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The Mechanism of Pyridine Hydrogenolysis on Molybdenum-Containing Catalysts

II. Hydrogenation of Pyridine to Piperidine

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The kinetics of pyridine hydrogenation was studied at high hydrogen pressures on a Mo–Al oxide and a Co–Mo–Al oxide catalyst. The rate equation was found to be $r = kP_{\mathrm{pyr}}P_{\mathrm{H_2}}{}^{n}/P_{\mathrm{pyr0}}$, in which n is 1.5 at 300 and 375°C and 1.0 at 250°C. This rate equation can be derived assuming strong adsorption of pyridine and its products with identical adsorption constants.

The (hydro)cracking of piperidine appears to have a low order in hydrogen, probably lower than 0.5.

The adsorption behavior of nitrogen bases and hydrogen on alumina and the molybdenum-containing catalysts was investigated by the gas chromatographic method. The adsorption of the nitrogen bases appeared to be very strong on both catalysts, and varied in the order piperidine > pyridine > ammonia.

Hydrogen also showed a strong adsorption. Hydrogen and nitrogen bases appeared to adsorb on different sites.

INTRODUCTION

In Part I (*1*) the preparation of a monolayer molybdena–alumina catalyst was discussed. Its activity for cyclohexane dehydrogenation and pyridine hydrogenolysis was compared with a cobalt-promoted molybdena–alumina catalyst. For the pyridine hydrogenolysis the product distributions were investigated as a function of the temperature. The same activity and selectivity pattern was found for both catalysts. This paper deals with the first step in the reaction scheme, namely the hydrogenation of pyridine. The reaction scheme can be simplified for this case into

$$\text{pyridine} \overset{k_1}{\rightleftharpoons} \text{piperidine} \xrightarrow{k_2} \text{consecutive products.}$$

Much work has been performed on the hydrogenolysis of thiophene in order to study the mechanism of the desulfurization process. However, only a little work has been published about the hydrogenolysis of pyridine and the mechanism of the hydrodenitrogenation process. Most hydrodenitrogenation 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 (*2–5*). Some authors investigated the hydrodenitrogenation process with the aid of model compounds like quinoline or pyridine (*6–9*). The catalysts used in these studies are mostly molybdenum-containing catalysts, e.g., the $CoO–MoO_3–Al_2O_3$ catalyst.

The overall order in nitrogen was found to be unity by many authors. This was the case for oil fractions containing different nitrogen compounds and for model compounds, mostly diluted with an organic solvent. The first order "rate constant," however, appears to be dependent on the nitrogen content of the feed (*3*, *9*). McIlvried (*8*) gives an explanation for this phenomenon by taking into account the strong adsorption of the reaction products on the catalyst. He studied the conversion of pyridine and piperidine on a sulfided catalyst containing nickel, cobalt and molybdenum on alumina. The nitrogen compounds were diluted with xylene (nitrogen level: 100–4000 ppm, $P_{N_0} = 10^3$–5×10^4 N/m^2). McIlvried showed that the conversion of *piperidine* could be described by an equation similar to

$$\text{reaction rate} = \text{constant} \times \frac{b_{\text{pip}} P_{\text{pip}}}{1 + b_{\text{xyl}} P_{\text{xyl}} + b_{\text{pip}} P_{\text{pip}_0}}.$$

in which P_{pip_0} = piperidine partial pressure at the reactor inlet

b_{xyl}, b_{pip} = adsorption constants for xylene and piperidine.

(The term $1 + b_{\text{xyl}} P_{\text{xyl}}$ in the denominator was represented as a constant in the equation given by McIlvried.)

This equation can be derived by assuming equally strong adsorption of piperidine and its products on the catalyst. McIlvried showed that the first order rate constants obtained by other authors were also inversely proportional to the nitrogen content of the feed (or partial pressure in the reactor).

The rate equation given above could not describe the conversion of *pyridine*. McIlvried concluded that equally strong adsorption of the nitrogen bases may occur on the cracking sites but not on the hydrogenation sites. Relatively very strong adsorption of ammonia on the hydrogenation sites could explain the results for the pyridine conversion.

The reaction order in hydrogen is not well known. Regarding the order of the denitrogenation reaction in respect to hydrogen, orders of 1 and 2 were reported (*4–5*). It is not clear whether these reaction orders apply for the hydrogenation reactions or for the (hydro)cracking reactions.

We investigated the hydrogenation of pyridine, ring opening and dehydrogenation of piperidine and the cracking and disproportionation of different amines, to obtain more information about the kinetics of the different reaction steps. The results of the hydrogenation of pyridine are presented in this paper together with the results of the adsorption experiments.

