

A STUDY OF HYDRODENITROGENATION OF PYRIDINE CATALYZED BY SULFIDED Ni-Mo/ γ -Al₂O₃

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(Received 9 September 1986 • accepted 26 January 1987)

Abstract— The hydropyrolysis of fuels containing relatively large amounts of organonitrogen compounds becomes increasingly important in the upgrading of hydrocarbon fuels. Therefore, to investigate the removal of organonitrogen compounds, the hydronitrogenation of pyridine dissolved in n-heptane was studied over sulfided Ni-Mo/γ-Al₂O₃ catalysts in the range of temperature between 513 K and 633 K and pressure between 30 bar and 50 bar in a fixed bed flow reactor. Pyridine conversion increased with the increased temperature and pressure, and the piperidine formation was found to be irreversible. Pyridine concentration reached a maximum at about 573 K and the apparent reaction order was found to be one with respect to pyridine.

INTRODUCTION

Liquid fuels derived from unconventional sources such as oil shale and coal contain significant amounts of organic nitrogen compounds as well as organic sulfur compounds being commonly found in most petroleum crudes. The concentrations of both groups of compounds must be greatly reduced to meet air pollution standards and to prevent catalyst poisoning in subsequent refining processes.

Much work has been performed on the hydrogenolysis of sulfur compounds like thiophene in order to study the mechanism of the desulfurization process. However, only a little work has been published about hydrogenolysis of pyridine and the mechanism of hydronitrogenation process. Most hydronitrogenation studies are carried out to study either the overall kinetics of the process or the difference in the rate of nitrogen removal of several types of nitrogen bases [1-4]. Some authors investigated the hydronitrogenation process with the aid of model compounds like quinoline or pyridine and with catalysts like Co-Mo-Al₂O₃ catalyst.

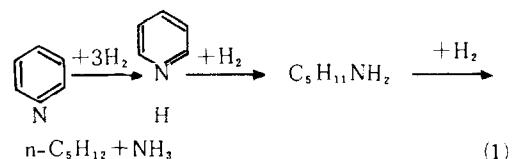
In this study, with pyridine as a nitrogen compounds and Ni-Mo-Al₂O₃ as a catalyst, experiments were performed using a fixed bed flow reactor. The experimental results are presented in this paper together with a literature survey.

BACKGROUND LITERATURE

Reaction networks

Literature on the mechanism of pyridine hydronitrogenation is reviewed by Goudriaan [5] and by Satterfield and Cocchetto [6] and that of other heterocyclic nitrogen compounds by Cocchetto and Satterfield [7].

The hydronitrogenation mechanism of pyridine proposed by McIlvried [8] begins with the saturation of pyridine to piperidine. The hydrogenolysis of the saturated ring to n-pentylamine is followed by the subsequent hydrogenolysis of the alkyl amine to n-pentane and ammonia.



Goudriaan [5] reported that n-pentylpiperidine was the principal intermediate product from piperidine at a pressure of about 8 MPa on a Co-Mo catalyst pre-reduced but in the absence of sulfur compounds. The formation of n-pentylpiperidine over pentylamine seemed to be favored by higher partial pressures of pyridine.

Reaction kinetics

The kinetics of pyridine hydrogenation was studied at high hydrogen pressures on a Mo-Al₂O₃ and also on a Co-Mo-Al₂O₃ catalyst by J. Sonnemans [9]. The rate equation was found to be

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$r = \frac{KP_Y P_H^n}{P_Y}$ in which n is 1.5 at 573 K and 648 K but 1.0 at 523 K. This rate equation can be derived under the assumption of strong adsorption of pyridine and its products with identical adsorption constants. Anabtawi, J.A. et al. [10] found that the saturation step of pyridine was irreversible and the rate equation could be described as follows:

$$r = -\frac{dP_Y}{dt} = KP_Y P_H \quad (2)$$

Equilibrium limitation

Equilibrium between pyridine and piperidine, the first product formed in the overall series of hydrodenitrogenation reaction of pyridine, can be a rate-limiting factor under some conditions. This equilibrium can affect the overall rate of reaction if hydrogenolysis step of the C-N bond is slower than hydrogenation step and if conditions are such that the equilibrium concentration of piperidine is severely limited. The rate of hydrogenolysis of the C-N bond is then less than it would be if there were no significant thermodynamic limitation on the concentration of piperidine. However, if hydrogenation was rate limiting, piperidine would react as it forms and the position of the ring saturation equilibrium would not influence the overall hydrodenitrogenation rate.

