Interactions Between Catalytic Hydrodesulfurization of Thiophene and Hydrodenitrogenation of Pyridine

Pyridine hydrodenitrogenation (HDN) is more difficult than thiophene hydrodesulfurization (HDS), and there is a thermodynamic limitation on the first step of the HDN reaction mechanism which occurs, for example, at 5 to 11 bars, at temperatures above about 350°C. Pyridine inhibits the HDS reaction as previously reported, but sulfur compounds have a dual effect on HDN. At low temperatures, thiophene inhibits the reaction by competing with pyridine for hydrogenation sites on the catalyst. This retards the hydrogenation of pyridine to piperidine, reducing the overall reaction rate. At high temperatures the dominant effect is interaction of hydrogen sulfide, an HDS reaction product, with the catalyst to improve its hydrogenolysis (hydrocracking) activity. This increases the rate of piperidine hydrogenolysis, which is rate determining at the latter conditions, and enhances the overall rate of HDN.

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SCOPE

The hydroprocessing of fuels containing relatively large amounts of organonitrogen compounds will become increasingly important in the future in the upgrading of synthetic fuels from oil shale and coal or processing of lower grades of crude petroleum. Organosulfur compounds are also always present, and the inhibiting effect of organonitrogen compounds on catalytic hydrodesulfurization is established. However, very little has been published on the effect of organosulfur compounds on hydrodenitrogenation. These two groups of effects were explored by using as model compounds thiophene and pyridine which represent some of the less reactive organosulfur and organonitrogen compounds, respectively.

Studies were made with a flow microreactor at temperatures of 200° to 500°C, 4.4 and 11.2 bars pressure, on commercial catalysts consisting of $CoMo/Al_2O_3$, $NiMo/Al_2O_3$, NiW/Al_2O_3 and $NiW/SiO_2\text{-}Al_2O_3$.

CONCUSIONS AND SIGNIFICANCE

Pyridine, a basic nitrogen compound, severely inhibits the hydrodesulfurization of thiophene on sulfided cobalt-molybdate type of catalysts, in agreement with previous studies. The pattern of this inhibition suggests there are two types of HDS sites involved. The first are postulated to be very active for HDS but very sensitive to nitrogen bases. Sufficient quantities of these bases will completely block these sites and render them inactive for HDS. The second type of sites are much less active for HDS, but they are also less susceptible to pyridine poisoning. These latter sites are responsible for HDS activity after the first type of sites have been blocked.

The hydrodenitrogenation of pyridine is more difficult than thiophene HDS, and there appears to be a thermodynamic limitation to the first step in the reaction mechanism. Sulfur compounds have a twofold effect on HDN. At low temperatures they are postulated to compete with pyridine for hydrogenation sites on the catalyst, thereby inhibiting the rate of the hydrogenation step in the pyridine decomposition mechanism. At high temperatures the HDS reaction product hydrogen sulfide interacts with the catalyst to improve the hydrogenolysis activity. This increases the rate of piperidine hydrogenolysis, which is the rate limiting step at high temperatures, and results in enhancement of the HDN reaction rate. For maximum effectiveness in HDN, both hydrogenation activity and hydrogenolysis activity are required for an active catalyst, but the relative emphasis on the two types of functionality will depend on processing conditions and, presumably, the type of compounds present.

Hydrodesulfurization (HDS), which is accompanied by some hydrodenitrogenation (HDN), is an important commercial process for removal of organosulfur compounds from petroleum feedstocks. The overall chemical reactions involved are

$$\left\{\begin{array}{l}\text{Organo-sulfur compound}\\ \text{Organo-nitrogen compound}\end{array}\right\}$$

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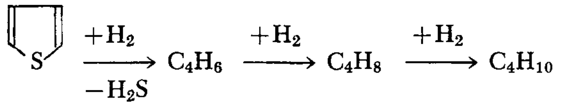
$$+ H_2 \xrightarrow[\text{catalyst}]{} \text{Hydrocarbon} + \left\{\begin{matrix} H_2S \\ NH_3 \end{matrix}\right\}$$

Sulfided cobalt-molybdenum on alumina or nickel-molybdenum on alumina are typical catalysts. Several excellent reviews of HDS reactions and processes are available (Schuman and Shalit, 1970; Schuit and Gates, 1973; Weisser and Landa, 1973*a*).

Hydrodenitrogenation will become increasingly important in the future to lower the organonitrogen content of synthetic crudes extracted from oil shale, some coals, or certain low-grade naturally occurring petroleum, which contains large amounts of both sulfur and nitrogen. HDS and HDN occur simultaneously at suitable temperatures and pressures, but the reactions interact with each other in ways which are little understood. As will be shown, under some circumstances mutual inhibition occurs; under others, hydrogen sulfide enhances HDN. This work was undertaken to elucidate these interactions by study of the HDS/HDN reactions of mixtures of thiophene and pyridine on four commercial hydrotreating catalysts. These compounds were chosen because they are representative of classes of sulfur and nitrogen compounds in petroleum and synthetic fuels which are difficult to desulfurize and denitrogenate by hydrogenation.

