

A STUDY OF HYDRODENITROGENATION OF PYRIDINE OVER MOLYBDENUM NITRIDE CATALYSTS AND THEIR CHARACTERIZATION

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Abstract—A series of molybdenum nitride (Mo_2N) catalysts were prepared by a topotactic synthesis method using a TPR (Temperature Programmed Reaction) at various conditions (temperature ramping rate, NH_3 gas flow rate, final preparation temperature). The surface property and acidity of Mo_2N catalysts prepared at various prepared conditions were studied by SEM, XRD, BET, FT-IR and TGA. The hydrodenitrogenation (HDN) of pyridine in *n*-heptane over Mo_2N catalyst (A1) was studied in a fixed bed continuous flow reactor (CATATEST) at the temperatures between 250–450°C, the pressure at $20\text{--}40 \times 10^5$ Pa and the contact time between 0.01–0.05 g cat.hr./ml feed. The microstructure of Mo_2N catalyst was not changed at various preparation conditions by topotactic reaction. The XRD and BET studies showed that the extent of the crystallinity and the surface area of the prepared Mo_2N catalysts increased when the final preparation temperature increased and the temperature ramping rate was lowered. In addition, from the TGA curve, the acid strength increased with the increase of the NH_3 gas flow rate. The results of pyridine hydrodenitrogenation (HDN) over Mo_2N catalyst showed that the catalytic activity (conversion %) increased as reaction temperature, reaction pressure, and contact time increases. The selectivity for piperidine possessed a maximum at 350°C regardless of the reaction pressure. Also, the selectivity for cracked products increased as reaction temperature and pressure increased. The activation energy was determined 7.16 kcal/mol by Arrhenius plot.

Key words: Molybdenum Nitride, Hydrodenitrogenation, Topotactic Reaction, Characterization

INTRODUCTION

The crude oil contains significant amounts of sulfur and nitrogen compounds. Therefore, they should be removed by hydrotreating processes to prevent poisoning of precious metal catalysts used in the conversion process such as hydrocracking and reforming reaction, also, to control the air pollution by SO_x and NO_x produced in the process of the combustion of petroleum-based fuels. The industrial importance of hydrotreating catalysts has led to a large number of studies relating to their specific surface properties [Arnolydy et al., 1985; Declerck-Grimee et al., 1978; Okamoto et al., 1989; Payen et al., 1989] and catalysis [Aubert et al., 1986; Cowley et al., 1978; Hargreaves et al., 1979; Kwart et al., 1982; Massoth et al., 1977; Nagai et al., 1983; Satterfield et al., 1975; Yang et al., 1983]. The commercial hydrotreating catalysts, such as Co- or Ni-promoted Mo and W catalysts, are usually supported on the $\gamma\text{-Al}_2\text{O}_3$ due to the low specific surface area and thermal stability of the catalytically active phase. Recently, high surface area molybdenum nitride (Mo_2N) catalysts have been developed by several research groups using a method called topotactic synthesis [Hargreaves et al., 1979; Levy, 1977; Ranhotra et al., 1987; Volpe et al., 1985]. It is well established that the Mo_2N catalysts are resistant to poisoning caused by S and N compounds and sintering even at 717°C [Volpe et al., 1985].

However, relatively few investigation have been devoted to the effect of the preparation variables on surface property of Mo_2N catalysts [Ranhotra et al., 1987]. The nitrogen compounds in crude oil are amines, anilines, nitriles and hetero-cyclic com-

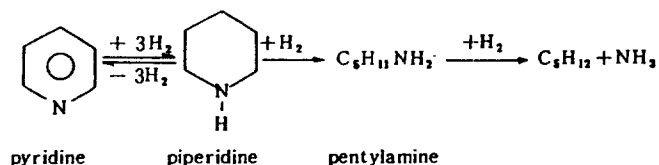


Fig. 1. Mechanism of HDN of pyridine.

pounds. The reactivity of hetero-cyclic compound is very low. Therefore, we select pyridine as a reactant in this study. Mechanism of HDN of pyridine is suggested by Gupta et al. [Gupta et al., 1978; LePage et al., 1978; McIvried, 1971] (see Fig. 1). The objectives of this study are: (1) to elucidate the influence of the preparation variables (temperature ramping rate, NH_3 gas flow rate, final preparation temperature) on the surface property and acidity of the prepared Mo_2N catalysts, (2) the effect of the reaction conditions (temperature, pressure, contact time) on the catalytic activity and selectivity of pyridine HDN over Mo_2N catalyst.

