r = instantaneous reaction rate
P = pyridine
T = thiophene
I, II = Type I, Type II HDS sites

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Pyridine Hydrodenitrogenation: An Equilibrium Limitation on the Formation of Piperidine Intermediate

Equilibration between pyridine and piperidine, the first product formed in the overall series of hydrodenitrogenation (HDN) reactions of pyridine, can be a rate-limiting factor under some conditions. Thus, on a commercial $NiMo/Al_2O_3$ catalyst at 11 bars pressure, a maximum in the pyridine HDN rate occurs at about 400°C, caused by a thermodynamic limitation on the allowable concentration of piperidine. From studies with pyridine and with piperidine, $NiMo/Al_2O_3$ appears to have greater hydrogenation-dehydrogenation activity than $CoMo/Al_2O_3$ but $CoMo/Al_2O_3$ appears to have greater hydrogenolysis activity than $NiMo/Al_2O_3$, at least at about 300°C and below.

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SCOPE

The denitrogenation of pyridine and piperidine is a good model for the initial hydrodenitrogenation (HDN) reactions encountered in the hydroprocessing of liquid fuels in that the heterocyclic nitrogen compounds are relatively unreactive, but pyridine is easier to study than the multi ring heterocyclic structures. The first step in HDN reactions in general is usually saturation of the heterocyclic ring, which is followed by hydrogenolysis of the C—N bond and by further reactions leading ultimately to the formation of hydrocarbons and ammonia. When rupture of the C—N bond is the rate limiting step, this rate is determined in part by the maximum allowable concentration of the hydrogenated heterocyclic compound, here piperidine. A clear understanding of the interactions between thermodynamics and kinetics is necessary to optimize processing conditions.

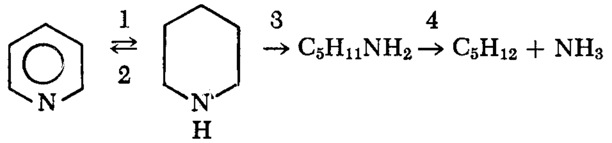
The hydrodenitrogenation of pyridine and of piperidine, its hydrogenated analogue, was studied in a continuous flow, isothermal microreactor at 11 bars, 200 to 425°C, and over NiMo/Al_2O_3 or CoMo/Al_2O_3 commercial catalysts. The study was prompted to explain an earlier observation of ours (Satterfield et al., 1975) that a maximum in the rate of HDN of pyridine occurred as temperature was increased.

CONCLUSIONS AND SIGNIFICANCE

Under some experimental conditions, the concentration of piperidine that can exist in equilibrium with pyridine indeed can be a limiting factor in the overall HDN rate. Since the equilibrium concentration drops at higher temperatures, a maximum in the rate with increased temperature can appear. Higher pressures are thus required in compensation to achieve desirable rates. An ideal catalyst for HDN reactions should have good hydrogenation functionality to cause the first (hydrogenation) step to proceed with dispatch but also good hydrogenolysis functionality to cause rupture of the C—N bond in the next step. Here a NiMo/Al_2O_3 commercial catalyst appeared to have greater hydrogenation-dehydrogenation activity than a CoMo/Al_2O_3 catalyst, but the CoMo/Al_2O_3 catalyst appeared to have greater hydrogenolysis activity, at least at 300°C and below.

In HDN reactions in general, hydrogenation of the heterocyclic ring is usually the first step, and this can cause a thermodynamic limitation on the overall rate. The subtle interplay between thermodynamics and kinetics and the consequent shift in emphasis on different functionalities of a catalyst under different conditions should be borne in mind in any kinetic or catalytic study of HDN reactions.

The removal of nitrogen compounds from petroleum and synthetic crudes derived from coal or oil shale is best achieved by catalytic hydrodenitrogenation (HDN). Most of this nitrogen is in the form of heterocyclic nitrogen compounds, which are the most resistant to HDN. Hydrodenitrogenation of these substances proceeds via saturation of the heterocyclic ring, followed by ring fracture and subsequent removal of the nitrogen as ammonia. The principle steps in HDN of pyridine, which is a good model compound for study (McIlvried, 1971; Sonnemans et al., 1972), are the formation in turn of piperidine, pentyl amine, and pentane plus ammonia. Alkyl transfer reactions can also occur, since Sonnemans et al. (1972) and Goudriaan (1974) reported substantial concentrations of N-pentyl piperidine in the products. Other compounds are also found.