METHODS

Kinetic Measurements

The apparatus used for kinetic measurements has been described elsewhere (*10*). Besides the U-type reactor we used a stainless steel reactor of a smaller size (I-type). The diameter was also 6 mm. A separate experiment showed that the walls of the reactor did not show any important activity for the pyridine hydrogenation. The pyridine partial pressure at the reactor inlet and the composition of the products were analyzed by means of gas chromatography.

The reaction time t is defined as: $t = mP/\phi_t$ in which m = mass of catalyst (kg); P = total pressure (N/m^2); ϕ_t = total moles fed to the reactor (moles/sec).

Adsorption Measurements

Adsorption measurements were carried out by the method of Roginskii (*11*). Both the pulse method and the frontal method were applied. For the pulse experiments a stainless steel reactor (d_i = 4 mm) was used. A thermal conductivity detector and recorder were used for a continuous registration of the composition of the output gas flow. For the frontal method a U-type glass reactor (d_i = 9 mm) was used. The breakthrough curves were obtained by taking samples at the reactor outlet and analyzing them by gas chromatography.

In both methods the temperature of the catalyst (1–3 g) was constant within 1°C, both as a function of the time and the bed length. The carrier gas used in the experiments was either hydrogen or argon, deoxidized by a copper catalyst and dried by molecular sieves. The gas flow rate was 1.44 or 3.6 ml/sec. A constant partial pressure of pyridine in the carrier gas was obtained with the aid of two saturators. The second one was thermostated. Ammonia was added to the carrier gas from a cylinder. A constant gas flow rate of ammonia was obtained by maintaining a constant pressure drop over a capillary. The partial pressures of the adsorbates were determined by titration of the ammonia and by freezing out and weighing the pyridine; the accuracy was 2–3%.

Materials

The catalysts used were: γ-Al_2O_3 (213 m^2/g), 4% CoO–12% MoO_3–Al_2O_3 (Ketjenfine, 235 m^2/g) and 22% MoO_3–Al_2O_3 (195 m^2/g). The γ-Al_2O_3 catalyst contained 1% SiO_2, 0.8% SO_4, 0.06% Na_2O and 0.02% Fe. (The alumina (and Ketjenfine) were kindly supplied by Ketjen Amsterdam. Analysis data obtained from Ketjen.) The 22% MoO_3–Al_2O_3catalyst was prepared by slow adsorption of molybdate on γ-alumina at pH 1. The MoO_3–Al_2O_3 catalyst is considered to have a very extensive MoO_3 surface and a low Al_2O_3 surface (*1*). In all the experiments the catalysts were pretreated for more than 16 hr at 450°C in hydrogen.

RESULTS

Kinetics of Pyridine Hydrogenation

The reaction *order in pyridine* of the hydrogenation was determined by changing the reaction time and the initial pyridine partial pressure. A first order in pyridine was found by changing the reaction time. This was clearly demonstrated at three temperatures, viz, 270, 310 and 350°C (*12*). Experiments at constant reaction time and different initial partial pressures of pyridine showed a serious deviation of the first order behavior. An increasing conversion of pyridine was found at decreasing partial pressures of pyridine (Table 1). The first order constant k_1 of the pyridine hydrogenation appears to be inversely proportional to the pyridine pressure at the reactor inlet (Table 1).

Next to pyridine and piperidine, ammonia and *N*-pentylpiperidine were observed in the products. The last two were formed in more or less equimolar amounts. Pentylamine was not found. This indicates that the most important consecutive reaction is not the formation of pentylamine by the opening of the piperidine ring, but the disproportionation of two piperidine molecules into ammonia and *N*-pentylpiperidine (*10*). Assuming an apparent first order reaction in piperidine the reaction rate constant k_2 was calculated (Table 1). This "rate constant" also increases with decreasing initial partial pressure of pyridine.