EXPERIMENTAL

1. Catalyst Preparation

The Mo_2N catalysts were prepared by a topotactic synthesis method using a TPR (Temperature Programmed Reaction) [Lee et al., 1987; Levy, 1977; Ranhotra et al., 1987; Volpe et al., 1985]. The materials used in this investigation were parent MoO_3 (Yakuri Chemical Co, 99.5% purity) and high purity NH_3 gas (Matheson Company, 99.97% purity). The detailed procedure of catalyst pre-

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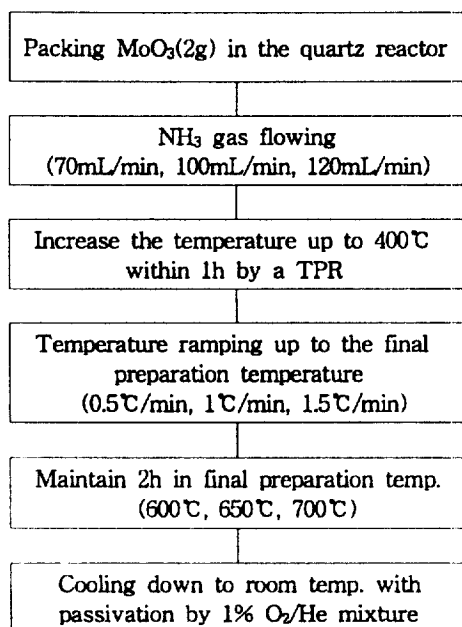


Fig. 2. Procedure of catalyst preparation.

Table 1. Notation of catalysts

Catalyst	NH ₃ gas flow rate (mL/min)	Ramping rate (°C/min)	Final temp. (°C)
A1	120	0.5	700
A2	120	1.0	700
A3	120	1.5	700
B1	100	0.5	700
B2	100	1.0	700
B3	100	1.5	700
C1	120	1.0	600
C2	120	1.0	650
C3	70	1.0	700

paration by a topotactic synthesis method at different preparation conditions is shown in Fig. 2. Two grams of parent MoO₃ were packed in the quartz reactor and purged by NH₃ gas. Then the temperature was increased up to 400°C within 1 hour by a TPR. When desired final preparation temperature was reached, the system was maintained for 2 hours and was cooled down to room temperature with passivation by 1% O₂/He mixture. The notation of Mo₂N catalysts prepared at various preparation conditions were listed in Table 1.

2. Characterization of Mo₂N Catalysts

Microstructure of parent MoO₃ and Mo₂N catalysts were observed by a scanning electron microscopy (SEM: Hitachi, H-601). X-ray powder diffraction (XRD) patterns of Mo₂N catalysts prepared at different conditions were obtained on a diffractometer (D/MAX-IIA, Rigaku, target: CuKα, 2θ=20°-100°). The surface area of catalysts was measured by a BET method (Micromeritics, ASAP 2200). The acidity was measured by a TGA (Shimadzu, TGA-50). The kinds of acid sites were found by a FT-IR (IFS88, Bruker) after Mo₂N catalysts were adsorbed by pyridine, and the IR bands of adsorbed pyridine are shown in Table 2 [Forni, 1974].

3. Catalytic Reactions

Pyridine HDN over Mo₂N catalyst (A1) was carried out at var-

Table 2. IR bands of adsorbed pyridine

Hydrogen-bonded pyridine	Coordinately-bonded pyridine	Pyridinium ion
1440-1447 (vs)	1447-1460 (vs)	1485-1500 (vs)
1485-1490 (vs)	1488-1503 (vs)	1540 (s)
1580-1600 (s)	1580 (v)	1620 (s)
	1600-1633 (s)	1640 (s)

"vs: very strong; s: strong; w: weak; v: variable.