Focussing on steps 1, 2 and 3, the equilibrium between pyridine and piperidine can affect the overall rate of reaction if step 3, hydrogenolysis of the C—N bond, is slower than step 1 and if conditions are such that the equilibrium concentration of piperidine is severely limited. The rate of hydrogenolysis of the C—N bond (and the overall HDN rate) is then less than it would be if there were no significant thermodynamic limitation on the concentration of piperidine. However, if step 1 were rate-limiting, piperidine would react as it forms and the position of the ring-saturation equilibrium would not influence the overall HDN rate.

Equilibrium towards piperidine becomes less favorable at higher temperatures and lower hydrogen pressures. Under the reaction conditions of McIlvried (315°C, 50-100 bars, NiCoMo/Al_2O_3 catalyst) hydrogenation was rapid and step 3 was rate-limiting. Equilibrium of steps 1 and 2 was far to the right. Stengler et al. (1964), as reported by Goudriaan (1974), stated that on a NiW/Al_2O_3 catalyst at 50 bar, step 3 was rate-limiting below 350°C and step 1 at higher temperatures. In a very recent study on CoMo/Al_2O_3 catalyst at 80 bars, Goudriaan (1974) concluded that the equilibrium of steps 1 and 2 may begin to limit the overall rate of reaction at temperatures higher than 350°C, and Sonnemans and co-workers (1973, 1974) discuss its implications for the mechanism of pyridine HDN. In an independent study at 11 bars we (Satterfield et al., 1975) found, unexpectedly, that the conversion of pyridine over some catalysts dropped with an increase in temperature about 400°C. This effect apparently has not been previously reported in HDN studies and it can be interpreted in terms of the development of an unfavorable equilibrium for the initial saturation step at higher temperatures. Piperidine could not be detected with the analytical system we used previously, so the present study was carried out to test this hypothesis by suitable experiments and analysis of products from the reaction of pyridine or of piperidine, respectively.

APPARATUS AND PROCEDURE

The experimental apparatus and procedure centered around a continuous flow, fixed bed, catalytic micro reactor, immersed in a fluidized sand bath furnace for controlled isothermal operation, described in more detail elsewhere (Satterfield et al., 1975; Mayer, 1974). Liquid pyridine or piperidine was pumped into the system, vaporized, and mixed with hydrogen before it entered the reactor. A gas chromatograph equipped with Pennwalt 223 analytical columns was used for quantitative analysis of the reactor off gas. Catalysts were commercial NiMo/Al_2O_3 or CoMo/Al_2O_3 as used previously, crushed and sieved to provide a 20/24 mesh size for study. A single charge of each catalyst was used for all experiments. All studies were made at a total pressure of 11.2 bars and temperatures varied from about 200° to 425°C. A great excess of hydrogen was present at all times.

Table 1
Experimental conditions
Total pressure = 11.2 bars

Reaction of pyridine

Catalyst	Partial pressure at reactor inlet, bars	Superficial residence time (s) at 250°C*
NiMo/Al_2O_3	0.13	3.04
CoMo/Al_2O_3	0.56	3.92
	0.55	7.91

Reaction of piperidine

Catalyst	Partial pressure at reactor inlet, bars	Superficial residence time (s) at 250°C*
NiMo/Al_2O_3	0.12	3.08
CoMo/Al_2O_3	0.60	10.8

* Residence time is calculated based on the superficial gas velocity at 250°C and 11.2 bars.

The ranges of reactant partial pressure and space velocity (expressed here as a superficial residence time calculated for 250°C) are given in Table 1. The catalysts were activated in situ by treatment with a 10% hydrogen sulfide 90% hydrogen mixture according to a procedure specified by the manufacturer and given by Mayer (1974). The analytical columns provided good separation of the heavier components (pyridine, piperidine, *n*-pentylamine), but the light reaction products such as ammonia and *n*-pentane, though they appeared as separate peaks on the chromatograms, were not resolved. Injection of known pyridine-piperidine solutions covering the full range of compositions indicated that the quantitative analysis of these components always involved absolute errors less than 0.5 mole per cent. Further details are given by Cocchetto (1974).

RESULTS AND DISCUSSION

The Equilibrium Limitation

The percent conversions of pyridine as a function of temperature agreed closely with those we found previously (Satterfield, et al., 1975) for similar residence times. As before, greater conversions were obtained with NiMo/Al_2O_3 than with CoMo/Al_2O_3 over the entire temperature range investigated, but even with NiMo/Al_2O_3 the conversion of pyridine reached a maximum of only 28% at about 375°C and then dropped (Figure 3). With piperidine HDN however, conversion increased with temperature on both catalysts, ultimately to the 100% level.

