THE KINETICS OF PYRIDINE FORMATION FROM TETRAHYDROFURFURYL ALCOHOL OVER Pd/γ-Al$_2$O$_3$

Joo Hong Choi, Hong Dae Kim* and Wha Young Lee**

Dept. of Chem. Eng., Kyeongsang National University, Chinju 660-701, Korea
*Technical Service Lab., Yukong Ltd., Co., Ulsan 680-130, Korea
**Dept. of Chem. Eng., Seoul National University, Seoul 151-742, Korea

Abstract—A kinetic study of pyridine formation from tetrahydrofurfuryl alcohol over Pd/γ-Al$_2$O$_3$ was carried out in a differential flow reactor. The best expression for the main reaction was determined from the experimental data. The rate was governed by the irreversible surface reaction between the dissociatively adsorbed ammonia on the hydrogenated surface and molecularly adsorbed tetrahydrofurfuryl alcohol.

INTRODUCTION

Synthesis of pyridine from tetrafurfuryl alcohol (THFA) has been studied over the transition metal catalysts supported on the acidic metal oxide. The product distribution was widely dependent on the catalysts and reaction condition. The base transition metals such as Cr [1], Cu or Ni [2] supported on alumina and a fused iron promoted by vanadium pentoxide or chromic oxide yield mainly piperidine as the main product. So further dehydrogenation process is required for pyridine synthesis. Manly [4] reported Pd/alumina enhanced the yield of pyridine. And recently Choi and Lee [5] reported that Pd/γ-Al$_2$O$_3$ achieved the pyridine selectivity more than 90% even at the integral conditions of the reaction.

On the mechanism of the reaction, Butler and Laundon [6-8] reported that tetrahydropyridine was formed as an intermediate. On the other hand, Bashkirov et al. [3] reported that 5-amino-1-pentanol was formed as an intermediate. These earlier studies were based on the contact time which revealed a few information about the mechanism. Our recent study [9] has demonstrated that ammonia is adsorbed dissociatively in the form of NH$_2$ on the hydrogenated surface of Pd/γ-Al$_2$O$_3$ at the reaction temperature. We propose in this paper a possible reaction mechanism. And the suitable rate equation for the pyridine formation was derived from the experimental results.

**Author to whom correspondences should be addressed.

EXPERIMENTAL

Palladium chloride dissolved in 1 N HCl solution was supported on γ-Al$_2$O$_3$ in an incipient wetness method and then calcined at 450C for 6 hrs. The dispersion and particle size of 4.5 wt% Pd/γ-Al$_2$O$_3$ determined by H$_2$ chemisorption were 32% and 36Å [5], respectively. Reaction was conducted in a differential flow reactor made of pyrex in 9 mm diameter [5]. 100 mg of calcined catalyst was placed at the reactor and reduced at 380℃ for 1 hr in the hydrogen stream. The reduced catalyst was cooled to a reaction temperature. Liquid product was collected in a sampling pot maintained at −5℃ and analyzed with FID using PEG 20 M as a column material. Gas phase was also analyzed with TCD. The conversion and selectivity were calculated on the carbon basis.
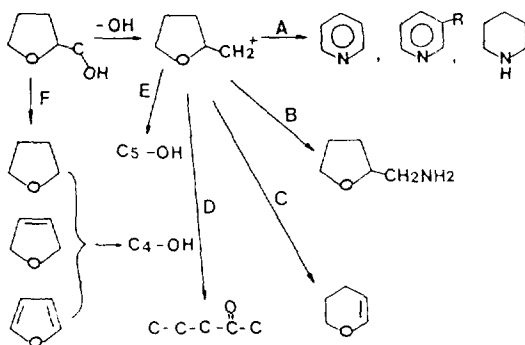
RESULTS AND DISCUSSION

The selective formation of pyridine from THFA requires the reducing or the oxidizing environment [7]. The reducing condition was prepared with hydrogen in this study. And nitrogen was used for balance gas. The effects of hydrogen and nitrogen on the reaction were shown at Table 1 which shows the product distribution and the conversion as the feed composition was changed successively. The first two and fourth results in Table 1 show that THFA was mainly fractured into furans in the absence of ammonia regardless of the presence of nitrogen and hydrogen. Com-