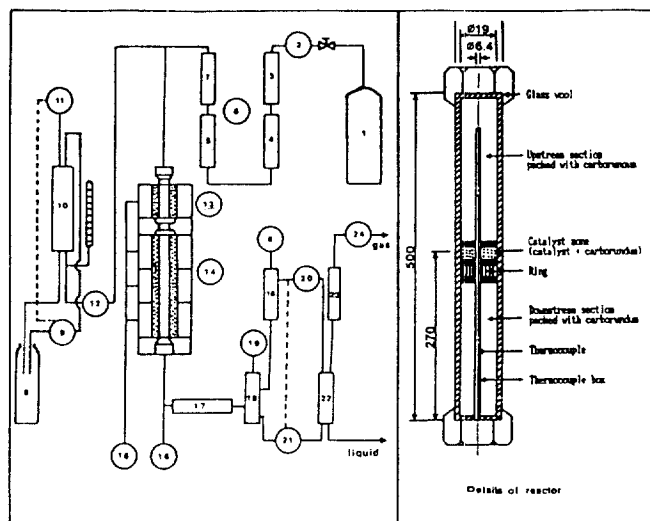


Fig. 3. Schematic diagram of experimental apparatus and details of reactor.

1. H₂ gas tank
2. Pressure regulator
3. Deoxo unit
4. Drying column
5. Gas mass flowmeter
6. Pressure gauges
7. Capillary tube
8. Supply tank
9. Supply pump
10. Feed tank
11. Feed tank level controller
12. Metering pump
13. Preheater
14. Stainless steel reactor
15. Temperature regulator
16. Temperature recorder
17. Condenser
18. H.P. separator
19. H.P. sep. level controller
20. Back pressure regulator
21. Level control electrovalve
22. L.P. separator
23. Gas sampler
24. Wet gas meter

ious reaction conditions using a continuous fixed-bed flow reactor (Geomecanique Cata-test, LPD model C). The reactant, which was simulated to be a similar mole ratio of pyridine in real residue, was prepared by dissolving 3 mol% of pyridine (Junsei Chemical Co., 99.9% purity) in n-heptane. The reactor (vertical position) made of 19 mm-I.D. stainless tube, and a mixture of catalyst and carborundum (SiC, 1/5 as weight base) was held between the layers of quartz wool. Prior to the reaction, the catalyst was stabilized for 24 hours and treated with standard conditions (reaction temperature 350°C, reaction pressure 30×10⁵ Pa, and the contact time 0.03 g cat.hr./ml feed). During the first step of reaction, the deactivation of catalyst occurred quickly and after 24 hours the conversion was stabilized. The mixture gas (H₂/pyridine = 200 mole ratio) flowed from top to bottom of the reactor. The pyridine HDN was carried out at different reaction temperatures (250-350°C), reaction pressures (20×10⁵-40×10⁵ Pa), and contact times (0.01-0.05 g cat.hr./ml feed). The schematic diagram of experimen-

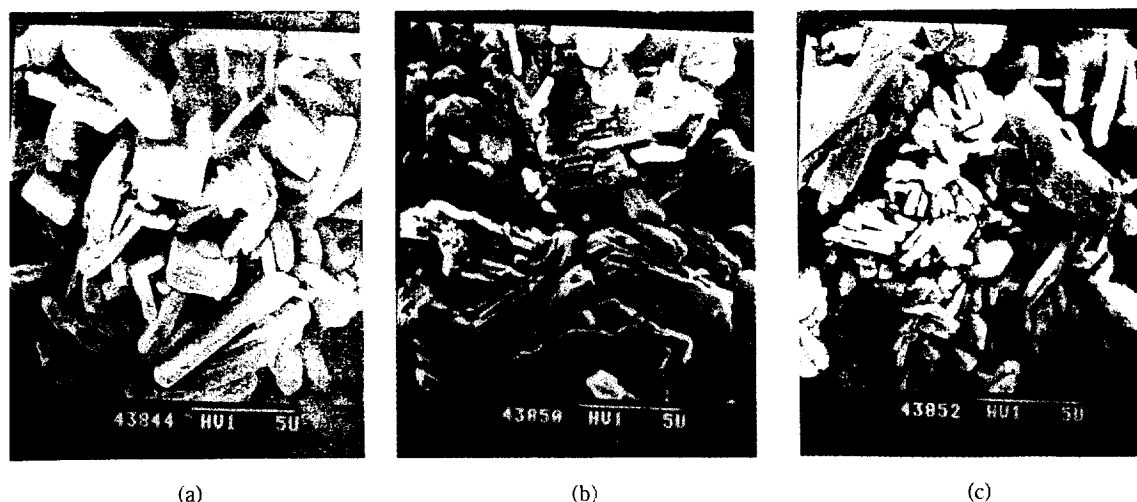


Fig. 4. SEM photographs of catalysts.