Equilibrium towards piperidine becomes less favorable at higher temperatures and lower hydrogen pressures. Under the reaction conditions of McIlvried [8] hydrogenation was rapid and hydrogenolysis was rate-limiting.

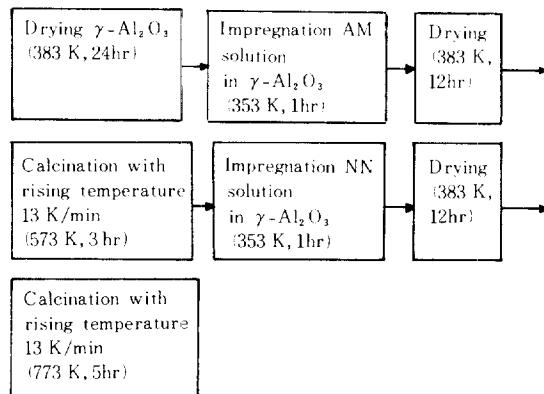
Stengler et al. [11], as reported by Goudriaan [5], stated that on a Ni-W-Al₂O₃ catalyst hydrogenolysis was rate-limiting below 623 K. In a very recent study on Co-Mo-Al₂O₃ catalyst, Goudriaan [5] concluded that the equilibrium may begin to limit the overall rate of reaction at temperatures higher than 623 K and Sonnemans and co-Workers [9, 12] discuss its implications for the mechanism of pyridine. In an independent study, Satterfield [13] found unexpectedly that the conversion of pyridine over some catalysts dropped with an increase in temperature about 673 K. This effect has not been previously reported in hydrodenitrogenation and it can be interpreted in terms of the development of an unfavorable equilibrium for the initial saturation step at higher temperature.

EXPERIMENTAL

Catalyst preparation

The catalyst was prepared via impregnation of γ -alumina with aqueous nickel nitrate [NN, Ni(NO₃)₂·6H₂O] and ammonium molybdate [AM, (NH₄)₆Mo₇O₂₄·

4H₂O]. The support was a γ -alumina, 0.16 cm³/g pellet type; 212 m²/g; containing by weight 96.65% Al₂O₃, 2.3% SiO₂, 0.26% Na and 0.28% Ca. After impregnation, the catalyst was air-dried for 12 hr at 383 K and then calcined in air for 3 hr-5 hr at 573-773 K.



The properties of prepared catalyst are given in Table 1.

Apparatus

LPD CATALYST UNIT (Model C, IFP License) was used. A schematic diagram of experimental apparatus is shown in Fig. 1. The reactor is a fixed bed flow reactor equipped with thermocouple. The catalyst was mixed with carborundum, an inert reactor packing material, by the weight ratio of 5:1 of inert material to catalyst.