The *order in hydrogen* of the pyridine hydrogenation was determined at 250, 300 and 375°C. By multiplying the apparent first order "rate constants" k_1 and k_2 by the initial partial pressure of pyridine, the corrected rate constants k'_1 and k'_2 were obtained. The composition of the products and these rate constants are presented in

TABLE 1
CONVERSION OF PYRIDINE ON THE CoO–MoO_3–Al_2O_3 CATALYST AS A FUNCTION OF THE INITIAL PYRIDINE PARTIAL PRESSURE[a]

Sequence of experiments:	7	2	6	5	4	3	8	1
P_{pyr_0} (10^5 N/m^2)	1.28	0.87	0.81	0.76	0.72	0.57	0.49	0.28
Pyridine (mole %)	64	53	49	48	40	37	33	12
Piperidine (mole %)	32	39	42	46	47	50	54	59
Consecutive products (mole %)	4	8	9	12	13	13	13	29
k_1[b](10^{-8} m^2 moles/kg N sec)	0.73	1.05	1.16	1.4	1.5	1.6	1.8	3.5
$k_1P_{pyr_0}$(10^{-3} moles/kg sec)	0.94	0.91	0.94	1.05	1.06	0.91	0.88	0.97
k_2[b](10^{-8} m^2 moles/kg N sec)	0.35	0.61	0.56	0.69	0.72	0.65	0.63	1.04

[a] $T = 300°C$; $P_{H_2} = 60 \times 10^5$ N/m^2, $t = 6.1 \times 10^7$ kg N sec/m^2 moles.

[b] The reaction scheme used was: pyridine $\overset{k_1}{\rightleftharpoons}$ piperidine $\xrightarrow{k_2}$ consecutive products.

TABLE 2

CONVERSION OF PYRIDINE AT 250, 300 AND 375°C AS A FUNCTION OF THE HYDROGEN PRESSURE[a]

Reaction conditions			Product compositoin			Rate constants	
	P_{H_2} (10^5 N/m²)	P_{pyr_0} (10^5 N/m²)	Pyridine (mole %)	Piperidine (mole %)	Consecutive products (mole %)	$k_1 P_{pyr_0} = k'_1$ (moles/kg sec)	$k_2 P_{pyr_0} = k'_2$ (moles/kg sec)
$T = 250°C$	15	0.75	92	7	1.3	5.8×10^{-5}	2.4×10^{-4}
7.5 g 22% MoO_3–Al_2O_3	30	0.59	80	17	3	1.2×10^{-4}	1.9×10^{-4}
	45	0.52	63	33	4	2.2×10^{-4}	1.1×10^{-4}
$t = 1.0 \times 10^8$ kg N sec/m² moles	60	0.41	54	42	4	2.3×10^{-4}	0.7×10^{-4}
$T = 300°C$	15	1.08	87	11	2.4	3.5×10^{-4}	0.9×10^{-3}
3.5 g CoO–MoO_3–Al_2O_3	30	1.08	63	31	6	1.1×10^{-3}	0.8×10^{-3}
	45	1.05	40	53	7	1.8×10^{-3}	0.6×10^{-3}
$t = 4.5 \times 10^7$ kg N sec/m² moles	60	1.07	29	54	17	3.1×10^{-3}	1.2×10^{-3}
$T = 375°C$	15	0.38	95	2.3	2.7	1.9×10^{-3}	3.5×10^{-2}
0.10 g 22% MoO_3–Al_2O_3	30	0.34	81	11	8	5.6×10^{-3}	2.8×10^{-2}
	45	0.40	73	19	8	9.2×10^{-3}	2.0×10^{-2}
$t = 1.44 \times 10^6$ kg N sec/m² moles	60	0.37	69	31	10	1.5×10^{-2}	1.4×10^{-2}
	61	0.58	64	27	9	1.9×10^{-2}	2.1×10^{-2}
	75	0.31	36	44	20	2.4×10^{-2}	1.4×10^{-2}

[a] The experiments at 300 and 375°C showed higher rate constants than normally obtained at these temperatures .The sequence of the experiments was at 375°C 60, 30, 15, 45, 75, 61 (10^5 N/m²), at 300°C 45, 60, 30, 15, 60 (10^5 N/m²) and at 250°C 30, 15, 45, 60 (10^5 N/m²). In the series at 250°C an intermediate reduction of the catalyst at 450°C was necessary before the Expt at 45 × 10^5 N/m² to avoid the influence of activity decline on the determination of the reaction order.

Table 2. The order in hydrogen of the ring hydrogenation was calculated by means of the least squares method. With a 90% confidence level the following values were obtained: 1.06 ± 0.40 at 250°C, 1.54 ± 0.21 at 300°C and 1.57 ± 0.15 at 375°C. There may be a possibility of 5% that the reaction order in hydrogen is the same at the three temperatures. However, taking into account the sequence of the experiments at 250°C a lower order in hydrogen for the pyridine hydrogenation at 250°C may be concluded. Other experiments support this conclusion.