(a) MoO_3 , (b) Mo_2N , Al, (c) Mo_2N , A3

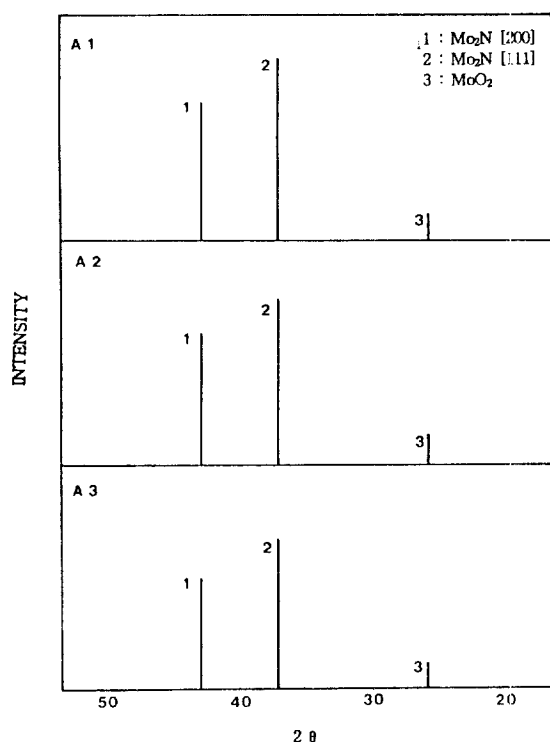


Fig. 5. XRD patterns of catalysts prepared at various temperature ramping rate.

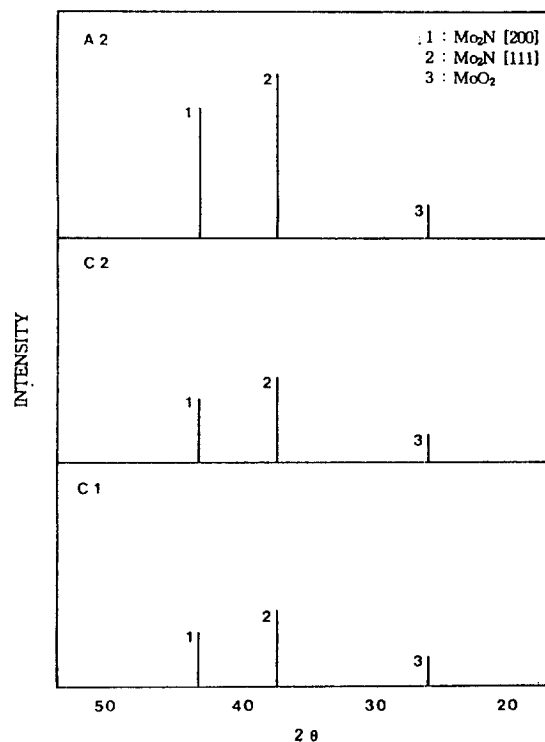


Fig. 6. XRD patterns of catalysts prepared at various final preparation temperature.

reactor apparatus and details of reactor are shown in Fig. 3. The reaction products were analyzed by an on-line gas chromatograph (Youngin Scientific Co. Ltd., M680A) analysing the contents in the column (Chromosorb W treated with 10% Carbowax 1000 and 1% NaOH) with a FID detector.

RESULTS AND DISCUSSION

1. Characterization of Mo_2N Catalysts

The SEM studies of Mo_2N catalysts provides further information about surface morphology of Mo_2N catalysts and the results

are presented in Fig. 4. The precursor (MoO_3), possesses a large orthorhombic structure of crystalline MoO_3 (Fig. 4a). The prepared Mo_2N catalysts (see Fig. 4b-c) possess a similar shape to that of MoO_3 precursor. This result supports our conclusion that the prepared Mo_2N catalysts possess topotactic Mo_2N particles.