Experimental procedure

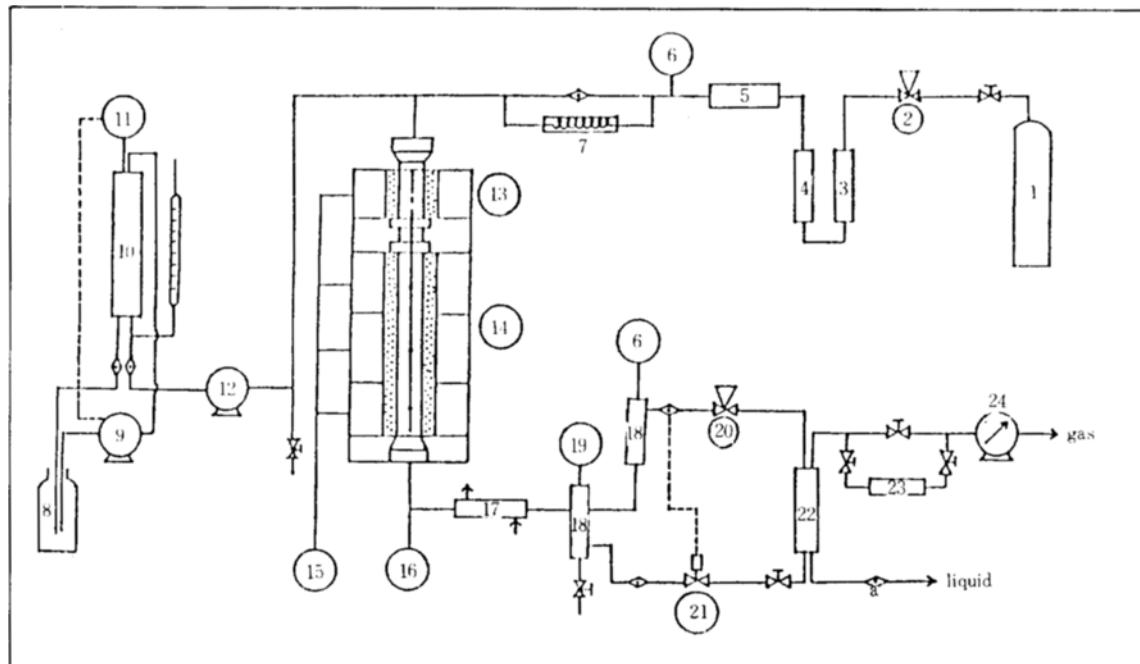
The catalyst was presulfided in situ for 5 hr with the flow rate of 12 l/hr of 10 vol % H₂S in H₂ at atmospheric pressure and 653 K. Pyridine was dissolved in n-heptane and the solution was used without further purification. The experiments were carried out at temperature of 513 to 633 K, pressure of 30 to 50 bar, and W/F of 0.03 to 0.05 gcat.hr/gmole of feed. The mole ratio of hydrogen to pyridine was fixed at 400.

Analysis

The products were analyzed on Shimadzu GC-7A gas chromatograph equipped with a flame ionization

Table 1. Physical properties of catalyst prepared.

Items	γ -Al ₂ O ₃	Ni-Mo/ γ -Al ₂ O ₃
NiO (wt %)	—	3.5
MoO ₃ (wt %)	—	16.5
Surface area (m ² /g)	211.83	158
Pore volume (mL/g)	0.8917	0.6570
Bulk density (g/mL)	0.71	0.79
Apparent density (g/mL)	1.49	1.54
Porosity	0.57	0.50



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

Fig. 1. Schematic diagram of experimental apparatus.

detector using a 3.5 m, 3 mmID column packed with 1% NaOH or 10% Carbowax 1000 on chromosorb W. Gas products were not detected.

RESULT AND DISCUSSION

Blank run

Blank runs with carborandum and no catalyst in the reactor under more severe conditions gave conversions of pyridine less than 0.05% and conversions of n-heptane less than 1%. This result indicates that there is no significant effect of both the reactor material and carborandum.

Mass and heat transfer effect

Preliminary experiments were done to ensure negligible effect of external mass transfer on conversions; that is, changing the catalyst loading from 1.5 g to 3 g led to no change in the conversion of pyridine. And the effect of internal mass transfer is also found negligible by testing on the catalyst particle size from 30 to 100 mesh. Heat transfer effects were found to be negligible through suitable calculation suggested by Broderick