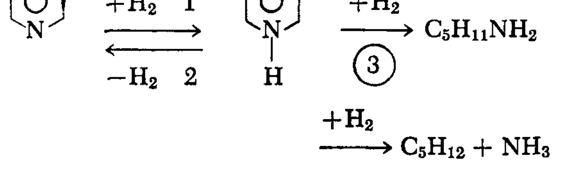
Studies on HDS of thiophene and HDN of pyridine have revealed substantial information about the reaction mechanisms for these compounds individually, although it is not too clear how these may be affected by pressure or by the nature of the catalyst. From studies at 1 atm. over chromia and supported cobalt molybdate catalysts, Owens and Amberg (1961) proposed the following for the desulfurization of thiophene:



(1)

Their results specifically indicated that the first step, at least under their conditions, is cleavage of a C—S bond rather than hydrogenation of thiophene. The reaction rate has been described by a Langmuir-Hinshelwood expression in which thiophene and hydrogen sulfide compete for catalyst sites (Satterfield and Roberts, 1968). Hydrogen sulfide also inhibits the subsequent hydrogenation steps.

Pyridine is less reactive than thiophene. From studies on a supported nickel cobalt molybdenum catalyst at 750 to 1 500 lb./sq.in.gauge, McIlvried (1971) concluded that the mechanism of pyridine denitrogenation is



(2)

Disproportionation reactions of piperidine and pentyl amine also occur (Sonnemans et al., 1972). The rate of pyridine denitrogenation can also be described by a Langmuir-Hinshelwood model in which adsorbed nitrogen compounds have a strong inhibiting effect on the rate.

Pyrrole has seldom been used in HDN studies, since its instability makes handling difficult.

Previous studies on simultaneous HDS/HDN indicate that nitrogen compounds inhibit the HDS process. In tests of thirty-five different crude oil fractions, Kiovsky and Berg (1964) concluded that the nitrogen content of the feedstock was the most important variable affecting catalyst HDS activity. Doelman (1962) studied the HDS of a cycle oil fraction (3.8 wt. % sulfur) to which he added pyridine and quinoline. With the processing conditions used, sulfur removal from the original cycle oil was 98%, while in the presence of the nitrogen compounds (1.0 wt. % nitrogen in feedstock) sulfur removal was 94%. Kirsch et al. (1959) experimented with a synthetic gasoline (0.4 wt. % sulfur) blended from heptane, heptene, and thiophene. With their experimental conditions, sulfur removal from this feedstock was 79%, while addition of pyridine (0.1 wt. % nitrogen in feed) reduced this to 59%. Ahuja et al. (1970) also observed pyridine inhibition of thiophene HDS over catalysts other than cobalt-molybdenum-alumina.

Two studies using pure compounds have also shown the detrimental effect of nitrogen compounds on HDS. Desikan and Amberg (1964) observed that pyridine poisoned thiophene HDS on a presulfided CoMo/Al_2O_3 catalyst in a manner indicating that there were two sites which have HDS activity. Pyridine apparently poisons these sites to different extents. Lipsch and Schuit (1969) also reported that pyridine poisons thiophene HDS, using a CoMo/Al_2O_3 catalyst that was prereduced but not presulfided, but the effect was not great as that of Desikan and Amberg. Both these studies utilized pulsed reactors, so the results are mainly qualitative.

The effects of sulfur compounds on HDN are only poorly understood. A patent by Gerald (1957) claimed the addition of a sulfur compound in great excess over the organonitrogen present to improve nitrogen removal over a catalyst containing molybdenum, attributed to the possible formation or maintenance of a particular sulfided form of the catalyst. A recent study by Goudriaan et al. (1973) reported that hydrodenitrogenation of pyridine over a CoMo/Al_2O_3 catalyst was enhanced if the catalyst were presulfided rather than being reduced in hydrogen. In the presence of hydrogen sulfide in molar excess over the pyridine, the nitrogen removal was further increased, attributed to an enhancement of the hydrocracking activity of the catalyst by the hydrogen sulfide.

APPARATUS AND PROCEDURE

The apparatus (Figure 1) centered around a steady state flow microreactor. An infusion pump fed a liquid feed (thiophene, pyridine, or a mixture of these compounds) to the system through a length of heated capillary which served as a vaporizer. Prepurified grade hydrogen was passed through a DEOXO purifier and molecular sieve (Type 4A) drying column to remove traces of oxygen and water. The hydrogen and vaporized reactants were then mixed and flowed through several feet of preheater tubing before entering the reactor.

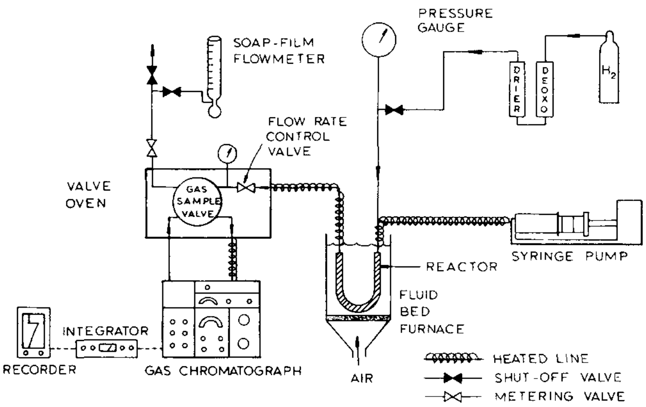


Fig. 1. Schematic diagram of apparatus.

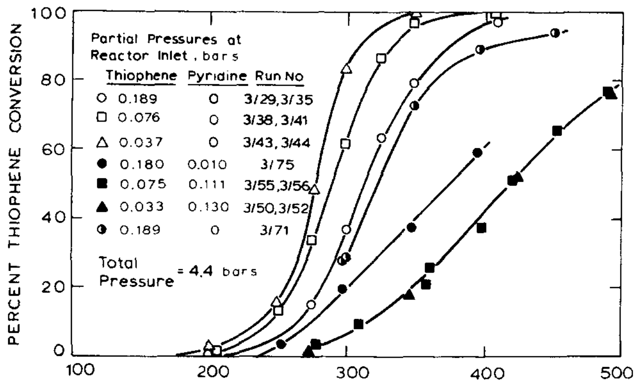


Fig. 2. Thiophene HDS with $CoMo/Al_2O_3$ catalyst (experimental conditions given in Table 2).

