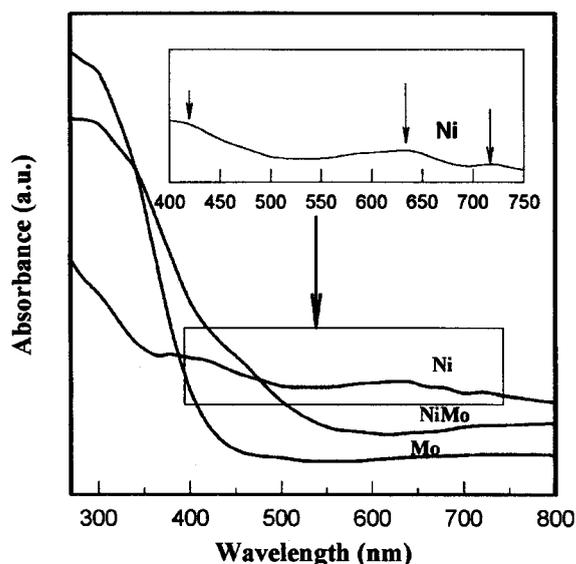


Fig. 5. DRS spectra of the oxidic $\text{Mo}/\text{Al}_2\text{O}_3$, $\text{Ni}/\text{Al}_2\text{O}_3$, and $\text{NiMo}/\text{Al}_2\text{O}_3$ ($r=0.3$) catalysts.

mentioned above. This band is different from the Ni bands of NiO , NiAl_2O_4 , and NiMoO_4 (720-800 nm). Therefore, the band at 450 nm represents Ni^{2+} species in the new phase which is dissimilar to NiO , NiAl_2O_4 , and NiMoO_4 phase. This implies that the new phase is formed by the interaction between Ni and Mo. Iannibello and Mitchell [1979] studied the DRS spectra of $\text{CoMo}/\text{Al}_2\text{O}_3$ to report that the effect of Co was to reduce the tetrahedral Mo^{6+} band and presumably to form Co-O-Mo bonds together with octahedrally coordinated Mo^{6+} species. Therefore, this phase may be related to the Ni-Mo-O phase, which is to be changed to Ni-Mo-S phase upon sulfidation [Ozkan et al., 1994].

5. Effect of Nickel on HDN Activity

Presented in Fig. 6 are the activities of $\text{Mo}/\text{Al}_2\text{O}_3$ and $\text{NiMo}/\text{Al}_2\text{O}_3$

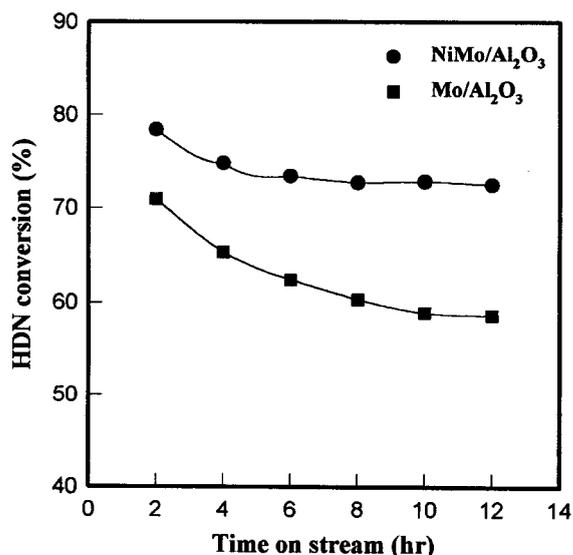


Fig. 6. Activities of sulfided $\text{Mo}/\text{Al}_2\text{O}_3$ and $\text{NiMo}/\text{Al}_2\text{O}_3$ ($r=0.3$) catalysts for the HDN of pyridine.

Al₂O₃ catalysts for the HDN of pyridine. According to Ledoux et al. [1984], piperidine denitrogenation requires only single Brönsted or Lewis acid site, whereas the pyridine hydrodenitrogenation needs at least one bifunctional site having the nature of both reduced site and acidic site. The reduced sites dissociate H₂ and perform the hydrogenation, while the acidic sites allow the removal of the nitrogen atom.