In order to focus on the reversible pyridine-piperidine reaction, Figure 1 (for NiMo/Al_2O_3) and Figure 2 (for CoMo/Al_2O_3) compare the experimentally observed ratios of piperidine to pyridine plus piperidine in the reactor effluent with the calculated equilibrium ratios (Cocchetto, 1974) as a function of temperature, for both pyridine HDN runs and piperidine HDN runs. The equilibrium curve corresponds to the hydrogen partial pressure of 11.1 bars. Figure 1 shows that for pyridine HDN, the amount of piperidine in the off gas increased at the expense of pyridine as the temperature was increased to nearly 300°C. At this point, the equilibrium begins to shift from piperidine to pyridine, and the observed quantities of piperidine began to decrease with temperature. Above approximately 400°C, equilibrium was established. With piperidine feed, no pyridine was observed below 300°C, but above this temperature its quantity increased steadily at the expense of the piperidine. At 400°C, equilibrium was again established. At high temperatures, equilibrium was established starting with either pyridine or piperidine.

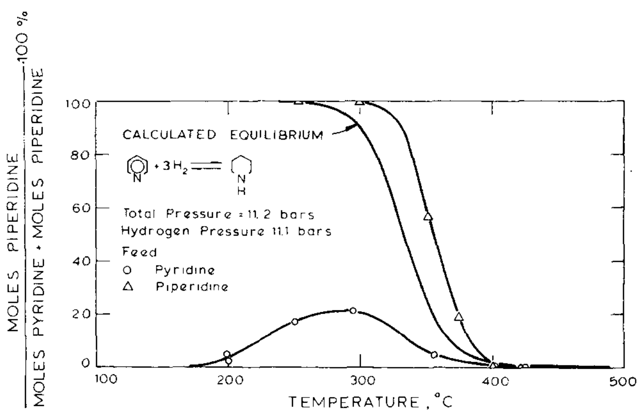


Fig. 1. Comparison of experimental and equilibrium quantities of pyridine and piperidine for HDN over NiMo/Al_2O_3 catalyst.

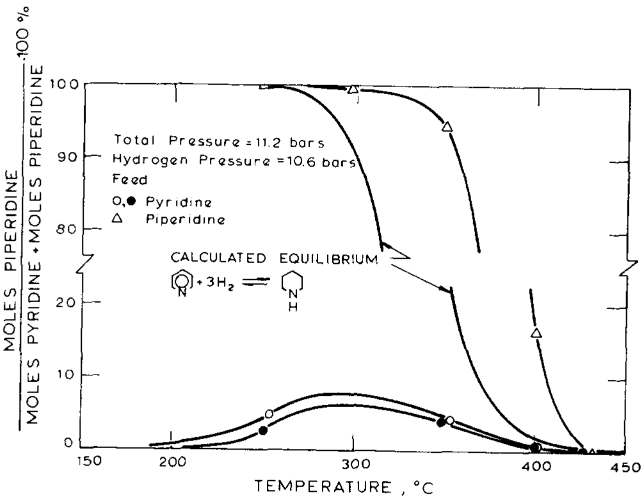


Fig. 2. Comparison of experimental and equilibrium quantities of pyridine and piperidine for HDN over CoMo/Al_2O_3 catalyst.

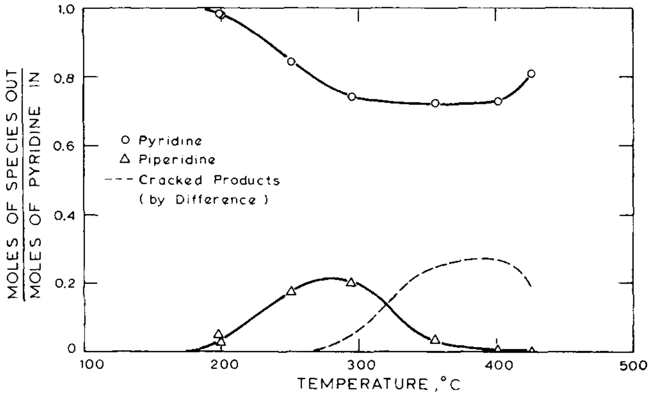


Fig. 3. Product distribution for pyridine HDN runs over NiMo/Al_2O_3 catalyst.