XRD patterns of Mo_2N catalysts prepared at different preparation conditions are shown in Fig. 5-6. XRD patterns of Mo_2N catalysts produce only the peaks attributed to the typical crystalline Mo_2N compounds at $2\theta = 37^\circ$ and 43.2° for [111] and [200] planes, respectively [Markel et al., 1990]. Markel et al. reports that low temperature ramping rate produces topotactic Mo_2N particles

Table 3. BET data of various catalysts

Catalyst	NH ₃ gas flow rate (mL/min)	Ramping rate (°C/min)	Final preparation temperature (°C)	Surface area (m ² /g)
A1	120	0.5	700	67.0
A2	120	1.0	700	62.1
B2	100	1.0	700	52.5
C1	120	1.0	600	34.7
C3	70	1.0	700	46.4

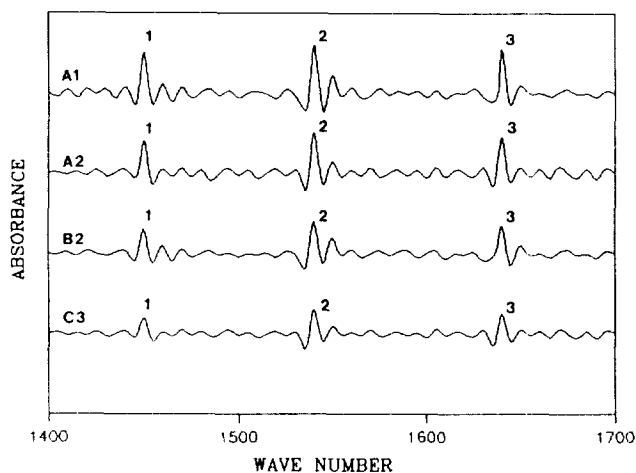


Fig. 7. FT-IR spectra of pyridine adsorbed catalysts.

- 1: 1450 cm⁻¹ (Lewis site, vs)
- 2: 1540 cm⁻¹ (Brönsted site, s)
- 3: 1630 cm⁻¹ (Lewis site, s)

with high surface area. They also suggested that the topotactic Mo₂N particles are not spherical so that the dimensions of the diffracting domains perpendicular to the [111] plane are slightly larger than those of perpendicular to the [200] plane [Markel et al., 1990]. The Mo₂N catalysts possess a sharp peak for [111] plane than that of [200] plane (see Fig. 5-6). Therefore, the prepared Mo₂N catalysts used in this investigation possess topotactic Mo₂N particles. Also it is worth noting that the final preparation temperature exerts a strong influence on the degree of the crystallinity and increases as a function of final preparation temperature.

The surface areas of Mo₂N catalysts prepared at different preparation conditions are summarized in Table 3. The surface areas of Mo₂N catalysts are influenced by the temperature ramping rate, NH₃ flow rate, and final preparation temperature. They increase as functions of final preparation temperature and NH₃ flow rate and also an inverse function of temperature ramping rate. It was found that the prepared Mo₂N catalysts have relatively higher surface area (34-67 m²/g) compared to the parent MoO₃ (precursor, ~0.6 m²/g). The generation of higher surface area for Mo₂N catalysts is attributed to the preferential beginning of the metal reduction at very small linear domains parallel to [120] plane of MoO₃ [Lee et al., 1988; Volpe et al., 1985]. In addition, Markel et al. suggested, when the metal lattice contracts and fractures, the crystal pores are produced during the reduction by NH₃, proceeds in these zones [Markel et al., 1990]. The catalyst A1 (see Table 1) possesses the highest surface area (67 m²/g). This is

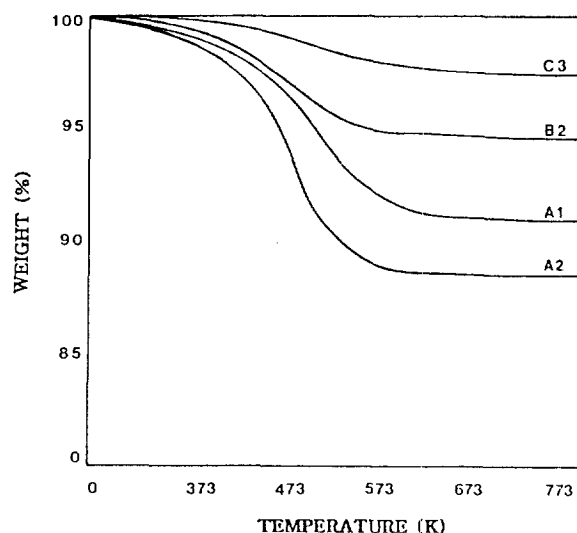


Fig. 8. TGA curves of pyridine desorption.

