Rate and Mechanism of Ruthenium-Catalyzed Hydrogenation of Pyridine in Slurry Reactors

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The hydrogenation of pyridine (C_5H_5N) at 330–930 psia of hydrogen, 140–240°C, was studied using unsupported Ru powder (<120 mesh) as catalyst in slurry reactors. Pyridine was hydrogenated completely to piperidine ($C_5H_{11}N$) with no other partially hydrogenated pyridine bases under present conditions. Kinetic studies show that there is a shift in the controlling mechanism from chemical control in the lower temperature region ($\Delta E_{app}^* = 14$ kcal/mol, <200°C) to mass transfer control in the higher temperature region ($\Delta E_{app}^* < 6$ kcal/mol, >200°C). The observed reaction rate at 170°C can be best described by the rate equation: $r = (k_s K_H K_{py} C_H C_{py})/(1 + K_H C_H) (1 + K_{py} C_{py} + K_{pi} C_{pi})$. The rate-limiting step for the surface reaction control region may involve the surface reaction between adsorbed pyridine and adsorbed hydrogen on two different active sites. The true activation energy was estimated to be about 44 kcal/mol.

INTRODUCTION

The catalytic hydrogenation of pyridine (C_5H_5N) to piperidine ($C_5H_{11}N$) is a system of great interest: it is the first step for hydrodenitrogenation on metal oxides catalysts (*1*), and the reaction itself is of industrial significance since piperidine is a versatile chemical.

The kinetics of catalytic hydrogenation of gaseous pyridine has been studied using Co–Mo/γ-Al$_2$O$_3$ as catalyst and the rate equation was described by Eq. (1),

$$-\frac{dP_{py}}{dt} = \frac{kK_{py}P_{py}P_H{}^a}{1 + K_{py}P_{py} + \Sigma K_{prod.}P_{prod.}} \quad (1)$$

where K is the equilibrium absorption constant, P is the partial pressure, and k is a surface reaction rate constant. The reaction order of hydrogen ($P_H{}^a$) was reported to be about 1.0–1.6 (*2, 3*). The rate-limiting step of the gas phase hydrogenation of pyridine was proposed by Sonnemans *et al.* (*3*) to be

the uptake of hydrogen atom by the adsorbed dihydropyridine intermediate (C_5H_7N). This conclusion is contradictory to the general belief that the most difficult step should involve the addition of first hydrogen molecule to the stable aromatic ring (*4*). It is the aim of this study to search for a more acceptable reaction mechanism.

On the other hand, the hydrodenitrogenation of petroleum is usually conducted in high-pressure trickle-bed reactors; and the large-scale hydrogenation of pyridine to yield piperidine can only be economically accomplished in slurry reactors. Consequently, this research was carried out in slurry reactors to investigate the kinetics of high-pressure pyridine hydrogenation.

EXPERIMENTS

An 600 rpm agitated 600 ml Parr mini reactor (model 4563) equipped with temperature controller and modified sampling system was used for this research (Fig. 1). Hydrogenation was started by charging the reactor with 160 ml of chemically pure pyridine liquid and an appropriate amount of RuO$_2$ powder (<120 mesh). Air was flushed out of the reactor with low-pressure hydro-

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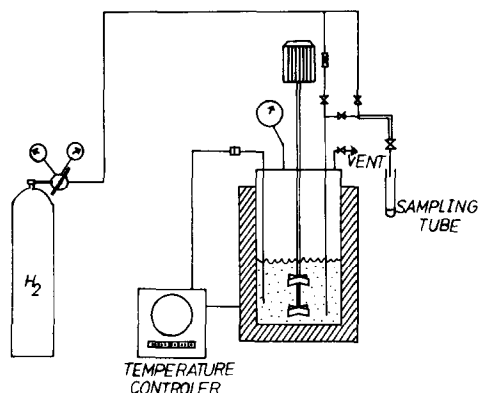
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FIG. 1. Experimental apparatus for the hydrogenation of pyridine.

FIG. 2. The concentration profile of pyridine vs reaction time.

gen, after which the inlet valve was closed and heating commenced. When the designated temperature was reached, hydrogen was fed to the predetermined pressure which was maintained throughout the reaction. During a reaction, about eight samples, 2 ml of each, were withdrawn periodically for analysis of pyridine and piperidine ratio by gas chromatograph. The GC column used was Carbowax 20 M on Chromosorb P 80-120 mesh.

A polynomial equation of the form (7)

$$C_{py} = a + bt + ct^2 \qquad (2)$$

was fitted to the data for each set of conditions. Differentiation of the best fit equation gave directly the hydrogenation rate $r(-dC_{py}/dt)$. The values of the initial rate r_0 and specific rate r_x at certain conversion yield were obtained by calculating the rates at the initial concentration (i.e., $t = 0$) or the designated concentration of pyridine.