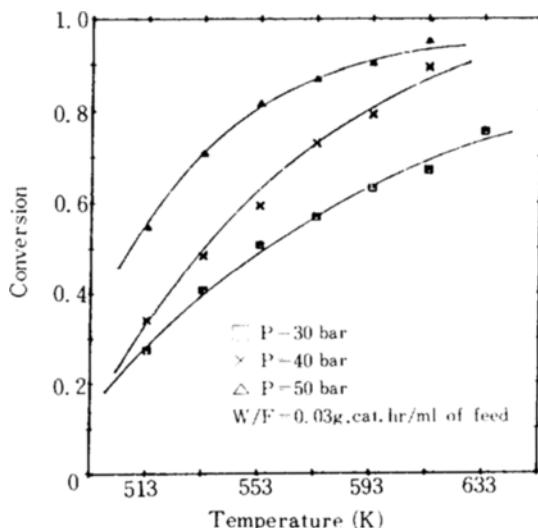


Fig. 2. Effects of the reaction temperature and the total pressure on the conversion.

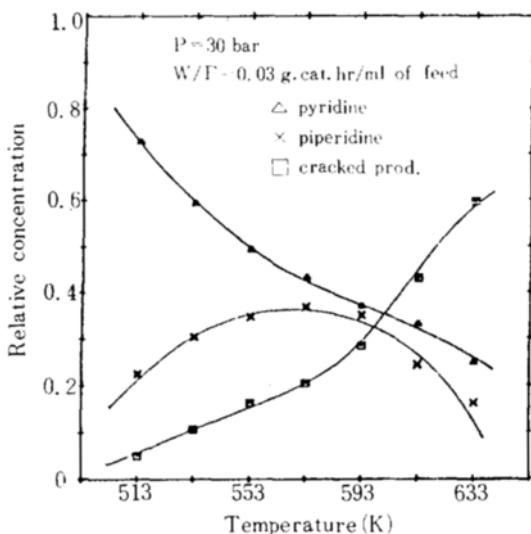


Fig. 3. Relative concentration of pyridine and products at various temperatures.

[14].

Effect of the reaction pressure and temperatures

The results of experiments conducted at three different reaction pressures, of 30 bar, 40 bar and 50 bar, are shown in Fig. 2. This demonstrates that increase in the reaction temperature increased the conversion of pyridine. This result shows that the reaction of pyridine to piperidine is irreversible.

The increased reaction pressure increased the conversion of pyridine. In this test most of pyridine was converted at 613 K and 50 bar.

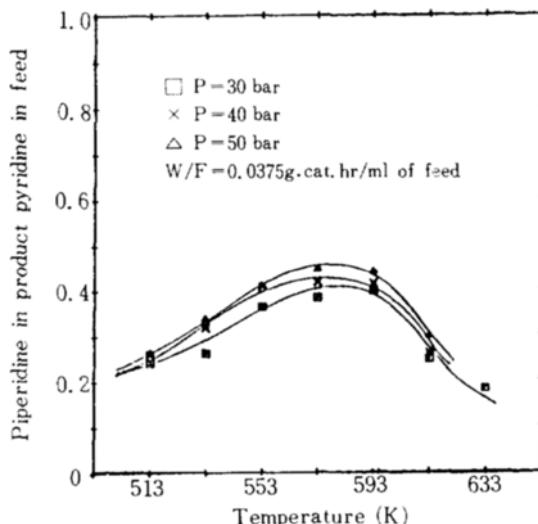


Fig. 4. Piperidine formed from pyridine.

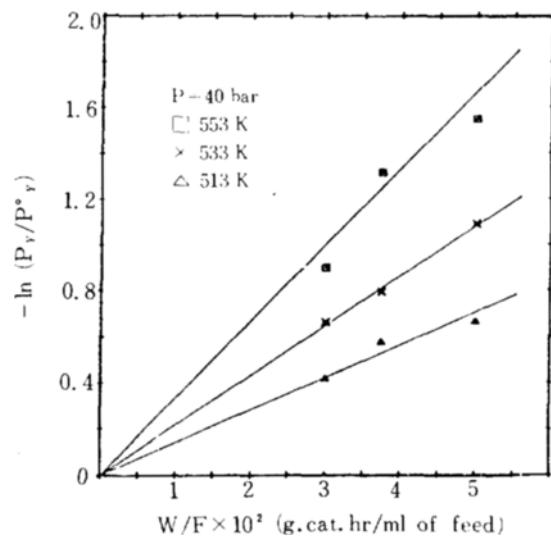


Fig. 5. Plot to test for reaction order.