The results shown in Figure 2 are quite similar, the two sets of data for pyridine feed representing two different residence times. The pyridine-piperidine reaction was generally farther from equilibrium with CoMo/Al_2O_3 than with NiMo/Al_2O_3, although the activities of the two catalysts cannot be precisely compared here since different partial pressures of reactant were used in the two

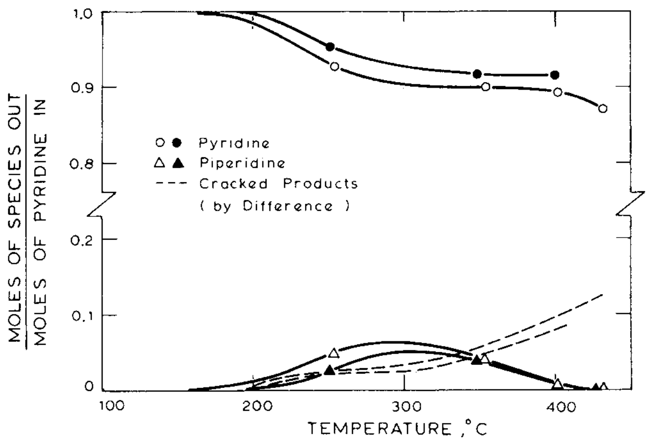


Fig. 4. Product distribution for pyridine HDN runs over CoMo/Al_2O_3 catalyst.

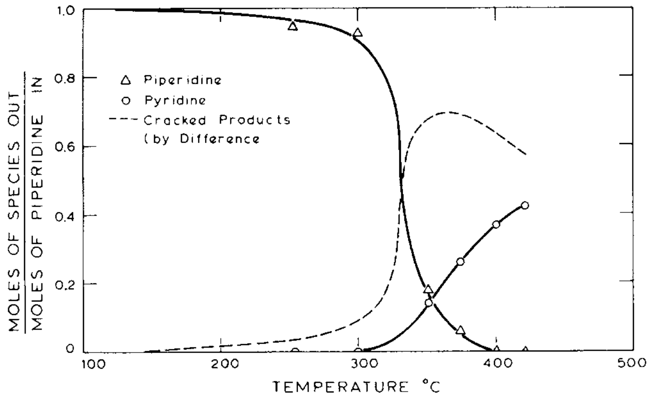


Fig. 5. Product distribution for piperidine HDN runs over NiMo/Al_2O_3 catalyst.

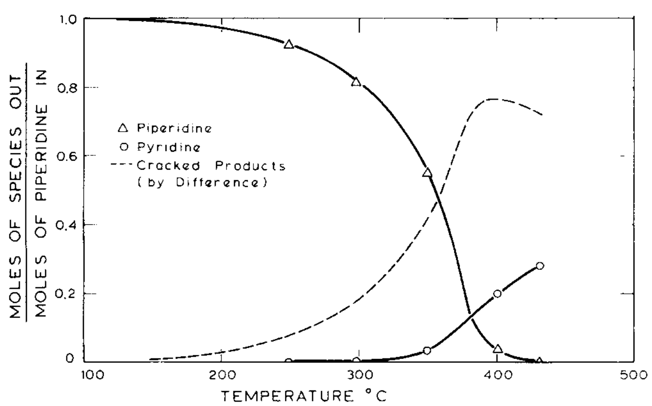


Fig. 6. Product distribution for piperidine HDN runs over CoMo/Al_2O_3 catalyst.

cases. Equilibrium was finally established at 430°C with the piperidine feed and at a slightly lower temperature (about 400°C) starting with pyridine. The results in the two figures clearly show the reversibility of pyridine saturation in the initial step of its hydrodenitrogenation.

Product Distribution

Some information about the relative hydrogenation and hydrogenolysis activities of the two catalysts can be gleaned from the product distributions as a function of temperature. For pyridine HDN, Figure 3 shows results over NiMo/Al_2O_3 and Figure 4 over CoMo/Al_2O_3. No *n*-pentylamine was detected in the reactor effluent, and the light reaction products (ammonia, *n*-pentane) could not be analyzed for quantitatively. The sum of ammonia, nitrogen-containing side products, and hydrocarbons such as *n*-pentane was determined by a material balance between the moles of pyridine fed to the reactor and the moles of pyridine and piperidine found in the products and is shown as the dashed lines. Ammonia was the principal nitrogen-containing cracked product, but at higher temperatures several light products other than ammonia and *n*-pentane appeared. With NiMo/Al_2O_3, below about 275°C piperdine was the only reaction product, and the material balance was within a few percent. The amount of piperidine in the reactor effluent reached a maximum just below 300°C and dropped to nearly zero at high temperatures. Ammonia and *n*-pentane were not observed at 251°C but were found in appreciable quantities at 295°C. Much greater quantities of ammonia and other light products appeared at 356° and 402°C, but a decrease was observed at 426°C consistent with the downturn in pyridine conversion. With CoMo/Al_2O_3 less piperidine was always formed than with NiMo/Al_2O_3 at the same temperature, and the ratio of cracked products to piperidine was higher.