RESULTS

Porous ruthenium oxide RuO_2 powder (<120 mesh), whose surface area was measured by BET method to be approximately 13 m²/g, was used as starting catalyst (5). It was assumed that the *in situ* reduced ruthenium metal might provide exact geometric configuration to adsorb pyridine (6). The exclusion of the γ-Al_2O_3 catalyst support was to minimize the weak interaction be-

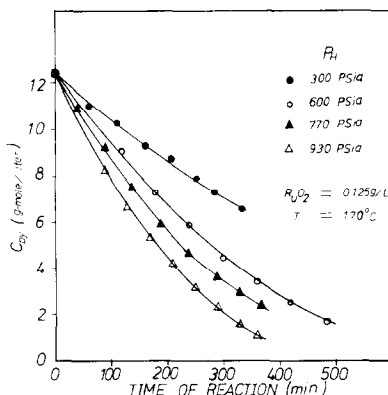tween the support and the pyridine base and to avoid a cracking reaction.

Figure 2 shows a representative concentration change of pyridine as hydrogenation proceeded. It is clear that the reaction rate diminished gradually. The possibility of catalytic activity decay was excluded by the following observation: the ruthenium catalyst, isolated by the end of one reaction, preserved at least 90% initial activity for another batch of pyridine. The only detectable product was piperidine in the present research.

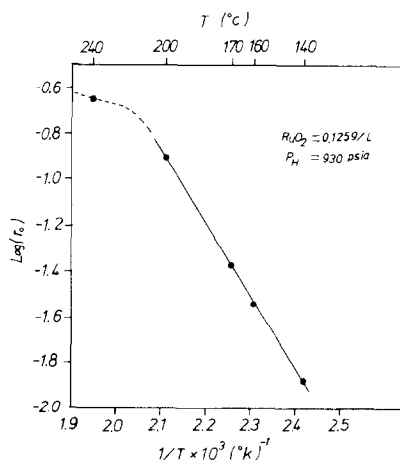The surface reaction controlled regime of ruthenium catalyzed hydrogenation of pyri-

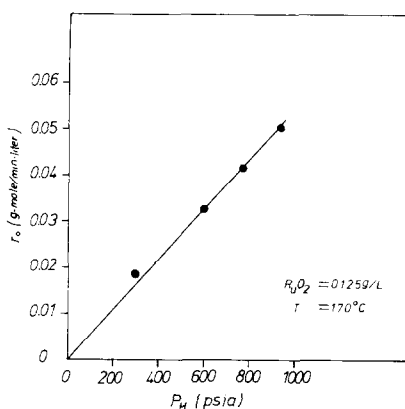FIG. 3. Arrhenius plot of ruthenium-catalyzed pyridine hydrogenation initial rates.

FIG. 4. Hydrogen pressure effect on the initial hydrogenation rate.

dine was determined. An Arrhenius plot of initial reaction rate r_0 vs $1/T$ is presented in Fig. 3 at constant catalyst loading of 0.125 g/l. It can be seen that there is a shift in the controlling mechanism from chemical control in the lower temperature region to mass transfer control in the higher temperature region. Apparent activation energies in the two temperature regions were estimated to be 14 kcal/mole (140–200°C) and less than 6 kcal/mol (200–240°C), respectively. Therefore, the following experiments were carried out at 170°C to study the kinetic model and the corresponding reaction mechanism.

The hydrogen pressure effect was observed to be first order at 330–930 psia at 170°C (Fig. 4). Moreover, the initial reaction rates were linearly dependent on the catalyst loading below 0.375 g/l and then gradually levelled off (Fig. 5).

KINETIC ANALYSIS

The purpose of this research is to develop an acceptable reaction mechanism of ruthenium-catalyzed pyridine hydrogenation. A variety of kinetic model and mechanism had been tested, but only one Langmüir–Hinshelwood type model was found to fit the experimental data and will be developed below as illustration.

The observation of reaction rate reduction can be rationalized by the competition

of piperidine (product) and pyridine (reactant) for the same active site. It was reported that the adsorption of pyridine and hydrogen occurs on different active sites (3). Therefore, it was assumed that there are two active sites, one for hydrogen and the other for pyridine and piperidine. One of the rate expressions fitting to this model can be expressed as Eq. (3).

$$r = - \frac{dC_{py}}{dt} = \frac{dC_{pi}}{dt}$$

$$= \frac{k_s K_H K_{py} C_H C_{py}}{(1 + K_H C_H)(1 + K_{py} C_{py} + K_{pi} C_{pi})} \quad (3)$$

where K_{py}, K_{pi}, and K_H are the equilibrium adsorption constants for pyridine, piperidine, and hydrogen, C_{py} and C_{pi} are the pyridine and piperidine concentrations, C_H is the dissolved hydrogen concentration which was assumed to be governed by Henry's law ($C_H = \beta_H \times P_H$), and k_s is the surface reaction rate constant.

