

Kinetic Studies on Diphenylamine Synthesis over HCl-treated Alumina

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Kinetic studies on diphenylamine synthesis from aniline have been carried out over 7 wt % HCl-alumina in the temperature range of 400-500°C.

The reaction rate is:

$$r = kp_A/(1 + Kp_D)$$

where k , K are constants; p_A , p_D are vapor pressure of aniline and diphenylamine, respectively.

This equation can be explained by the mechanism in which the rate-determining step is the adsorption of aniline.

The apparent activation energy of this process is about 13.0 kcal/mole and this value is considerably low in comparison with 25.0 kcal/mole obtained by using γ -alumina catalyst. On the other hand, it could be noted that the active sites of the HCl-treated alumina have decreased to about one thousandth that of the untreated alumina.

INTRODUCTION

It is well known that halogenation of alumina and silica-alumina increases their catalytic activity over the nonhalogenated forms as has previously been presented by many workers (1-6).

We observed the ir spectra of pyridine on HCl-treated alumina at different treatment temperatures of HCl and confirmed the existence of the following chemical types, discussed in another report: (i) coordinated pyridinium ion on protonic acid sites at room temperature (7), (ii) coordinated pyridine on the Lewis acid sites at higher temperature (8).

In a previous report (9), it was found that the vapor phase condensation of aniline to diphenylamine and ammonia over HCl-treated alumina and the activity of the alumina catalyst were greatly improved by HCl treatment of the catalyst. It could be also deduced from the results (9) that the increased activity was based on both the geometric configuration of the active

sites and an increase of the Lewis acidity of HCl-treated alumina.

Studies of this reaction system were carried out by Hoelscher *et al.* (10) and Ohta *et al.* (11), but no kinetic studies have been performed so far.

This report deals with studies of the kinetics and reaction mechanism of diphenylamine synthesis from aniline over HCl-treated alumina.

EXPERIMENTAL

The conventional flow type apparatus was used for the reaction at atmospheric pressure. The reaction tube was a quartz tube, 26-mm ϕ i.d., and the reactant was fed into the reactor with nitrogen gas by a micro-feeder which was operated by an electric motor. An ordinary Nichrome wound-electrically heated furnace was used to maintain the reaction temperature. An outline of the apparatus is shown in Fig. 1.

Since the reaction temperature was so high, nitrogen gas was used as a carrier to

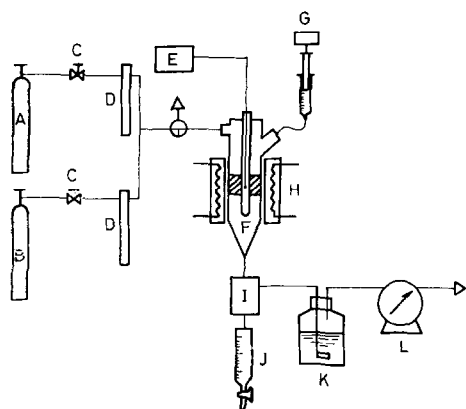


FIG. 1. Schematic diagram of flow apparatus: A, N₂ Bomb; B, Air Bomb; C, Needle valve; D, Flow meter; E, Temp. recorder; F, Reactor; G, Microfeeder; H, Heater; I, Condenser; J, Receiver; K, Washing bottle; L, Gas meter.

prevent the thermal decomposition of both products and reactants in the reaction zone. The feedstock aniline was purified by distillation with zinc dust.

The catalysts were prepared by immersing γ -alumina into a known concentration of HCl solution, left standing overnight, and then drying. Before reaction, the catalysts were activated at 500–550°C for 1–2 hr in air.

The products obtained in the receiver were analyzed by gas chromatography at various time intervals. Analytical conditions were as follows: column, stainless-steel tube (4-mm ϕ i.d.), 2-m long; silicon gum SE-30 (3%) on Neosorb NF (20/80 mesh); operation temp., 260°C; carrier gas, He 25 ml/min.

Unknown compounds were detected in the products in addition to the main product, diphenylamine (DPA), but their amounts were too small to consider. Conversion of aniline was calculated using the following equation:

$$\text{Conversion of aniline (\%)} = \frac{2 \text{ moles of DPA obtained}}{\text{moles of aniline supplied}} \times 100$$

RESULTS

In a previous report, it was shown that the optimum reaction temperature was at

400–500°C and the activity was improved by HCl treatment of the catalyst. It was also found that a decline of catalytic activity was observed owing to the high reaction temperature, but a constant activity could be obtained as the amount of HCl added to the catalyst was increased. Therefore, the present studies were carried out by using 7.4 wt% HCl–Al₂O₃ catalyst which had a constant activity.