The hydrogen pressure appears to have little effect on the rate of the piperidine hydrogenolysis. At 300 and 375°C a more or less constant value for k'_2 was obtained. At 250°C the k'_2 even seems to decrease with increasing hydrogen partial pressure. So it may be concluded that the order in hydrogen of the opening of the piperidine ring is about zero. However, only a rough estimate of the reaction order was possible due not only to the inaccuracy of the determination of the partial pressures of consecutive products but also because the conversion of piperidine turns out to be rather complex. For instance, piperidine is formed again from one of its products, namely *N*-pentylpiperidine (*10*). More experiments have to be carried out in order to formulate in detail the kinetics for the piperidine conversion.

Adsorption Measurements

Nitrogen Bases

We were not able to determine the isotherms for the adsorption of the nitrogen bases integrally due to several reasons. Gravimetric measurements showed already a maximum coverage of pyridine, on for instance the MoO_3–Al_2O_3 catalyst, at partial pressures of less than 10^3 N/m^2 (7 mm Hg). The pulse technique described by Roginskii (*11*) also failed due to the strong adsorption of the nitrogen bases, even at temperatures of 450°C. Moreover, several nitrogen compounds like piperidine or pentylamine reacted above 250°C.

With the pulse technique some qualitative results were obtained. An estimate of the heat of adsorption on the molybdena-alumina catalyst was possible by comparing the retention time for pyridine at 450°C and benzene at about 200°C. The ratio $\Delta H_{\text{pyr.ads}}/\Delta H_{\text{benzene.ads}}$ was found to be 1.5. From adsorption isotherms a value of 14 kcal/mole was calculated for the $\Delta H_{\text{benzene.ads}}$. Hence, the heat of adsorption for pyridine will exceed 20 kcal/mole. Hydrogen appeared to have little effect, if any, on the adsorption of pyridine and ammonia on the MoO_3–Al_2O_3 catalyst. Identical gas chromatographic curves were obtained using either hydrogen or helium as carrier gas.

With the aid of the frontal technique (*11*) the number of moles of nitrogen bases adsorbed per square meter (σ) was determined for the different catalysts. The results are given in Table 3. The values are characteristic for the maximum amounts chemisorbed (except for the value $\sigma = 1.63$ at $P_{\text{NH}} = 2.1$ mm Hg). However, only a part of the surface is covered by the nitrogen compounds (10^{-6} moles/m^2 = 160 Å^2/molecule). The total number of moles adsorbed per square meter appears to be the same for ammonia and pyridine. (Preliminary experiments carried out with piperidine showed that its adsorption is of the same order, viz, 2.4×10^{-6} mole/m^2 at 225°C on the 22% MoO_3–Al_2O_3 catalyst.) The amount adsorbed on the molybdena–alumina catalyst is about twice as high as for the alumina. The temperature did not appear to be an important variable for the amounts adsorbed. At a pyridine partial pressure of 3.75 mm Hg the values found at 350°C were only 10% less than at 300°C for all catalysts. At 400°C we obtained for the pyridine adsorption on the Ketjenfine catalyst the values 0.93×10^{-6} moles/m^2 at 3.75 mm Hg and 1.15×10^{-6} moles/m^2 at 8.7 mm Hg. Hence, even at high temperatures maximum adsorption of the nitrogen bases takes place at low partial pressures of the bases.

At the end of the adsorption experiments some information about the desorption was obtained by flushing the catalyst

TABLE 3

ADSORPTION OF PYRIDINE AND AMMONIA ON DIFFERENT CATALYSTS AT 300°C[a]

	Pyridine		NH_3	
	σ (10^{-6} moles/m^2)	P (mm Hg)	σ (10^{-6} moles/m^2)	P (mm Hg)
Al_2O_3	1.02	3.75	0.85	4.0
	0.95	8.7	0.83	6.25
$CoO-MoO_3-Al_2O_3$	1.21	3.75	—	—
22% $MoO_3-Al_2O_3$	1.78	3.75	1.63	2.1
	1.81	8.7	1.90	4.9

[a] The reproducibility is 3%. In comparing different catalysts the accuracy of the surface area determination has to be taken into account (3%).

with pure hydrogen. The amounts of pyridine or ammonia still adsorbed after different times of desorption are given in Table 4. The table shows that a part of the nitrogen compounds desorbed rather fast; a part did not desorb, even after flushing the catalyst for 18 hr. The values for the Ketjenfine catalyst are in between those for alumina and the monolayer MoO_3–Al_2O_3 catalyst. Similar experiments, carried out at higher temperatures, showed a decrease of the amounts adsorbed; for the CoO–MoO_3–Al_2O_3 catalyst the values 0.65 and 0.3 were obtained for desorption of pyridine at 400°C during 30 min and 18 hr, respectively. It may be stated that a part of the pyridine is irreversibly adsorbed. However, discussion about irreversible adsorption appears to be somewhat arbitrary because Fransen (*13*) in our laboratory has observed by ir spectroscopy that already at low temperatures desorption of the strongly chemisorbed molecules took place when other nitrogen compounds were present in the gas phase (*13*).