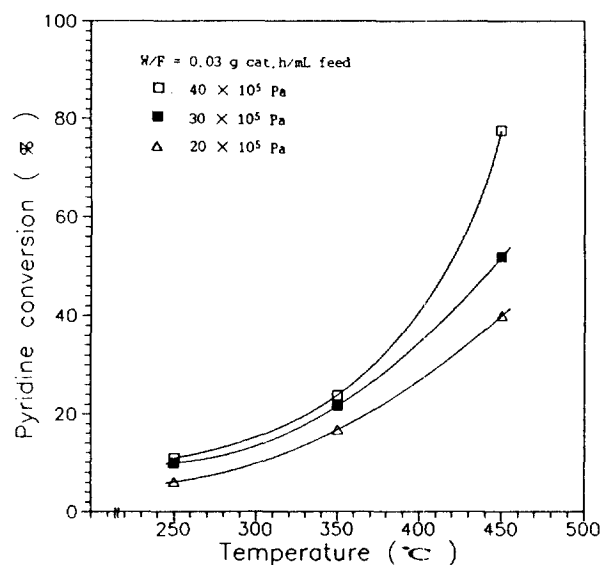


Fig. 9. Effect of temperature on the conversion of pyridine.

attributed to the increase in diffusion of NH₃ gas into the particle at this preparation conditions. The FT-IR peaks are shown in Fig. 7. The IR bands of adsorbed pyridine were observed at 1450 cm⁻¹ (Lewis acid, vs), 1540 cm⁻¹ (Brönsted acid, s) and 1630 cm⁻¹ (Lewis acid, s). From this result, more Lewis acid sites relative to Brönsted acid sites existed in Mo₂N catalyst. The TGA curves of pyridine desorption are shown in Fig. 8. The acid strength depends on the NH₃ gas flow rate rather than ramping rate or final preparation temperature. The acidity increased with the increase of the NH₃ gas flow rate.

2. Catalytic Reactions

The catalytic activities for pyridine HDN over Mo₂N catalyst at different reaction temperatures, pressures, and contact times are shown in Fig. 9-13. In order to determine the influence of packing material (SiC) on the catalytic activity, the blank test of the SiC was performed at standard conditions. It was found that the catalytic activity (<0.2% conversion) caused by SiC itself is minimal compared to the Mo₂N catalyst (>20% conversion) used