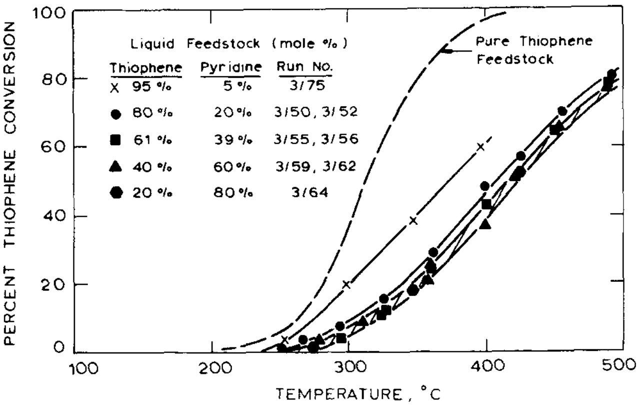


Fig. 3. Thiophene HDS in mixed feedstocks with $CoMo/Al_2O_3$ catalyst (experimental conditions given in Table 2).

The reactor was a stainless steel tube (0.5 cm I.D., 11 cm long) bent into a U shape and packed with catalyst. Catalyst particles were commercial extrudates crushed and sieved to 20/24 mesh. A typical catalyst charge was 1.5 g, and a single charge was used throughout an entire series of experiments. Table 1 shows the catalysts used. Each was activated prior to the first experimental run by treatment with a mixture of hydrogen sulfide (10%) and hydrogen (90%) according to a temperature-time program specified by the manufacturer.

The reactor and preheater tubing were immersed in a fluidized sand bath which served as a constant temperature medium. Reactor temperature was monitored with a thermocouple mounted in the exit gas stream so that its tip was just above the end of the catalyst bed. Temperature was controlled to ± 1°C below 350°C and ± 2°C above 350°C.

TABLE 1. CATALYSTS USED IN THIS STUDY

Manufacturer	Designation and type	Surface area(1)	Bulk density(2)
American Cyanamid	Aero HDS-2A, $CoMo/Al_2O_3$	270 m^2/g	0.531 g/cm^3
American Cyanamid	Aero HDS-3A, $NiMo/Al_2O_3$(a)	180 m^2/g	0.684 g/cm^3
Harshaw	Ni4303, NiW/Al_2O_3(b)	152 m^2/g	0.765 g/cm^3
Harshaw	Ni4301(3) $NiW/(SiO_2\text{-}Al_2O_3)$(b)	228 m^2/g	0.847 g/cm^3

Notes

(1). Surface area reported by manufacturer.

(2). Bulk density of 20/24 mesh fraction used in experiments.

(3). Analysis indicated the support composition was 66% SiO_2, 34% Al_2O_3.

(a). 3.1 wt% NiO, 15.0 wt% MoO_3.

(b). 6% nickel and 19% tungsten, as metal content.

Samples were taken from the reactor effluent stream with a gas sampling valve and injected into a Varian 2820 gas chromatograph. The sampling valve was mounted in an oven heated to 150°C to prevent condensation of reactants or products. The columns used in the chromatograph were 20 ft Carbowax 20M on Chromosorb W. These highly polar column packings separated the reactants (thiophene, pyridine) very well, but the light reaction products (butanes, ammonia, hydrogen sulfide, etc.) were unresolved and appeared as a single peak. Since hydrogen was used as the carrier gas in the chromatograph, the hydrogen in samples of the reaction mixture did not appear on the chromatograms. Peak areas were determined with an electronic digital integrator.

A single experimental run consisted of determining the steady state fractional conversion of thiophene and of pyridine at each of several different reactor temperatures for a fixed quantity of catalyst, feedstock, pressure, and total molar gas flow rate (hydrogen plus heterocyclic compounds). In a series of experimental runs pressure, quantity of catalyst and gas flow rate were held constant, but the ratio of thiophene and pyridine to each other and to hydrogen was varied from run to run. The feed rate of hydrogen was consequently adjusted slightly to keep the total molar flow rate constant as feed rates of thiophene and pyridine were changed. Hydrogen was always present in great excess; the mole ratio of hydrogen to heterocyclic compound varied from 22 to 90.

The raw data taken during a run were the reactant peak areas (thiophene, pyridine) and the overall flow rate through the system. Fractional conversions of the reactants were calculated for each reaction temperature of interest by taking the ratio of thiophene and pyridine peak areas to those found when no reaction was occurring.