With the aid of the frontal method we also investigated the competitive adsorption of the nitrogen bases by supplying a mixture to the catalyst and analyzing the breakthrough curves. A typical curve is given in Fig. 1, from which the ratio of the mean b values of ammonia and pyridine was calculated assuming a Langmuir type of adsorption. The ratio of the amounts of pyridine and piperidine adsorbed equals $b_{\mathrm{pyr}}P_{\mathrm{pyr}}/b_{\mathrm{pip}}P_{\mathrm{pip}}$. The results are given in Table 5. Pyridine showed a stronger adsorption than ammonia on both alumina and the molybdena–alumina catalyst. This stronger adsorption was found at 300 and 400°C indicating that the mean heats of adsorption of both compounds only differ slightly. Piperidine, in its turn, showed a stronger adsorption than pyridine. The adsorption was measured at lower tempera-

TABLE 4

MOLES OF PYRIDINE AND AMMONIA STILL ADSORBED AFTER DIFFERENT TIMES OF DESORPTION[a]

	$\sigma_{\mathrm{pyridine}}$($10^{-6}$ moles/m^2)			σ_{NH_3}(10^{-6} moles/m^2)		
Time of desorption:	0 min	20 min[b]	18 hr[c]	0 min	20 min	18 hr[c]
Al_2O_3	1.0	0.6	0.3_5	0.8_5	0.5	0.1_5
$CoO-MoO_3-Al_2O_3$	1.2	1.0	0.5			
22% $MoO_3-Al_2O_3$	1.8	1.5	1.0	1.9	1.4_5	0.9_5

[a] $\phi_{H_2} = 3.6$ liters/hr, $T = 300$°C.

[b] After a desorption time of 20 min the rate of desorption was below the detection level (0.04 mm Hg).

[c] Analyzed by the Dumas-method.

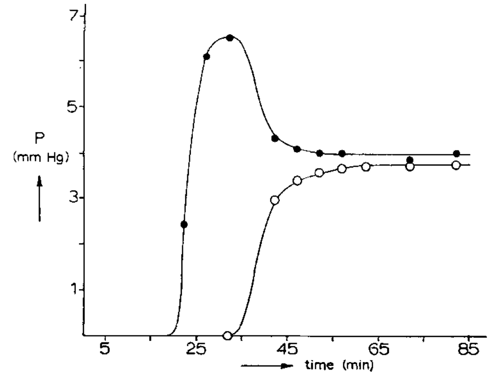

FIG. 1. Breakthrough curves obtained by supplying continuously both ammonia and pyridine to 1 g of the 22% MoO_3-Al_2O_3 catalyst (T = 300°C, ϕ_{Ar} = 0.45 ml/sec); (○)pyridine, (●) ammonia.

tures to avoid the decomposition of the piperidine.

Hydrogen Adsorption

Hydrogen chemisorption was also investigated with the pulse technique. Mostly this technique is used to determine adsorption isotherms, e.g., by Roginskii (*11*); the establishment of the adsorption equilibrium is one of the most essential points in this method. We demonstrated that this pulse method also can be used to determine the rate of adsorption, if the adsorption is far from equilibrium. The method is semiquantitative and has the advantage, in comparison with the usual volumetric technique, that the effect of other compounds, e.g., nitrogen bases, on the rate of hydrogen chemisorption can easily be investigated. In a future paper we intend to publish details of this method.

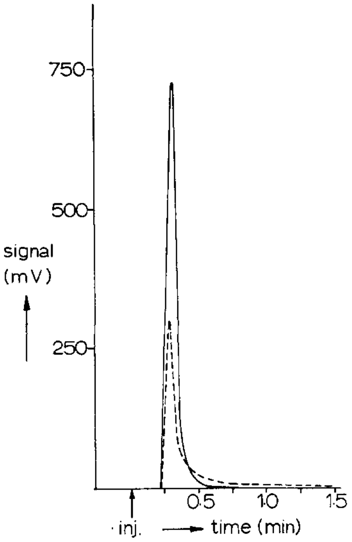

FIG. 2. Breakthrough curves obtained after injection of pulses of 0.76 ml hydrogen on 2.73 g catalyst (T = 350°C; ϕ_{Ar} = 1.0 ml/sec; p_{Ar} = 10^5 N/m²); (—) 4% CoO-Al_2O_3; (- - -) 4% CoO-12% MoO_3-Al_2O_3.