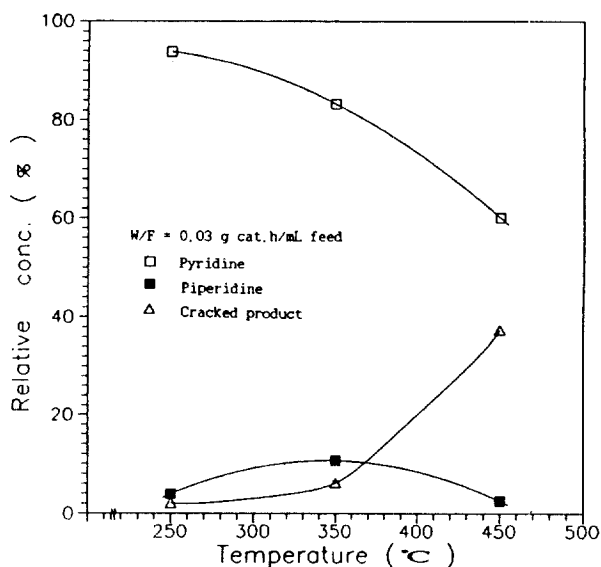
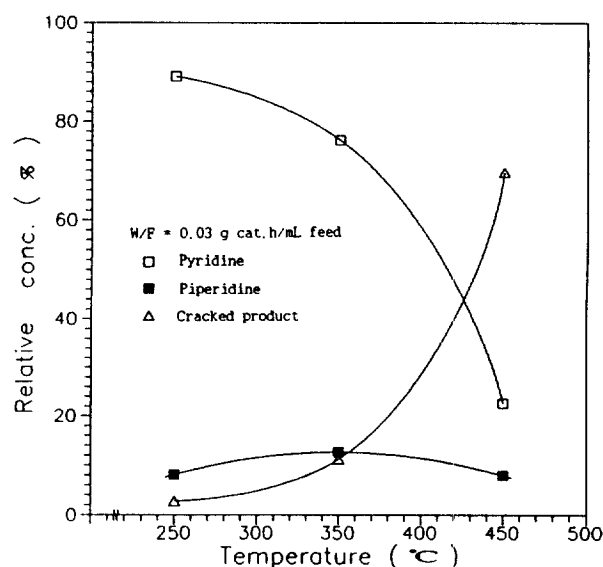
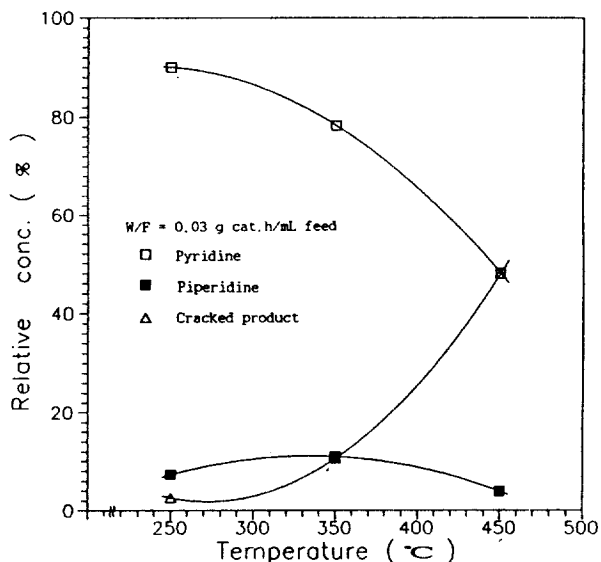
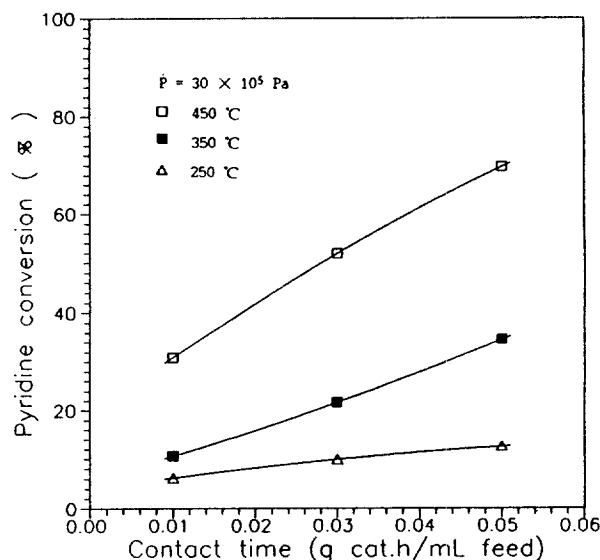
Fig. 10. Product distribution at 20×10^5 Pa.Fig. 12. Product distribution at 40×10^5 pa.Fig. 11. Product distribution at 30×10^5 Pa.

Fig. 13. Effect of contact time on the conversion of pyridine.

in this study. The catalytic activity of pyridine HDN over Mo_2N catalysts is dependent on the reaction temperature and pressure. The catalytic activity slightly increased up to 350°C while it increases drastically above 350°C at given pressures (see Fig. 9). In addition, the reactivity for pyridine HDN over Mo_2N catalysts also increased when increasing the reaction pressure at given reaction temperatures. The product distribution for pyridine HDN over the Mo_2N catalyst are shown in Fig. 10-12. The main reaction products are piperidine and cracked products such as pentylamine and pentane. The selectivity for piperidine rose slightly when increased up to 350°C and then decreased in reaction temperature regardless of the reaction pressure (see Fig. 10-12). On the other hand, the selectivity for cracked products increased slightly up to 350°C but then drastically increased with reaction temperature independent of the reaction pressure (see Fig. 10-12). The obtained results suggest that reaction temperature as well as reaction pressure control the catalytic activity for pyridine HDN over Mo_2N