As shown in Fig. 6, the addition of nickel as a promoter enhances the catalytic activity for the HDN of pyridine. When molybdenum is impregnated into alumina, both acidic and reduced sites are formed. The acidic sites offer proton to pyridine, whereas the reduced sites facilitate the hydrogenation reaction. When a promoter is present in Mo/Al₂O₃ catalysts, it enhances the decomposition of H₂ and the migration of hydrogen to polymolybdates by spill-over. Ozkan et al. [1994] suggested the existence of two major types of active sites promoting HDN of pyridine over NiMo/Al₂O₃ catalyst. The active sites of type I are pyridine hydrogenation sites consisting of sulfur vacancies associated with Mo or Ni in Ni-Mo-S phase and those of type II are piperidine hydrogenolysis sites consisting of Brönsted acid sites associated with Mo atoms only. It is by virtue of this effect of Ni in Ni-Mo-S phase that the NiMo/Al₂O₃ catalyst showed higher activity for the HDN of pyridine than Mo/Al₂O₃ catalyst.

The role of Ni can be further elucidated from the results of the TPR and the DRS analyses. As can be seen in Fig. 1, the TPR result shows that nickel introduced enhances the reducibility of Mo/Al₂O₃ catalyst. This effect on the reducibility is caused by the interaction between nickel and molybdenum.

In addition, the DRS profile of NiMo/Al₂O₃ catalyst obtains a new band at 450 nm as shown in Fig. 5. This new band represents Ni²⁺ species located in the new phase formed by the interaction between Ni and Mo. Therefore, one may deduce that this species is related to the Ni-Mo-O phase known as the precursor of the Ni-Mo-S phase. The reducibility of Mo and the Ni in Ni-Mo-S phase are related to the hydrogenation

activity [Thomas et al., 1982, 1983; Ozkan et al., 1994]. Since hydrogenation plays a crucial role in HDN reaction, the HDN activity of NiMo/Al₂O₃ becomes higher than that of Mo/Al₂O₃ catalyst.

Fig. 7 presents the HDN conversion of pyridine as a function of the Ni content. The NiMo/Al₂O₃ catalyst with atomic ratio [Ni/(Ni+Mo)]=0.3 shows the maximum activity. According to Yang and Satterfield [1983], sulfided NiMo/Al₂O₃ catalyst contains two active sites: one is the sulfur vacancy site associated with the molybdenum atom that performs hydrogenation and the other is the acidic site that participates in the hydrogenolysis and ring opening reaction. It is understood that such an optimum content of Ni exists because of the formation of HDN active sites by addition of Ni.

On the other hand, it is observed from the TPR results of Fig. 2 and the HDN activity of Fig. 7 that the reduction peak in the intermediate temperature range (500-600 °C) is closely related to the catalytic activity. When the reduction peak in this temperature range appears at the lowest temperature, the catalyst obtains the highest activity. In other words, the lower the intermediate reduction temperature, the higher the hydrogenation activity and thus the HDN reaction progresses more readily.

CONCLUSIONS

The NiMo/Al₂O₃ catalyst obtains the highest activity for the HDN of pyridine with the atomic ratio [Ni/(Ni+Mo)] of 0.3. According to the TPR result and the HDN activity test, the reduction peak in the intermediate temperature range (500-600 °C) is closely related to the catalytic activity. Therefore, the lower the intermediate reduction temperature, the higher the HDN activity of pyridine. The interaction between Ni and Mo apparently gives rise to the formation of the Ni-Mo-O phase that is the precursor of the Ni-Mo-S phase known as the active site for the HDN reaction. Consequently, Ni added as a promoter to Mo/Al₂O₃ catalyst enhances the HDN activity by improving the reducibility of Mo and forming the Ni-Mo-O phase.

ACKNOWLEDGMENT

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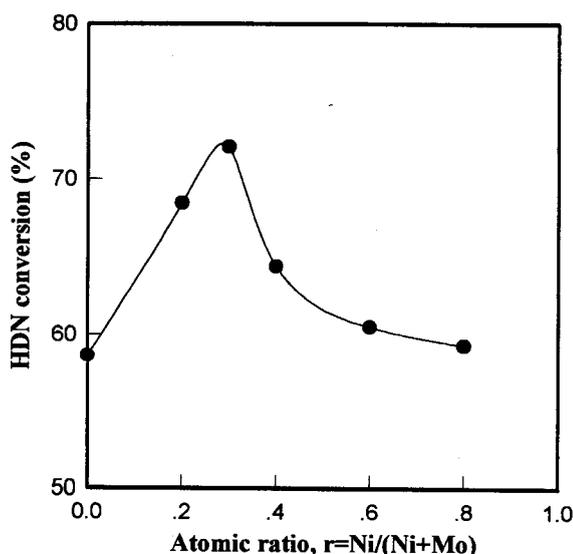


Fig. 7. Activity of sulfided NiMo/Al₂O₃ catalyst as a function of the Ni content for the HDN of pyridine.

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