The results showed very good reproducibility. The fractional conversions observed under a given set of conditions could be reproduced in separate experimental runs. With the analytical

TABLE 2. EXPERIMENTAL CONDITIONS FOR RESULTS DEPICTED IN FIGURES

Figure no.:	2,3	4,5	8	7	9
Pressure, bars:	4.4	11.2	4.4	11.2	11.2
Catalyst:	1.31 g (≃2.46 cm^3) $CoMo/Al_2O_3$ 20/24 mesh	1.48 g (≃2.17 cm^3) $NiMo/Al_2O_3$ 20/24 mesh	1.49 g (≃2.85 cm^3) $CoMo/Al_2O_3$ 16/28 mesh	1.48 g $NiW/SiO_2\text{-}Al_2O_3$ 20/24 mesh	1.48 g $CoMo/Al_2O_3$ NiW/Al_2O_3 20/24 mesh
Liquid feed rate, ml/hr.	1.30 to 6.53	0.65 to 2.60	2.60	0.65 to 2.6	0.65 to 2.6
Hydrogen feed rate, avg., cc(STP)/min.	714	271	350	273	273
Residence time,[*] s	0.52 to 0.32	3.1 to 2.1	≃1	2.44 to 1.65	3.77 to 2.55 2.65 to 1.80

[*] Based on superficial linear velocity at reaction conditions (varies inversely with temperature).

procedure used, however, a mass balance over the system was not possible. Application of correlations for heat transfer limitations (Mears, 1971) and mass transfer limitations (Satterfield, 1970) to worst case conditions showed that no significant temperature or concentration gradients existed in the reactor. Further details on experimental procedures are given by Mayer (1974).

RESULTS

HDS of Thiophene

Figures 2 and 3 show the percent conversion of thiophene obtained over a series of experimental runs with pure thiophene or mixed thiophene/pyridine feedstocks, each studied over a wide range of temperature. (See Table 2 for a summary of experimental conditions.) The entire series of experiments was carried out with one catalyst charge. No reaction of the pyridine occurred in any of these runs. As shown in Figure 2, with pure thiophene feedstocks, the fractional conversion of thiophene increased as initial partial pressure was decreased, and further analysis showed that the rate was nearly zero order with respect to initial partial pressure over this range of conditions.

The presence of pyridine in the feedstock has a severe inhibiting effect on HDS and changes the order of the HDS reaction, as is evident by comparison of the results with pure thiophene and those with mixtures of thiophene and pyridine. Comparison of runs 3/50 and 3/52 with 3/55 and 3/56 (Figure 2) shows that in the presence of pyridine the observed conversion of thiophene was independent of the initial concentration, indicating a rate expression which is first order with respect to initial thiophene partial pressure. Run 3/71, done as a reproducibility test (compare to 3/29, 3/35) after completion of the mixed feedstock experiments, showed an approximately 10% loss in HDS activity of the catalyst. This was the only permanent catalyst deactivation observed, and it probably was caused by coke formation at the very high temperatures (500°C) reached in some of the mixed feedstock runs. Subsequent experiments were limited to 425°C. The inhibiting effect of pyridine was reversible.

Figure 3 shows the effect of varying the ratio of pyridine to thiophene, keeping the initial partial pressure of the two heterocyclic compounds constant at 142 torr. Small additions of pyridine have a major inhibiting effect, but larger additions do not depress the rate further.

Figure 4 shows the results of a similar series of runs but at higher pressure (11.2 bars) and longer contact times, and using a NiMo/Al_2O_3 catalyst. HDN did occur in these runs, and those results will be discussed immediately below. As was observed at the lower pressure on the CoMo/Al_2O_3 catalyst, adding an equimolar amount of pyridine to a thiophene feedstock significantly reduces the fractional conversion of thiophene (compare 5/26 with 5/13, 5/16), while further increments of pyridine have very little additional effect (compare 5/34 and 5/36 with 5/26). As with the CoMo/Al_2O_3 catalyst, in the presence of large quantities of pyridine the HDS of thiophene follows nearly first-order rate behavior, with conversion approximately independent of initial thiophene concentration (compare 5/29 and 5/31 with 5/26). Similar studies with NiW/Al_2O_3, NiW/SiO_2-Al_2O_3, and CoMo/Al_2O_3 catalysts at the same conditions (Mayer, 1974, pp. 86-87) showed virtually identical results to those obtained with NiMo/Al_2O_3. Although the same weight of each catalyst was used in this comparison, the surface area per unit weight and the concentration of the active ingredients were somewhat different on different catalysts, so that a detailed comparison cannot be made quantitatively.

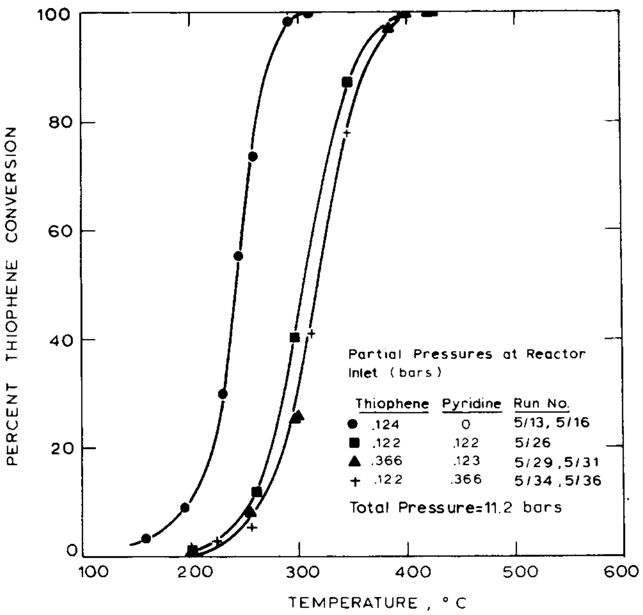


Fig. 4. Thiophene HDS with NiMo/Al_2O_3 catalyst (experimental conditions given in Table 2).