Table 1. The effects of reactant on the product distribution at 300°C

Molar feed ratio THFA[a] : NH$_3$: H$_2$: N$_2$	Time[b] (hr)	Product distribution (%)								Conversion (%)
		Furans[c]	DHP[d]	2-Pentanone	1-Butanol	Pyridine	Alkyl-pyridine	THFAM[e]	Others	
1 : 0 : 10 : 10	12	66.00	3.46	2.13	15.43	—	—	—	10.33	29.76
1 : 0 : 20 : 0	13	66.77	3.23	2.16	17.43	—	—	—	7.78	30.36
1 : 5 : 20 : 0	15	2.62	0.38	—	0.97	75.96	—	19.47	0.60	52.58
1 : 0 : 0 : 20	16	74.18	3.02	0.61	0.50	—	—	—	18.18	29.32
1 : 5 : 0 : 20	17	4.42	0.68	—	—	1.49	93.41	—	—	18.18
1 : 5 : 10 : 10	20	1.73	0.39	—	0.10	17.34	80.31	—	0.12	33.04

[a]6.3 cc/min, [b]The time elapsed after the start of reaction, [c]Furan+Dihydrofuran+Tetrahydrofuran, [d]Dihydrofuran, [e]Tetrahydrofurfuryl amine.

Scheme 1.

paring the first two rows, nitrogen insignificantly affected the activation of THFA. Third row shows ammonia reduces the fracture of THFA and induces the reaction to form pyridine. The effect of hydrogen on the selective formation of pyridine was demonstrated from the results of third and the last two rows. Pyridine selectivity was remarkably reduced by the interruption of hydrogen in the reaction stream. And pyridine selectivity and catalytic activity was recovered by the addition of hydrogen. Thus, hydrogen enhanced the catalytic activity and pyridine selectivity. It was understood that hydrogen promoted the dissociative adsorption of ammonia in the form of NH$_2$ [9]. We also think hydrogen inforces surface residuals desorbed to clean the catalyst surface.

The catalytic activity was decreased sharply at the initial stage of the reaction and roughly maintained steady state after 20 hr [5]. So the kinetic data was obtained after 24 hr from the initial start. The dependence of the reaction temperature and the contact time on this reaction was reported in a previous paper [5]. The selectivity of pyridine was maximized at 320 °C.

The main reaction for pyridine formation is progressed by the path A of Scheme 1 in which N substituted
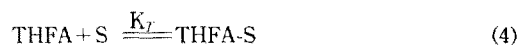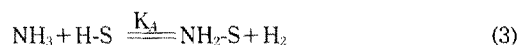
ring-enlargement occurs. The possible by-products were also predicted in Scheme 1. The direct fracture of THFA yields furans and finally ring-opened fragments such as C$_4$-alcohols (path F). Pentanol (path E) and 2-pentanone (Path D) are formed from the ring-opening of tetrahydrofurfuryl carbonium ion (THFCI). Furans are formed by the ring-enlargement of THFCI (Path C). The amine addition on THFCI forms tetrahydrofurfuryl amine (path B). Alkyl pyridines and fragments appeared in significant amounts at high temperature above 350°C and long contact time [5].

These side reactions and the multi-stage path of reaction make the kinetic study seriously complicated. So the kinetic data of this paper were limited in the narrow temperature range of 270-320°C.

The reaction rate of pyridine formation (R$_p$) was expressed by Eq. (1). Where F$_T^0$ is

$$R_p = \frac{F_T^0 X_T S_p}{W \cdot 100} , \text{ [mole/hr·g Catal.]} \qquad (1)$$

the feed flow rate of THFA, X$_T$ is the conversion of TFHA, S$_p$ is pyridine selectivity, and W is the amount of catalyst. The reaction was modeled as follows; (1) Ammonia is adsorbed dissociatively as Eq. (3) on the hydrogenated surface. (2) Molecular adsorption of THFA occurs at the vicinity of aminated and hydrogenated sites where pyridine is formed. And these are expressed by Eqs. from (2) to (6). Where S is active site.
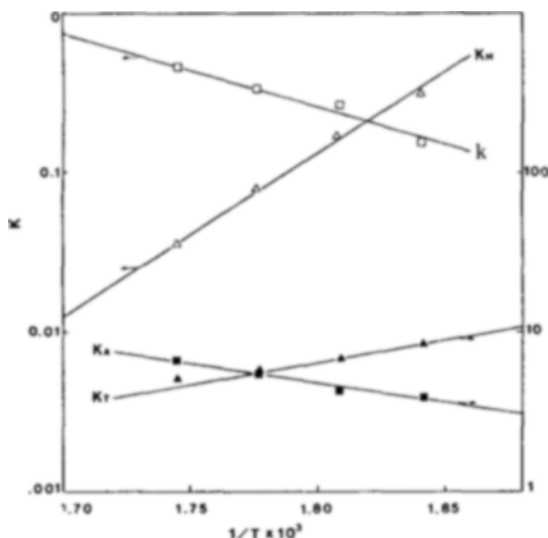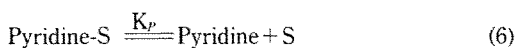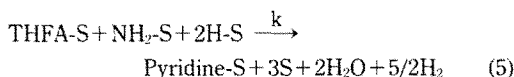
$$H_2 + 2S \xrightarrow{K_H} 2H\text{-}S \qquad (2)$$