The observed first order for hydrogen pressure implies that the $K_H C_H$ term in the denominator of Eq. (3) may be much less than one under the present reaction conditions.

If the only product is piperidine as experimentally observed, C_{pi} can be substituted by ($C_{py0} - C_{py}$). C_{py0} is the initial pyridine concentration which was calculated to be 12.44 M under STP conditions (8).
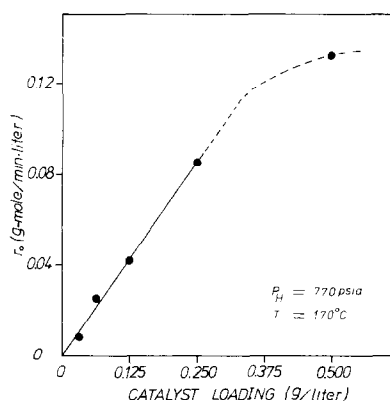

FIG. 5. The effect of ruthenium catalyst loading on the initial hydrogenation rate.

Equation (3) may be rearranged to give Eq. (4),

$$\frac{C_{py}}{r} = \frac{(1 + K_H C_H)(1 + K_{pi} C_{py0})}{k_s K_H K_{py} C_H}$$

$$- \frac{(1 + K_H C_H)(K_{py} - K_{pi})}{k_s K_H K_{py} C_H} C_{py} \quad (4)$$

which can be used to test the validity of the proposed kinetic model by plotting (C_{py}/r) vs C_{py} under constant hydrogen pressure which should yield a straight line. The plot is presented in Fig. 6 which shows a linear relationship.

The rate Eq. (3) of the proposed model may be rewritten as Eq. (5) in terms of fraction conversion X instead of concentration.

FIG. 6. The plot of (C_{py}/r) vs C_{py} as determined by Eq. (4).

$$r = \frac{(1 - X)}{\dfrac{(1 + K_H \beta_H P_H)(1 + K_{py} C_{py0})}{k_s K_{py} K_H \beta_H P_H C_{py0}} + \dfrac{(1 + K_H \beta_H P_H)(K_{pi} - K_{py})}{k_s K_{py} K_H \beta_H P_H} X} \quad (5)$$

where C_H is expressed as $\beta_H P_H$. Equation (5) can be recast as

$$r = \frac{(1 - X)}{C_1 + C_2 X} \quad (6)$$

where C_1 and C_2 are $1/r_0$ and $((1 - X)/r - 1/r_0)(1/X)$, respectively. C_2 values can therefore be obtained by calculating r_0, r, and X values.

The values of C_2 can also be expressed as Eq. (7),

$$C_2 = \frac{(1 + K_H \beta_H P_H)}{k_x \beta_H P_H} \quad (7)$$

which can be rearranged as Eq. (8)

$$C_2 = \left(\frac{1}{k_x \beta_H}\right)\left(\frac{1}{P_H}\right) + \frac{K_H}{k_x} \quad (8)$$

where constant k_x represents $(K_{pi} - K_{py})/(k_s K_{py} K_H)$.

Figure 7 shows the expected linear relationship between representative C_2 and $1/P_H$ for the proposed kinetic model. It is noted that the C_2 parameter is dependent on
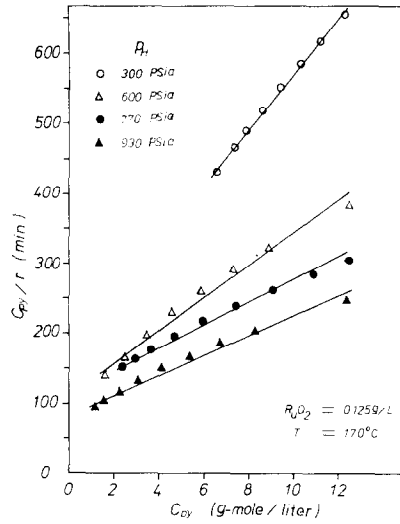
Henry's constant β_H and should be affected by the solution composition. The solution composition is gradually changed from pure pyridine to piperidine as the reaction proceeds.