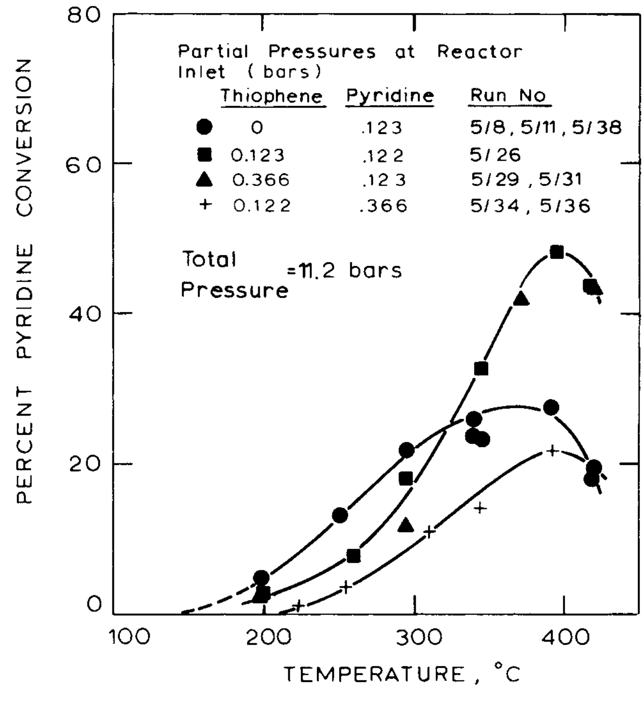


Fig. 5. Pyridine HDN on NiMo/Al_2O_3 catalyst (experimental conditions given in Table 2).

In summary, the principal observations on the HDS reaction are: (1) small additions of pyridine cause a major inhibition of the HDS of thiophene but larger additions have little effect, (2) thiophene HDS is zero order in the absence of pyridine and first order in the presence of substantial quantities, and (3) there is no significant difference between the behavior of the four catalysts studied.

HDN of Pyridine

Figure 5 presents the results for the HDN of pyridine alone on a NiMo/Al_2O_3 catalyst and in mixtures with thiophene as discussed above. Pyridine is much less reactive

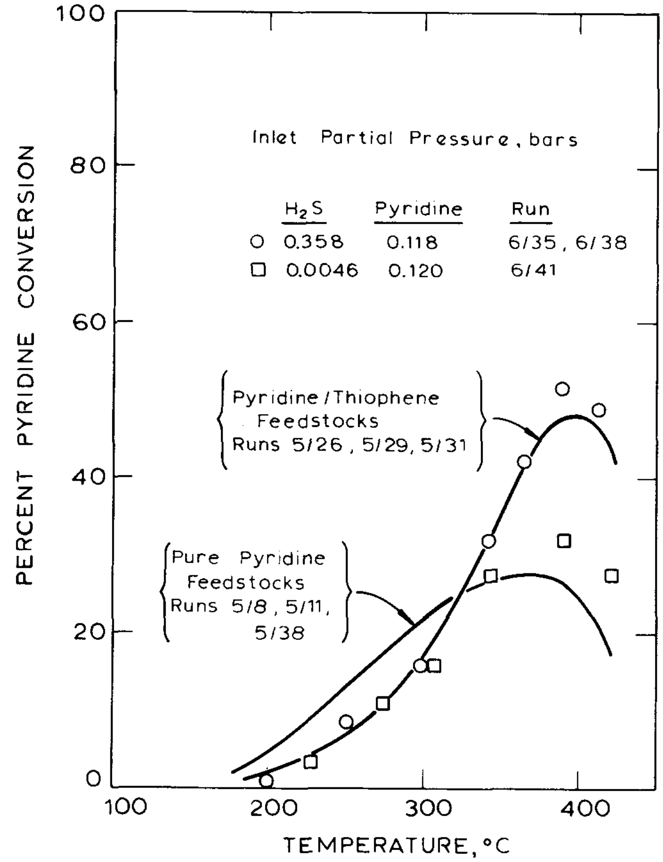


Fig. 6. Pyridine HDN in presence of hydrogen sulfide (NiMo/Al_2O_3 catalyst). Data points are for hydrogen sulfide. Solid lines show results in presence of thiophene feed. (See Figure 5.)

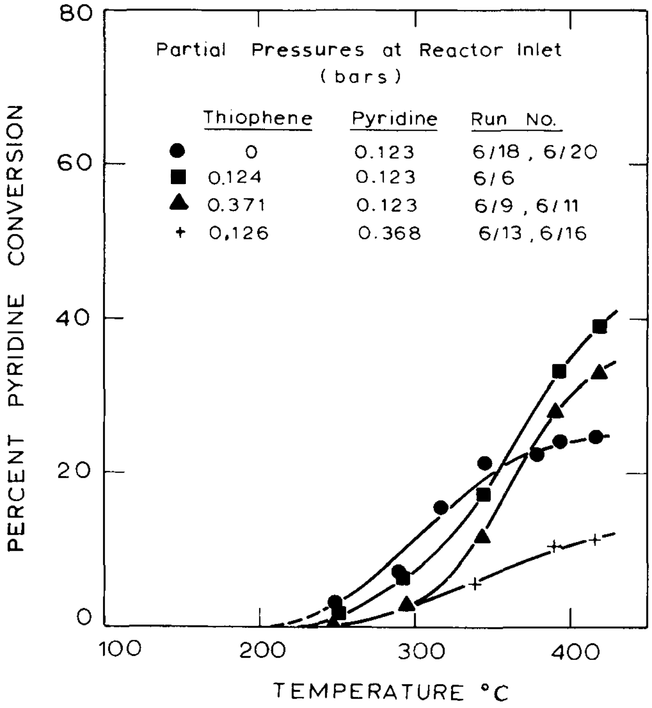


Fig. 7. Pyridine HDN with NiW/(SiO_2-Al_2O_3) catalyst (experimental conditions given in Table 2).

than thiophene. The maximum pyridine conversion ever observed was 50%, whereas thiophene could be 100% converted. The effect of temperature on HDN is unusual in that the fractional conversion goes through a maximum and turns downward above 380°C. This is probably because of the onset of a thermodynamic limitation on the reaction as discussed below. Comparison of runs 5/34 and 5/36 with run 5/26 and other observations indicates that the HDN reaction here is between zero and first order over the entire temperature range.