Typical curves obtained after injection of hydrogen are given in Fig. 2. The CoO-Al_2O_3 catalyst did not show adsorption of the hydrogen: injection of helium gave the same type of curve. The curve for the CoO-MoO_3-Al_2O_3 catalyst showed a lower peak height indicating that adsorption of hydrogen takes place. The decrease in peak height is related to the rate of chemisorption.

By varying the temperature, the volume of the hydrogen pulse, and the composition of the carrier gas, the following results were obtained. Above 250°C the

TABLE 5

RELATIVE ADSORPTION CONSTANTS OF THE NITROGEN BASES

	Catalyst	Temp (°C) 245	300	400
$b_{pyridine}/b_{NH_3}$	Al_2O_3		4.7	
$b_{pyridine}/b_{NH_3}$	22% MoO_3-Al_2O_3		4.3	4.2
$b_{piperidine}/b_{pyridine}$	22% MoO_3-Al_2O_3	6.1		
$b_{piperidine}/b_{pyridine}$	22% MoO_3-Al_2O_3	6.8[a]		

[a] In this case the method was slightly different. A mixture of pyridine and piperidine was added to the catalyst which already contained the maximum amount of piperidine adsorbed. Desorption of a part of this piperidine took place. The temperature was 225°C.

chemisorption of hydrogen was observed; the rate of chemisorption increases with increasing temperature. The hydrogen chemisorption was found to have a low order in hydrogen (<1). The presence of ammonia and pyridine in the carrier gas appears to increase the rate of hydrogen chemisorption on the CoO–MoO_3–Al_2O_3 catalyst, but did not have any effect on the MoO_3–Al_2O_3 catalyst. Hence, the strongly bonded nitrogen bases do not poison the hydrogen chemisorption. The conclusion can be drawn that hydrogen and the nitrogen bases adsorb on different, perhaps neighboring, sites.

DISCUSSION

The Order of the Reaction in Pyridine

The results given in Table 1 indicate that for the hydrogenation of pyridine the same applies as described in literature for the denitrogenation process, namely an apparent first order process with a reaction rate constant which is dependent on the initial partial pressure of the nitrogen compound. The model of the equally strong adsorption of reactant and products can explain this result, as was shown by McIlvried (*8*). Based on the assumptions of a first order reaction $A \rightarrow B$ and Langmuir type adsorption of A and B the following rate equation applies:

$$-\frac{dP_A}{dt} = \frac{k_A b_A P_A}{1 + b_A P_A + b_B P_B}, \qquad (1)$$

b_A, b_B = adsorption constants of compounds A and B (m^2/N); $P_A P_B$ = partial pressures of A and B (N/m^2).

Integration of this equation gives ($P_{B_0} = 0$):

$$\ln\frac{P_{A_0}}{P_A} = \frac{kb_A t - (b_A - b_B)(P_{A_0} - P_A)}{1 + b_B P_{A_0}}. \qquad (2)$$

From this correlation it follows that equally strong adsorption of A and B gives a first order reaction with a "reaction rate constant" depending on the initial partial pressure of A:

$$\ln\frac{P_{A_0}}{P_A} = \frac{kb_A t}{1 + b_A P_{A_0}}. \qquad (3)$$

If $b_A P_{A_0} \gg 1$ the equation may be simplified to:

$$\ln\frac{P_{A_0}}{P_A} = \frac{kt}{P_{A_0}}. \qquad (4)$$

In Fig. 3 the data from Table 1 have been plotted as $t/\ln(P_{A_0}/P_A)$ as a function of P_{A_0} in order to test whether Eq. (3) or (4) applies for the pyridine hydrogenation. It appears that the intercept practically equals zero. Hence, the ring hydrogenation of pyridine can be described by Eq. (4). The kinetics support the supposition of the equally strong adsorption of pyridine and