(i) Reaction order

In order to obtain the reaction order, experiments were performed under the following conditions: reaction temp., 432°C; catalyst, 7.4 wt% HCl–Al₂O₃, 3 g; S.V., 3000 (ml/g hr) (STP).

Nitrogen gas was used to maintain a constant space velocity.

Since the results were obtained under low conversion of aniline, the reaction rate obtained could be regarded as an initial rate. Figure 2 shows the correlation between the initial partial pressure of aniline and the initial rate; the linear relationship shows a first order reaction.

(ii) Inhibiting Effect of DPA

Both reactant and products in this reaction are basic substances while the catalyst is a solid acid. Since one of the products, diphenylamine, has a basic property and high boiling point, it should be noted that the decline of the catalytic activity was caused by these properties of DPA. On the other hand, another product, ammonia, has stronger basicity than DPA, but it may be presumed that the inhibiting effect of ammonia is small because of the higher re-

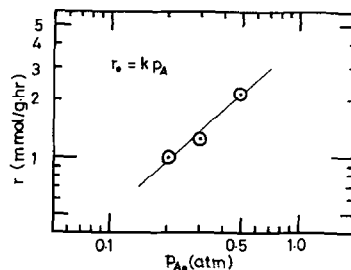


FIG. 2. Reaction order for DPA synthesis. React. temp., 432°C; Cat. wt., 3 g.

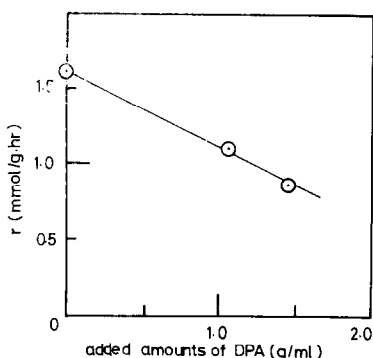


Fig. 3. Inhibiting effect of DPA on the rate.

action temperature. Therefore, the effects of DPA on the rate were investigated by adding the known amounts of DPA into the reactant. The results are shown in Fig. 3.

It was found that the reaction rate decreased as the amount of DPA added increased. The decline in rate was probably due to the added DPA, because the conversion of aniline was not more than 2–4% under the reaction conditions.

From consideration of the above results, the following rate equation was inferred as the experimental one.

$$r = \frac{ap_A}{1 + bp_D} \quad (1)$$

r , reaction rate; p_A , partial pressure of aniline; p_D , partial pressure of DPA; a , b , constants.

(iii) Effect of Space Velocity on the Rate

In order to examine whether Eq. (1) holds for the reaction, effects of the time factor on the rate were investigated. The correlation of aniline conversion and reciprocal space velocity based on catalyst weight are shown in Fig. 4 for various reaction temperatures.

The amount of conversion was determined by changing the flow rate of the feed which had a constant composition (aniline:nitrogen (mole ratio) = 0.3:0.7).

The reaction rate in a flow system can be obtained from the tangent of the curves at a given W/F in Fig. 4. The results thus obtained are presented in Table 1.

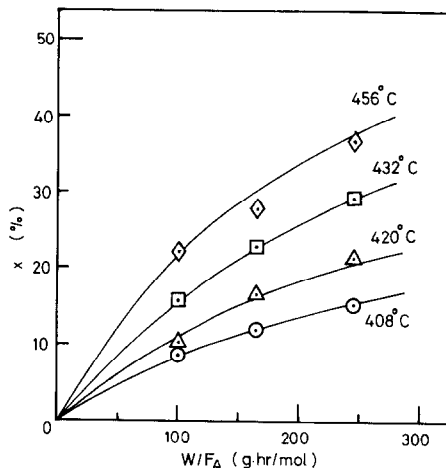


Fig. 4. Conversion of aniline vs. contact time.

When aniline conversion is expressed as x and Eq. (1) is rearranged, the following equation is obtained:

$$\frac{1-x}{r} = \frac{1}{ap_{A0}} + \frac{b}{2a}x, \quad (2)$$

where p_{A0} is the initial pressure of aniline.

The left term, $(1-x/r)$, was calculated from the results in Table 1 and its linearity examined as a function of x , at various temperatures, as shown in Fig. 5.