$$NH_3 + H\text{-}S \xrightarrow{K_A} NH_2\text{-}S + H_2 \qquad (3)$$

$$THFA + S \xrightarrow{K_T} THFA\text{-}S \qquad (4)$$

Fig. 1. Plot of the rate constant of the surface reaction (k) and equilibrium constants of the adsorption (K) vs. 1/T in the reaction of pyridine formation from FHFA.

Fig. 2. Effects of H$_2$ partial pressure on the pyridine formation. Solid curves represent the theoretical values at 270°C (●), 280°C (▲), 300°C ( ), and 320°C (△) (Total flow rate 196.0 cc/min, P_T 0.0323 atm, P_A 0.1613 atm, and N$_2$ balanced).

$$\text{THFA-S} + \text{NH}_2\text{-S} + 2\text{H-S} \xrightarrow{\text{k}}$$
$$\text{Pyridine-S} + 3\text{S} + 2\text{H}_2\text{O} + 5/2\text{H}_2 \qquad (5)$$

$$\text{Pyridine-S} \xrightarrow{\text{K}_P} \text{Pyridine} + \text{S} \qquad (6)$$

Subscripts A, T, P, and H represent ammonia, THFA, pyridine, and hydrogen, respectively. P, k, and K are partial pressure, the rate constant of the reaction, and the equilibrium constant of the adsorption, respectively. The rate of pyridine formation is written as Eq. (7) by the assumptions; (1) quasi-equilibrium exists on adsorption and desorption rate, (2) the rate determining step is the irreversible surface reaction, and (3) partial pressure

$$R_P = \frac{k\,K_H{}^{3/2}\,K_A\,K_T\,P_A\,P_T P_H{}^{1/2}}{(1 + K_H{}^{1/2}P_H{}^{1/2} + K_A K_H{}^{1/2}P_A/P_H{}^{1/2} + K_T P_T)^4} \qquad (7)$$

of product is ignored. The constants in Eq. (7) K_H, K_A, K_T and k were obtained by the multiple regression of the linearized equation. The equilibrium constants of adsorption were expressed as EXP (ΔS/R-ΔH/RT). And the rate constant of the reaction was expressed by Arrhenius equation. This mechanism is different from that of Butler and Laundon [8] on the views of explaining the role of palladium and hydrogen. They propose that amine (from ammonia dissociation) contacted with previously ring expanded-THFA on
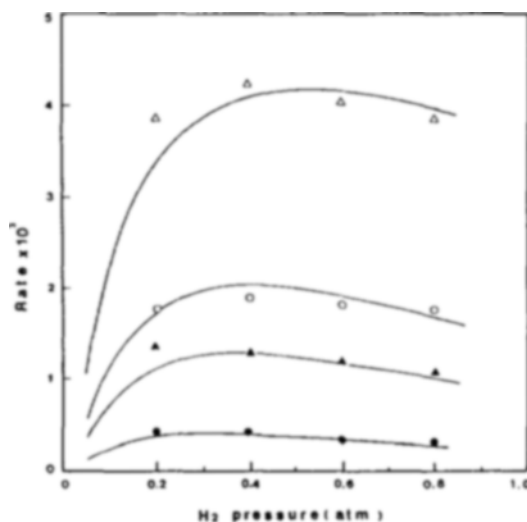
alumina to form tetrahydropyridine which was dehydrogenated into pyridine on palladium surface. Their mechanism contains no information about the role of palladium and hydrogen in the stage of reaction occurs. But we think palladium and hydrogen play an important role in the formation of active site for pyridine [9, 10]. Hydrogen, particulary, performs quasi-active sites [9] so that gives a suitable environments for the partial dissociation of ammonia [Eq. (3)] and for the selective formation of pyridine (Table 1). The rate equation showed a reasonable temperature dependence as shown at Fig. 1. And these were Eqs. from (8) to (11). Eq. (10) shows abnormal behavior in the adsorption constant, which indicates the adsorption rate of ammonia slightly increase with temperature.