Figures 5 and 6 are analogous to Figures 3 and 4 and show the product distribution as a function of temperature for piperidine HDN over NiMo/Al_2O_3 or CoMo/Al_2O_3. With NiMo/Al_2O_3, up to about 40% of the piperidine was dehydrogenated to pyridine but the conversion of piperidine to cracked products (dashed line) reached a maximum at about 370°C and then decreased. This behavior is similar to the downturn in pyridine conversion observed for this same catalyst. With CoMo/Al_2O_3 (Figure 6), pyridine was again formed only above 300°C but in smaller quantities than with NiMo/Al_2O_3. Small quantities of *n*-pentylamine were observed in the off gas from 300° to 400°C. With both catalysts, ammonia was the principal nitrogen containing cracked product and was produced in greater quantity than *n*-pentane. Qualitative examination of chromatogram peaks revealed trends consistent with the quantities of cracked products as calculated by difference.

Below 300°C only cracked products were formed with both NiMo/Al_2O_3 and CoMo/Al_2O_3, since the dehydrogenation of piperidine to pyridine was thermodynamically unfavorable. Comparison of the product distributions for pyridine and piperidine HDN over each catalyst suggest that below about 300°C, the hydrogenation of pyridine to piperidine was easier than piperidine hydrogenolysis for NiMo/Al_2O_3, but hydrogenolysis was easier than hydrogenation for CoMo/Al_2O_3. This could account for the low activity of CoMo/Al_2O_3 for pyridine HDN at low temperatures. The larger quantities of pyridine formed with NiMo/Al_2O_3 than with CoMo/Al_2O_3 for piperidine HDN also imply that the former catalyst had greater dehydrogenation activity. This is consistent with the fact that the piperidine dehydrogenation reaction was closer to equilibrium with NiMo/Al_2O_3 than with CoMo/Al_2O_3 (compare Figures 1 and 2).

Comparison with Previous Studies

Sonnemans et al. (1972) studied pyridine HDN over reduced CoMo/Al_2O_3 at 60 bars hydrogen partial pressure and Goudriaan (1974) at 80 bars pressure. No downturn in pyridine conversion was observed, though it appeared that the pyridine/piperidine equilibrium may have been established at 400°C. At the higher hydrogen pressures the equilibrium is much more favorable for piperidine than at the 11 bars hydrogen pressure used in the present study. The product distributions shown in Figures 3 and 4 exhibit the same trends as the distributions reported by Sonnemans and Goudriaan, except for the downturn.

McIlvried (1971) studied the hydrodenitrogenation of pyridine at 315°C and pressures of 50 to 100 bars on a NiCoMo/Al_2O_3 catalyst. He did not analyze for piperidine in his products but he observed that the nitrogen content of the total product was about the same for a given set of reaction conditions starting with either pyridine or piperidine. In his case, the rate of hydrogenation of the pyridine ring was presumably rapid relative to subsequent steps, and at his higher pressure there was no thermodynamic limitation on the concentration of piperidine that could exist in equilibrium with pyridine. Here the rates of hydrogenation of pyridine to piperidine and of the hydrogenolysis step both appeared to affect the overall rate at the overall rate at the lower temperatures. At the higher temperatures the rate limiting step was solely hydrogenolysis of piperidine present in low concentration because of a thermodynamic limitation. The maximum in pyridine conversion at 375-400°C is caused by the decrease in the equilibrium concentration of piperidine with increased temperature being more important than the increase in the kinetic rate constant for piperidine cracking.

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A New Technique for Collecting Binary Vapor-Liquid Equilibrium Data without Measuring Composition: the Method of Intersecting Isochores

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The Burnett coupled isochoric *PVT* experiment possesses many advantages for determining volumetric properties. In this study, we suggest that it also provides an excellent vehicle for determining VLE data. Incorporating a magnetic densimeter into the apparatus encompasses a VLE experiment in which the phases are not sampled to determine composition. Material balances allow composition calculation; the Gibbs-Duhem equation is not necessary and thus remains available for consistency checks.

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