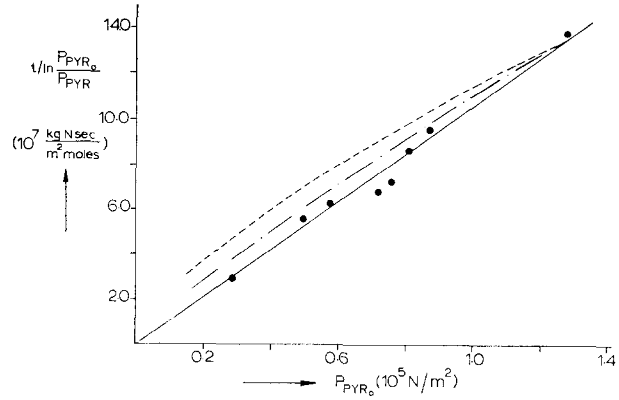

FIG. 3. Plot to test Eq. (3) for the pyridine hydrogenation (see also Table 1); (—) line calculated by means of the least squares method; (– · –) line calculated by means of Eq. (2) assuming $b_B/b_A = 2$; (- - -) line calculated by means of Eq. (2) assuming $b_B/b_A = 5$; (A = pyridine, B = piperidine; $b_A P_A \gg 1$; the reaction rate constant was calculated from the point at $P_{pyr_0} = 1.28 \times 10^5\ N/m^2$).

piperidine. Figure 3 shows that curved lines have to be expected when the adsorption constants differ. The figure suggests the ratio b_{pip}/b_{pyr} to be smaller than two.

McIlvried showed that an equation similar to Eq. (3) very well describes the conversion of piperidine. A less strong adsorption of the nitrogen bases on his catalyst compared with our catalyst might be concluded.

The adsorption experiments can give evidence on the application of Eq. (3) or (4). Table 3 shows that at 300°C and a partial pressure of pyridine or ammonia of $\sim$4 mm Hg (500 N/m^2) at least 90% of the maximum adsorption was obtained; this means that $b_{\text{N-bases}} > 10^{-2}$ m^2/N, if a Langmuir type adsorption is assumed. The kinetic experiments were carried out at a pyridine partial pressure of $>10^4$ m^2/N. $b_{pyr}P_{pyr}$ amounts therefore to $>10^2$, so the adsorption data show that in our case Eq. (4) is principally correct. The reason that Eq. (4) failed to describe the piperidine conversion of McIlvried is not due to a less strong adsorption of piperidine on his catalyst but to the presence of xylene in the feed. The intercept for this case is $(1 + b_{xyl}P_{xyl})/kb_{piP}$. From his results we calculated a value of 3×10^{-3} for the ratio b_{xyl}/b_{pip}; this corresponds to a difference in the heat of adsorption of about 7 kcal/mole. We found about the same value for the difference in heat of adsorption of pyridine and benzene in our experiments.

If the relation between the kinetics and the adsorption data is studied in greater detail a problem arises. The assumption between Eq. (2) and (3), namely, equal values for the adsorption constants of the nitrogen bases, is supported by the kinetics (Fig. 3), but is not in accordance with the results of the adsorption measurements (Table 5). The b value for piperidine appeared to be about 6 times as high as the value for pyridine which in its turn was 4 times as high as the b value for ammonia. The ratio b_{pyr}/b_{NH_3} was found to be the same at 300 and 400°C; hence the quotients of the b values may be only slightly dependent on the temperature.

A possible explanation for the discrepancy may be the following. Desorption experiments reported above as well as infrared spectroscopic measurements of the pyridine adsorption (*13*) point to a strong heterogeneity of the catalyst surface. The Langmuir type adsorption will therefore certainly only be a rough approximation of the adsorption behavior of the nitrogen bases on the MoO_3–Al_2O_3 catalyst. The molybdena surface may only be partly active in the pyridine hydrogenation.

Till now we did not discuss the results McIlvried obtained for the pyridine hydrogenation. He observed a deviation of the first order kinetics for this reaction (Fig. 3 in Ref. (*9*); P_{pyr_0} was kept constant). He concluded that there was a very strong adsorption of ammonia on the hydrogenation sites of his sulfided catalyst, which will have separate hydrogenation and cracking sites. However, we did not find evidence for a stronger adsorption of ammonia than of pyridine. The deviation of the first order in pyridine for the pyridine hydrogenation can be explained by the fact that some of their measurements were too close to the equilibrium of pyridine, piperidine and hydrogen. He neglected to take into account the reverse reaction.

The Order of the Reaction in Hydrogen

The order in hydrogen of the pyridine hydrogenation was 1.0 at 250°C and 1.5 at 300 and 375°C. Lipsch and Schuit (*14*) also observed at about the same temperature a change in the hydrogen order for butene hydrogenation on CoO–MoO_3–Al_2O_3. An explanation cannot yet be given. It was shown that the observed activity decline and the inaccuracy in the determination of the equilibrium constant of the pyridine–piperidine equilibrium (*12*) did not have an important effect on the observed order in hydrogen. The effect of diffusion limitation was also examined. Calculations showed that the influence of internal diffusion on the rate of hydrogenation is very small. Moreover, this effect will decrease the reaction order.