The effect of thiophene on HDN is twofold. Below 325°C the presence of the sulfur compound inhibits the HDN reaction in that lower fractional pyridine conversions were observed with mixed feedstocks than with pure pyridine feedstocks. Above 325°C the presence of thiophene enhances the HDN reaction. However, thiophene itself is probably not responsible for the enhancement effect, since it is more than 60% converted to hydrogen sulfide at 325°C (see Figure 4). To determine the role of hydrogen sulfide, three runs were performed with a pure pyridine feedstock at 10.3 bars total pressure but with a hydrogen sulfide partial pressure of 0.358 or 0.0046 bar in the reaction gas (Figure 6). With the higher hydrogen sulfide partial pressure the results duplicated those of runs 5/29 and 5/31, thus confirming the hypothesis that hydrogen sulfide, not thiophene, is responsible for the enhancement effect on HDN. With 0.0046 bar hydrogen sulfide, inhibition effects similar to those observed with thiophene appear, but enhancement of HDN at the higher temperatures, although evident, is much reduced in magnitude from that observed in the other runs.

The effect of hydrogen sulfide is corroborated by the observation of Goudriaan (1974, p. 157) on the hydrodenitrogenation of pyridine on a CoMo/Al_2O_3 catalyst at 75 bars pressure and 250° to 350°C. With a previously sulfided catalyst, a two to sixfold increase in HDN activity was found in the presence of 4 bar pressure of hydrogen sulfide over that found in the absence of hydrogen sulfide.

Similar studies were made with the other three catalysts. As with the NiMo catalyst, in the presence of thiophene a maximum was observed with CoMo/Al_2O_3 or NiW/Al_2O_3, but somewhat different behavior occurred on NiW/SiO_2-Al_2O_3 (Figure 7). These effects will be discussed below.

The enhancement of HDN by hydrogen sulfide may be associated with the maintenance of the catalyst in a completely sulfided state which has better HDN activity, since the catalyst loses sulfur in the presence of hydrogen alone, as shown by some simple experiments. Correctly sulfided CoMo/Al_2O_3 had a sulfur content of 1.9 to 2.1 wt. % S, but after exposure to hydrogen at either 300° or 400°C for 35 to 40 hr. this was reduced to 1.0%.

Some scouting experiments (Mayer, 1974, p. 100) indicated that the HDN activity will drop rapidly just after hydrogen sulfide is removed from the reactant gas stream, but further prolonged exposure to hydrogen will have little further effect beyond the initial decline. For example, at 350°C, on CoMo/Al_2O_3 catalyst, a 50/50 thiophene-pyridine feed gave a 31% conversion of pyridine and 93% conversion of thiophene. With pyridine alone at the same conditions, about 18% conversion was obtained after a freshly sulfided catalyst had been exposed to the pyridine-hydrogen mixture for only 1 hr., which dropped to 16% conversion after 38 hr. The rate of sulfur loss from the catalyst was not established quantitatively, but chromatographic analyses showed appearance of substantial hydrogen sulfide in the exit gas during the first hour at a rapidly decreasing rate. The active sulfur containing species on the catalyst surface must be unstable and rapidly decomposed in the absence of sufficient sulfur in the feed gas.

Effect of Other Additives

A few runs under limited conditions were performed with pyrolle, with results as shown in Figure 8. Although pyrolle is nonbasic, it exhibits almost exactly the same inhibiting effect as pyridine. Work with pyrolle is difficult experimentally because of its thermal decomposition, so no further studies were made with it.

Dilution of the feedstock with 1,3,5 triethylbenzene showed a mild increase in thiophene conversion, a trend that was also observed for pure thiophene feedstock as the initial reaction partial pressure was decreased. These results indicate that the reaction rate is close to zero order in initial thiophene concentration and that the aromatic compound is essentially inert under these sets of circumstances.

DISCUSSION

HDS of Thiophene

The HDS of thiophene is inhibited by hydrogen sulfide, and a kinetic expression for this reaction on $CoMo/Al_2O_3$ catalyst was developed by Satterfield and Roberts (1968) from studies with a differential reactor. Present data for thiophene HDS alone could be most readily compared with that expression for studies at low fractional conversion (< 20%). These showed quite good agreement (Mayer, 1974).

Present data were insufficient to construct a complete kinetic model for HDS in the presence of pyridine. Nevertheless, certain features of a satisfactory model can be developed from the following considerations. The inhibition of thiophene HDS by pyridine is presumably caused by competition between these compounds for active sites on the catalyst. The pattern of inhibition can be interpreted in terms of a two-site model analogous to that of Desikan and Amberg (1964). It is postulated that two kinds of sites (Type I and Type II) on sulfided catalysts are capable of catalyzing the HDS reaction. Type I sites are postulated to be very active and to be responsible for the majority of the HDS activity with pure thiophene feedstocks but to be extremely sensitive to basic nitrogen compounds. In the absence of pyridine, the rate is approximately zero order in thiophene. In the presence of sufficient quantities of pyridine, these sites will be completely blocked and, therefore, inactive for HDS.