N catalysts. The observation of high selectivity for cracked products above 350°C is attributed to the facilitation of hydrogenolysis and thermal cracking of pyridine at this high reaction temperature and pressure used in this experiment. The effect of contact time on the catalytic activity for pyridine HDN over Mo_2N catalyst at 30×10^5 Pa is shown in Fig. 13. The catalytic activity for pyridine at 250°C increases slightly as contact time increase. Above 350°C the catalytic activity increases drastically when increasing the contact time. The values of $\ln(1-X)^{-1}$ were plotted to the contact time, and by the result of Arrhenius plot (see Fig. 14) at the temperatures of 250, 350 and 450°C . Its activation energy was determined 7.16 kcal/mol.

CONCLUSION

The Mo_2N catalysts can be obtained by a topotactic synthesis method using a TPR. It was found that the preparation variables

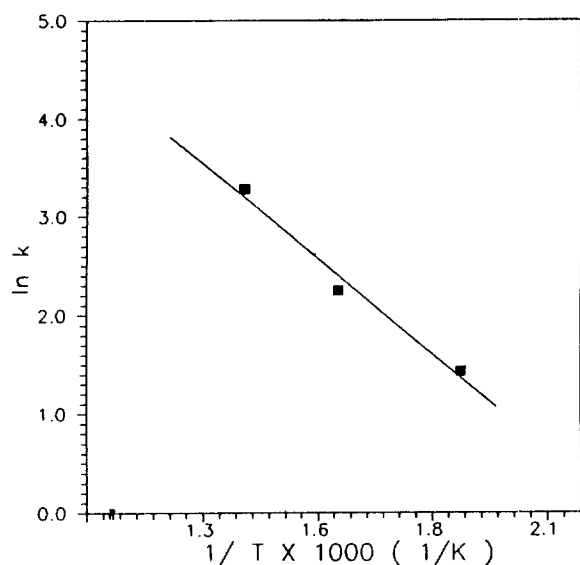


Fig. 14. Arrhenius plot.

exert an influence on the surface property of prepared Mo₂N catalysts. The BET study showed that the specific surface area of prepared Mo₂N catalysts increased at low temperature ramping rate, high flow rate of NH₃ gas and high final preparation temperature. In addition, the extent of the crystallinity of prepared Mo₂N catalysts increased when the final preparation temperature increased and the temperature ramping rate was lowered. The microstructure of Mo₂N catalyst was not changed at various preparation conditions by topotactic reaction. From the FT-IR peaks, relatively more Lewis acid sites existed in Mo₂N catalyst, and the TGA curves showed that the acid strength increased with the increase of the NH₃ gas flow rate. The results of pyridine HDN over Mo₂N catalyst showed that the catalytic activity (conversion %) increased as reaction temperature, pressure, and contact time increased. The selectivity for piperidine possessed a maximum at 350°C regardless of the reaction pressure. Also, the selectivity for cracked products increased as reaction temperature and pressure increased. The activation energy was determined 7.16 kcal/mol by Arrhenius plot.

ACKNOWLEDGEMENT

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NOMENCLATURE

MoO₃ : molybdenum trioxide
 Mo₂N : molybdenum nitride
 C_p : heat capacity [cal/mol K]
 ΔG : change of Gibbs free energy [Kcal/mol]
 ΔH : change of enthalpy [Kcal/mol]
 F : flow rate of feed [mL/hr]
 K : equilibrium constant
 k : rate constant [mol/g cat. h]
 n : reaction order of partial pressure of hydrogen
 P : total pressure [Pa]
 P_{pyr} : partial pressure of pyridine [Pa]
 P_{pyr,0} : initial partial pressure of pyridine [Pa]
 r : reaction rate [mol/g cat. h]

T : temperature [K, °C]
 W : catalyst weight [g]
 X : conversion [%]
 W/F : contact time [g cat. hr./mL feed]

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