If Eq. (4) is simplified to Eq. (9),

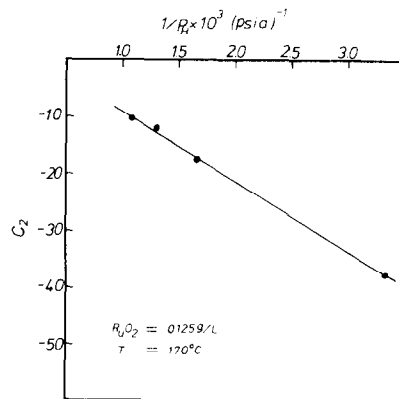$$r \simeq \frac{k_y C_{py} P_H}{1 + K_{py} C_{py} + K_{pi} C_{pi}} \quad (9)$$

FIG. 7. The plot of C_s vs $1/P_H$ as determined by Eq. (8) at $C_{py} = 0.8$ g-mol/liter.

where k_y is $(\beta_H k_s K_H P_H)/(1 + \beta_H K_H P_H)$. Regressional analysis (7) yielded $K_y = 2.1 \times 10^{-4}$ min^{-1} atm^{-1}, $K_{py} = 0.177$ liter/g-mol, and $K_{pi} = 0.009$ liter/g-mol at 170°C with average deviation of 10.8%.

Other rate expressions ranging from surface reaction-controlled to adsorption-controlled kinetic models were also analyzed by the above method and were all inferior to the proposed kinetic model Eq. (3).
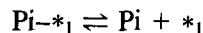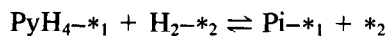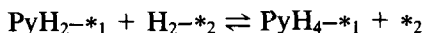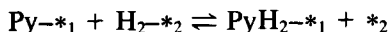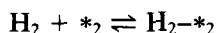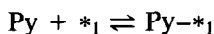
Nevertheless, the estimated activation energy 14 kcal/mol of chemical reaction control regime seems to be relatively small for aromatic nitrogen-containing compounds. This may be explained by the complex kinetic form of Eq. (3) which can be simply reduced to Eq. (10).

$$r_0 \simeq (0.68)k_s K_H C_H \qquad (10)$$

by assuming $1 \gg K_H C_H$ and $K_{py}C_{py0}$ equals $0.177 \times 12.44 = 2.20$ by substituting K_{py} and C_{py0} values into Eq. (3) for initial rates. The term $K_{pi}C_{pi}$ is negligible under initial conditions. Equation (10) reflects the fact that the observed apparent activation energy, derived from the r_0 vs $1/T$ plot, should be composed of surface reaction energy (k_s) and hydrogen adsorption energy (K_H). The hydrogen adsorption energy on noble metals were estimated to be approximately 30 kcal/mol (10). Therefore, the true activation energy of ruthenium-catalyzed hydrogenation of pyridine should exceed 14 kcal/mol to reach 44 kcal/mol. This value is high enough to open an aromatic ring compound such as pyridine whose resonance energy was reported to be 31.9 kcal/mol (11).

CONCLUSION

The foregoing analysis indicates that the most plausible mechanism to fit the proposed kinetic model (Eq. (3)) can be represented as follows,

$$Py + *_1 \rightleftharpoons Py\text{--}*_1$$

$$H_2 + *_2 \rightleftharpoons H_2\text{--}*_2$$

$$Py\text{--}*_1 + H_2\text{--}*_2 \rightleftharpoons PyH_2\text{--}*_1 + *_2$$

$$PyH_2\text{--}*_1 + H_2\text{--}*_2 \rightleftharpoons PyH_4\text{--}*_1 + *_2$$

$$PyH_4\text{--}*_1 + H_2\text{--}*_2 \rightleftharpoons Pi\text{--}*_1 + *_2$$

$$Pi\text{--}*_1 \rightleftharpoons Pi + *_1$$

in which two different active sites $\overset{*}{1}$ and $\overset{*}{2}$ are required to hydrogenate pyridine. Both pyridine and piperidine compete for the same active site. The rate-limiting step under the present reaction conditions is believed to involve the surface reaction between the adsorbed pyridine and adsorbed hydrogen to generate an PyH$_2$ intermediate which is subsequently hydrogenated rapidly to yield piperidine. Both PyH$_4$ and PyH$_2$ intermediates should not be released from the catalyst surface and are more easily hydrogenated than pyridine itself. This mechanism may well represent the Ru catalyzed hydrogenation of pyridine in slurry reactors.

APPENDIX 1: NOMENCLATURE

C Concentration in solution (g-mol/liter)
C_1 $1/r_0$
C_2 $((1 - X)/r - 1/r_0)(1/X)$
H Hydrogen
k Reaction rate constant
K Equilibrium adsorption constant
k_x $(K_{pi} - K_{py})/(k_s K_{py} K_H)$
k_y $(\beta k_s K_H K_{py})/(1 + \beta K_H P_H)$
p Pressure (psi)
pi Piperidine (C$_5$H$_{11}$N)
py Pyridine (C$_5$H$_5$N)
r Reaction rate (g-mol/liter-min)
r_0 Initial reaction rate
s Surface
t Time (min)
T Temperature (°C, °K)
X Conversion
β Solubility constant (Henry's law)

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