In terms of a Langmuir-Hinshelwood model, the results are consistent with the following rate expression:

$$r_I = \frac{k_I p_T}{1 + K_{I,T} p_T + K_{I,P} p_P} \times f(p_{H_2}) \qquad (3)$$

where $K_{I,T} p_T >> 1$, and $K_{I,P} p_P >> K_{I,T} p_T$. (For a more complete model a term for hydrogen sulfide should be included in the denominator, and the adsorptivity of hydrogen sulfide relative to thiophene and pyridine should be considered.)

Type II sites are postulated to have less HDS activity but to be less susceptible to poisoning, and therefore are responsible for the HDS activity of the catalyst after all Type I sites are blocked. Thiophene and pyridine probably compete for Type II sites, but the competition is less one-sided than on Type I sites.

Under moderate to high concentrations of pyridine, the rate of HDS is first order in thiophene and relatively insensitive to variations in pyridine concentration. These results are consistent with the following rate expression:

$$r_{II} = \frac{k_{II} p_T}{1 + K_{II,T} p_T + K_{II,P} p_P} \times f(p_{H_2}) \qquad (4)$$

where $K_{II,T} p_T << 1$ and $K_{II,P} p_P << 1$. The total rate of HDS is

$$r = r_I + r_{II} \qquad (5)$$

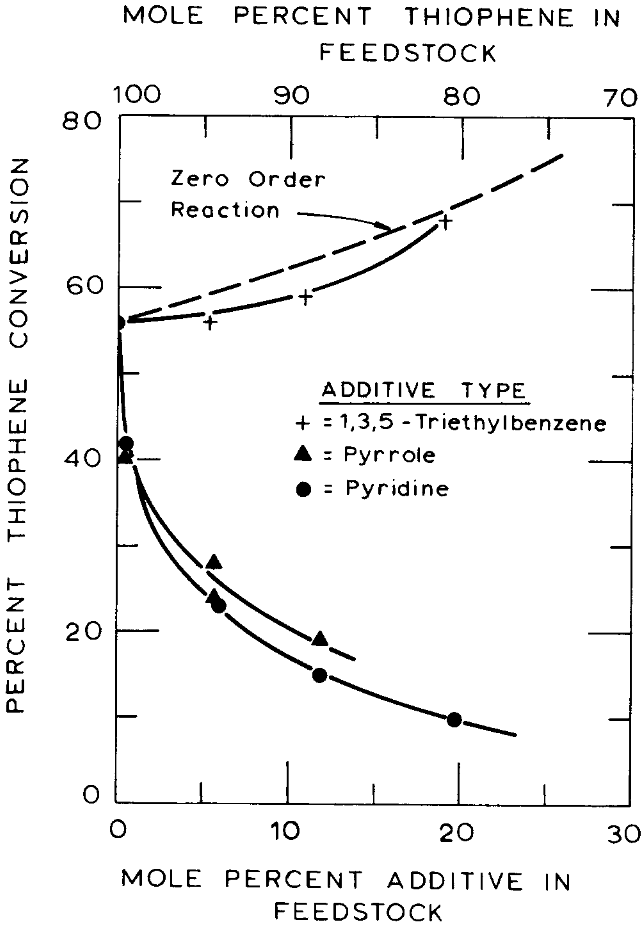


Fig. 8. Effect of additives on thiophene HDS at 300°C (other experimental conditions given in Table 2).

In the absence of pyridine, the Type I sites carry the reaction. That is, $k_I >> k_{II}$, or

$$r = \frac{k_I}{K_{I,T}} \times f(p_{H_2}) \qquad (6)$$

On the other hand, Type II sites are much less sensitive to pyridine poisoning. Thus, in the presence of pyridine

$$\begin{aligned} r &= \frac{k_I p_T}{K_{I,P} p_P} \times f(p_{H_2}) + k_{II} p_T \times f(p_{H_2}) \\ &\simeq k_{II} p_T \times f(p_{H_2}) \end{aligned} \qquad (7)$$

The inhibiting effects of pyridine on thiophene HDS found here follow the same trends observed by investigators studying the effects of nitrogen compounds on the HDS of real or simulated petroleum feedstocks. These results indicate that sulfur removal by HDS from feedstocks having a high nitrogen content will be more difficult than sulfur removal from conventional, low-nitrogen feedstocks. This means more severe and, consequently, more expensive processing conditions will be required, such as higher pressures, higher temperatures, and longer contact times.

HDN of Pyridine—Effect of Sulfur Compounds

The effect of sulfur compounds on pyridine HDN can be interpreted in terms of the reaction mechanism [Equation (2)] and the results of Goudriaan et al. (1973).