Product distribution

Figure 3 shows relative concentration profiles for pyridine, piperidine and cracked products as a function of the reaction temperature at a total pressure of 30 bar. Up to approximately 573 K the relative concentration of piperidine was two fold of that of cracked products and above 603 K the concentration of cracked products was increased rapidly.

Meanwhile, the normalized concentration of piperidine is shown in Fig. 4. The concentration reached a

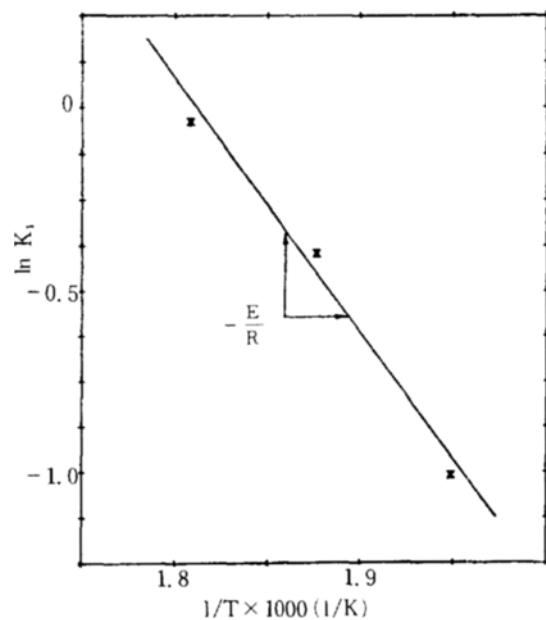
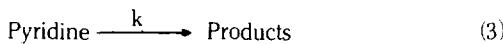


Fig. 6. Arrhenius plot for the rate constant.

maximum at approximately 573K at each reaction pressure. The maximum value increased as the reaction pressure became higher.

Reaction order and activation energy

The reaction order with respect to pyridine was determined by changing the reaction time and the initial pyridine partial pressure. Assuming an apparent first order reaction with respect to pyridine, the reaction rate is expressed as follows:



$$r = -\frac{dP_Y}{dt} = K P_Y P_H \quad (4)$$

Since P_H remains constant, intergration of this equation gives:

$$-\ln \frac{P_Y}{P_Y^0} = K P_H t \quad (5)$$

In Fig.5. the experimental results have been plotted as $-\ln (P_Y/P_Y^0)$ versus t ($= W/F$).

From this result, we find that the reaction order is one with respect to pyridine. From the Arrhenius plot as shown in Fig. 6 the activation energy was calculated to give 13.75 Kcal/gmole.

CONCLUSION

1. The conversion of pyridine increased with increasing temperature and pressure. The conversion of pyridine to piperidine was found to be an irreversible process.
2. Piperidine concentration reached a maximum at approximately 573K at each reaction pressure and increase in the reaction pressure increased the maximum amount formed.
3. The apparent reaction order was found to be one with respect to pyridine and the activation energy for this hydrodenitrogenation of pyridine was found to be 13.75Kcal/gmole.

ACKNOWLEDGEMENT

The authors truly appreciate the financial support from the Korea Science and Engineering Foundation.

NOMENCLATURE

AM	: ammonium molybdate
F	: feed rate, ml/hr
k	: rate constant, gmole/g of cat. hr
n	: reaction order
NN	: nickel nitrate
P_H	: partial pressure of hydrogen, bar
P_Y^0	: initial partial pressure of pyridine, bar
P_Y	: partial pressure of pyridine, bar
r	: reaction rate, gmole/g. hr
t	: time, hr
W	: catalyst weight, g

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