For the calculation of the order in hydrogen we assumed that the hydrogen pressure was an independent variable in the rate equation. Investigations into the chemisorption of hydrogen and of the N-bases support this view. The ammonia and pyridine adsorption was not affected by hydrogen (between 0 and 1 atm). The nitrogen bases were shown to have some effect on the hydrogen chemisorption. However, it has not to be expected that this interferes with the determination of the order in hydrogen because this effect could only be found at very low partial pressures of the nitrogen compounds.

Preliminary results indicate that the hydrogen chemisorption is not rate determining for the pyridine hydrogenation at temperatures above 250°C. The relation between the hydrogen chemisorption and the change in the kinetics of the pyridine hydrogenation will be subject of further research.

Several problems arise when comparing our results with literature data. First, the catalysts are different. However, in our laboratory we found that the kinetics of pyridine hydrogenation were similar on oxidic and sulfidic catalysts (*12*). Secondly, the interference of other products may be important; Rosenheimer and Kiovsky (*5*) reported even the presence of liquid in their reactor.

The order in hydrogen reported by Wilson, Voreck, and Malo (*4*) and by Rosenheimer and Kiovsky (*5*) was obtained by following the decrease of the nitrogen content as a function of the hydrogen pressure. It is not clear whether the order applies to the ring hydrogenation or the ring opening reaction. Assuming a reaction scheme

$$3H_2 + A \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} B \xrightarrow{k_2} C,$$

n_1 as the order in hydrogen of the first reaction and n_2 as the order in hydrogen for the second reaction, the following possibilities may be present.

The first reaction is rate determining: order in hydrogen of the denitrogenation reaction is n_1.

The second reaction is rate determining: the dependence of the denitrogenation rate on the hydrogen pressure will be

$$\frac{KP_{H_2}{}^{(3+n_2)}}{1 + KP_{H_2}{}^{3}}$$

(K = equil. const. of the first step).

Therefore experimentally an order in hydrogen in between n_2 and $3 + n_2$ may be found depending on the value of the equilibrium constant.

Calculation on the piperidine–pyridine equilibrium showed that some of the experiments of the investigators of the denitrogenation process were performed at

TABLE 6

Comparison of Reaction Orders in Hydrogen, Found by Several Investigators

		Order in hydrogen of		
Authors	Denitrogenation of	Pyridine hydrogenation	Piperidine (hydro)cracking	Denitrogenation
This work	Pyridine	1.5	≈0	
McIlvried (*8*)	Pyridine	2–3[a]		
McIlvried (8)	Piperidine		≈0[b]	
Wilson, Voreck, and Malo (*4*)	Me-isoquinoline in naphtha			1
Rosenheimer and Kiovsky (*5*)	Cracked diesel oil			2
Flinn, Larson, and Beuther (*2*)	Cracked light furnace oil			2–3[c]

[a] Calculated by us from two experiments far from the pyridine-piperidine equilibrium.

[b] Calculated by us from the last three lines of the upper section of Table 1 of McIlvried's paper.

[c] Calculated by us from Fig. 3 of the paper of Flinn, Larson, and Beuther (*2*).

reaction conditions in which the hydrogenation equilibrium might be on the side of the aromatics. Depending on the rate determining step an order in hydrogen of n_1 or in between n_2 and $3 + n_2$ has to be expected.

In Table 6 the orders in hydrogen are summarized. The table shows that our conclusions are in agreement with the results of McIlvried: the hydrogenation has a high order in hydrogen and the ring opening reaction has a low order in hydrogen. Different orders in hydrogen for the denitrogenation process were found. The hydrogenation of the aromatic ring as well as the ring opening may be rate determining; in the last case the position of the hydrogenation equilibrium may influence the rate of denitrogenation.

CONCLUSIONS

1. The kinetics for the pyridine hydrogenation are

$$-\frac{dP_{\mathrm{pyr}}}{dt} = k\,\frac{P_{\mathrm{pyr}}P_{\mathrm{H_2}}{}^{n}}{P_{\mathrm{pyr_0}}}$$

($n = 1.0$ at 250°C and 1.5 at 300–375°C).

2. The dependence of the hydrogenation rate on the pyridine partial pressure can be derived assuming strong adsorption of pyridine and its products on the catalyst; the adsorption constants (b values) have to be equal.

3. Adsorption experiments support the conclusion concerning the strong adsorption of the nitrogen bases, but failed to demonstrate the equally strong adsorption of the bases. The strength of adsorption was found to be piperidine > pyridine > ammonia.

4. The order in hydrogen of the ring opening was found to be low (<0.5).

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