$$k = 1.6933 \times 10^{16}\ \text{EXP}(-21924/T),\ [\text{mol/g catal} \cdot \text{hr}] \qquad (8)$$

$$K_H = 1.0453 \times 10^{-13}\ \text{EXP}(18561/T),\ [\text{atm}^{-1}] \qquad (9)$$

$$K_A = 3.7108\ \text{EXP}(-721/T),\ [1] \qquad (10)$$

$$K_T = 2.5403 \times 10^{-5}\ \text{EXP}(7650/T),\ [\text{atm}^{-1}] \qquad (11)$$

This result was understood by the reason that the dissociative adsorption of ammonia [as shown at Eq. (3)] occurs by way of a kind of surface reaction be-
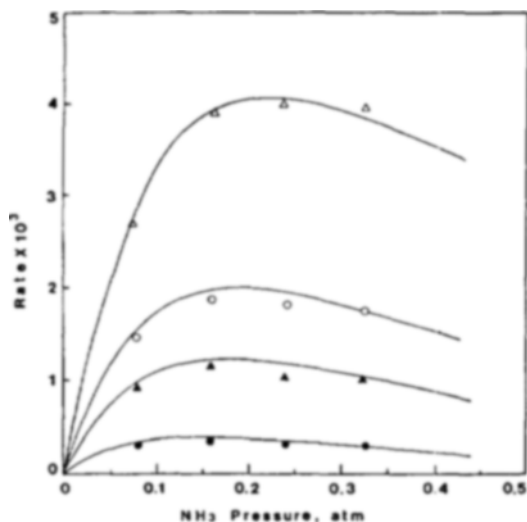
Fig. 3. Effects of NH_3 partial pressure on the pyridine formation. Solid curves represent the theoretical values at 270°C (●), 280°C (▲), 300°C (○), and 320°C (△) (Total flow rate 196.0 cc/min, P_T 0.0323 atm, P_H 0.3225 atm, and N_2 balanced).
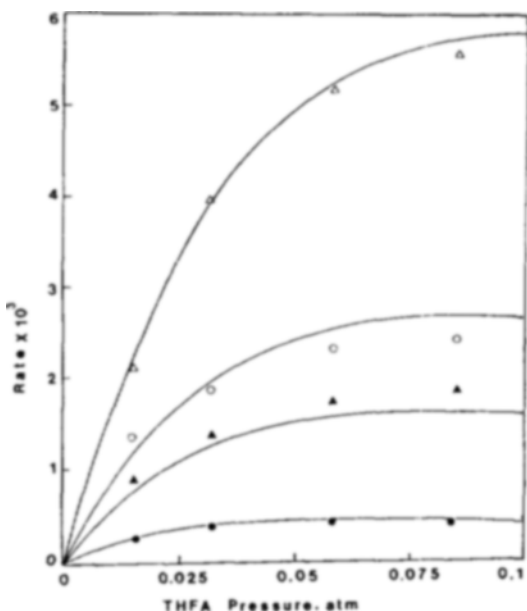

Fig. 4. Effects of THFA partial pressure on the pyridine formation. Solid curves represent the theoretical values at 270°C (●), 280°C (▲), 300°C (○), and 320°C (△) (Total flow rate 196.0 cc/min, P_H 0.3225 atm, P_A 0.1613 atm, and N_2 balanced).

tween ammonia and hydrogen atom.

The partial pressure dependence of the rate were shown at Figures 2, 3, and 4. The theoretical values from the model was well fitted with the experimental data. Fig. 2 shows that hydrogen enhances pyridine formation at low composition but slightly decreases it at excess condition. The composition of ammonia had also the optimum value for pyridine formation as shown at Fig. 3. And the rate was tediously increased with the increase of the partial pressure of THFA over 0.1 atm. So the optimum mole ratio of THFA : NH_3 : H_2 for pyridine formation has been pointed out [4, 5] as 1 : 5 : 10.

Inspite of the simplification of surface reaction shown in Eq. (5) and the assumption of homogeneous active site in the present study, the rate expression [Eq. (7)] was suitable for discription the formation of pyridine from the reaction of ammonia and THFA.

CONCLUSIONS

The suitable rate expression of pyridine formation from the reaction of THFA and ammonia was obtained from the following assumptions; Ammonia is adsorbed dissociatively in the form of NH_2 on the hydrogenated catalyst surface and molecular THFA is adsorbed near the amine. And irreversible surface reaction of these adsorbates was the rate limiting step. The model describes well the experimental data. And the rate of pyridine formation was expressed as the following equation.

$$R_p = k\, K_H^{3/2}\, K_A\, K_T\, P_A\, P_T\, P_H^{1/2}/(1 + K_H^{1/2}\, P_H^{1/2} + K_A\, K_H^{1/2}\, P_A\, P_H^{1/2} + K_T\, P_T)^1$$

ACKNOWLEDGEMENT

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