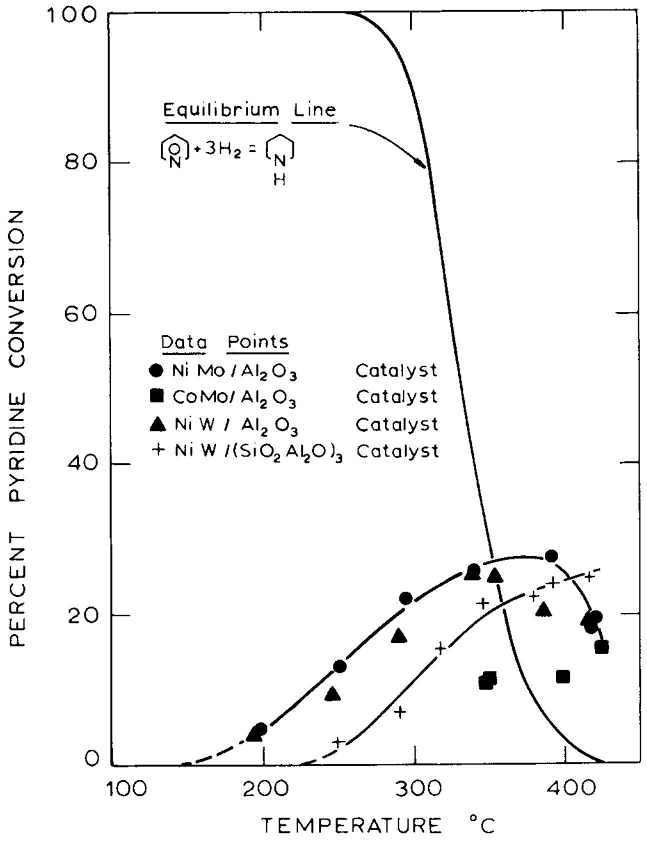


Fig. 9. Comparison of experimental and equilibrium pyridine conversion (experimental conditions given in Table 2).

Below approximately 325°C the rate of pyridine hydrogenation (Step 1) is postulated to influence the overall rate of reaction. Sulfur compounds such as thiophene or hydrogen sulfide can compete for hydrogenation sites on the catalyst, slowing down this important step in the reaction mechanism, resulting in an inhibition by thiophene of the pyridine conversion.

Above 325°C the overall rate of HDN is probably limited by the hydrogenolysis of piperidine (Step 3) rather than by hydrogenation of pyridine. At these temperatures we postulate that the dominant effect of hydrogen sulfide is to improve the activity of the catalyst for rupture of the C—N bond. This effect increases the speed of the rate limiting step and results in the increase of pyridine conversion observed with mixed feedstocks compared to a pure pyridine feed. The way in which hydrogen sulfide improves this hydrogenolysis activity is unknown. It may be by maintaining the catalyst in a fully sulfided and more active state. Cobalt-molybdenum-alumina catalysts lose sulfur on exposure to a high temperature reducing atmosphere (Tanatarov et al., 1972), an observation confirmed during this research. In the presence of sufficient hydrogen sulfide, however, the catalyst will remain fully sulfided. Alternatively, the effect of hydrogen sulfide may be due to its acidity. In this case the hydrogen sulfide molecules may aid in removing strongly adsorbed nitrogen compounds from the catalyst surface. This interpretation is consistent with the observations of other investigators who observed improved rates of HDN in the presence of hydrogen chloride gas (Madkour et al., 1969; McCandless and Berg, 1970).

HDN of Pyridine—Effect of Thermodynamic Equilibria

The curious drop in pyridine conversion with increasing temperature (Figure 5) can be explained by considering the influence of the thermodynamic equilibria for Steps 1 and 2 on the reaction. For the overall HDN reaction, there is no thermodynamic limitation on complete pyridine removal in the temperature and pressure range studied here. However, there is a severe equilibrium limitation in the first step in the reaction mechanism which may be responsible for the observed downturn in conversion. If hydrogenation (Step 1) is rate limiting, the piperidine formed will quickly react to products. However, if Steps 1 and 2 are fast relative to Step 3, pyridine and piperidine could approach chemical equilibrium.

A test of this hypothesis is to compare the thermodynamically predicted pyridine conversion for reactions 1 and 2 with the experimentally determined values, using known free energies (McCullough et al., 1957; Scott, 1971). Calculations were made for a reactant gas taken to be 1% pyridine and 99% hydrogen at 11 bars, the conditions used in the experiments with a pure pyridine feedstock. The results are shown in Figure 9 together with experimentally observed pyridine conversions for four different catalysts studied. The results for $NiMo/Al_2O_3$ and for NiW/SiO_2-Al_2O_3 are the same as those depicted on Figures 5 and 7. By taking the percent conversion at temperatures below 350°C as a measure of hydrogenation activity, on a weight basis the NiMo and NiW catalysts are the most active, the CoMo least, and NiW on an acidic support is less active than on an Al_2O_3 support.

Comparison of calculation with experiment indicates that thermodynamic equilibrium may indeed become a limiting factor. Above 325°C the equilibrium shifts increasingly in favor of pyridine at the expense of piperidine. The hydrogenolysis reaction can become starved of its reactant source, thus slowing piperidine removal and resulting in a decrease in pyridine conversion. Conversions greater than the equilibrium values in Figure 9 are possible because the hydrogenolysis reaction was neglected in calculating equilibrium conversions. All the alumina supported catalysts displayed the same pyridine conversion at 420°C, while the silica-alumina supported catalyst showed greater conversion at this temperature. This can be attributed to a slightly better hydrogenolysis activity of the silica-alumina support compared to pure alumina (Weisser and Landa, 1973*b*).

Although thermodynamic arguments can explain the observed downturn in fractional pyridine conversion at high temperatures, our evidence to support this interpretation comes primarily from an associated study reported on elsewhere (Satterfield and Cocchetto, 1975). Piperidine has been identified as a product of pyridine HDN (Beugeling et al., 1971), but was not detected in the present study because of analytical problems.

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NOTATION

k = intrinsic rate constant
K = adsorption coefficient
p = partial pressure

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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