The linear relationships observed in Fig. 5 support the validity of Eq. (2) for the process. The constants a and b in Eq. (2) were calculated from the ordinate and slope of the lines. The values of a and b obtained were presented in Table 2 for each reaction temperature. It should be noted that constant a corresponds to an apparent rate constant k and b is equivalent to an adsorption equilibrium constant K of DPA.

Therefore, the apparent activation energy and the heat of adsorption of DPA can be calculated by plotting $\ln k$ and $\ln K$ from Table 2 against $1/T$ where T is in absolute temperature. Figure 6 shows the dependence of the constants on $1/T$ and the following values are determined.

Apparent activation energy $E = 13.0$ kcal/mole

Heat of adsorption of DPA $-\Delta H = 36.0$ kcal/mole

TABLE 1
 CALCULATED RESULTS FOR EQUATION (2)

React. temp. (°C)	408			420			
	W/F (g hr/mol)	x (%)	r ($\times 10^4$)	$1 - x/r$ ($\times 10^{-2}$)	x (%)	r ($\times 10^4$)	$1 - x/r$ ($\times 10^{-2}$)
101		8.5	6.2	14.8	11.5	8.8	10.1
165		11.8	4.6	19.3	16.4	6.6	12.7
245		15.0	3.9	21.8	21.2	5.2	15.2

React. temp. (°C)	432			456			
	W/F (g hr/mol)	x (%)	r ($\times 10^4$)	$1 - x/r$ ($\times 10^{-2}$)	x (%)	r ($\times 10^4$)	$1 - x/r$ ($\times 10^{-2}$)
60		10.5	14.6	6.1	13.2	20.0	4.34
101		16.0	12.0	7.0	20.2	15.0	5.32
165		22.7	8.8	8.8			

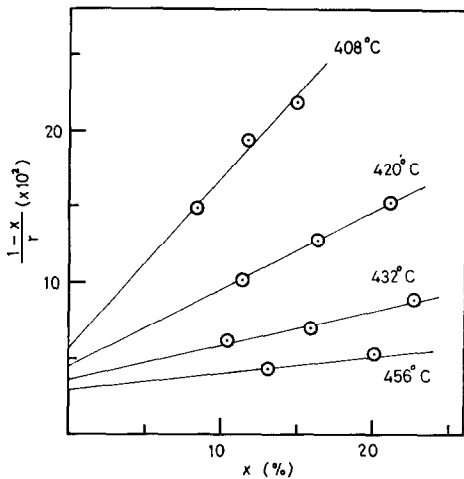


FIG. 5. Examination of Eq. (2).

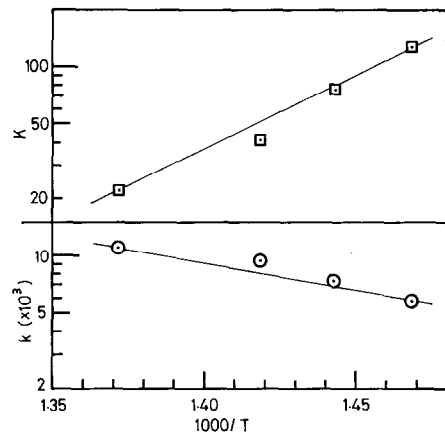


FIG. 6. Arrhenius plot for the apparent rate constant and adsorption equilibrium constant of DPA.

 TABLE 2
 APPARENT RATE CONSTANT AND ADSORPTION EQUILIBRIUM CONSTANT OF
 DPA $p_{A0} = 0.3$ (atm)

(°C)	$1000/T$	$1/ap_{A0}$ ($\times 10^{-2}$)	$b/2a$ ($\times 10^{-2}$)	$a (= l)$ ($\times 10^3$)	$b (= K)$
408	1.4684	5.8	11.0	5.75	126.6
420	1.4430	4.5	5.1	7.4	75.5
432	1.4184	3.6	2.2	9.3	40.9
456	1.3714	3.0	1.0	11	22.0

Therefore, the rate constant and the adsorption equilibrium constant of DPA are expressed by the following equations,

$$\log k = 1.920 - \frac{13.0 \times 10^3}{2.3RT} \quad (3)$$

$$\log K = -9.395 + \frac{36.0 \times 10^3}{2.3RT} \quad (4)$$

(iv) *Integrated Form*

The following equation is obtained from integration of Eq. (1):

$$\begin{aligned} W/F_A &= -(\alpha + \beta) \ln(1-x) - \beta x \\ \alpha &= 1/ap_{A0}, \beta = b/2a. \end{aligned} \quad (5)$$

Since we can calculate k and K by using both Eqs. (3) and (4) at any temperature, the aniline conversion can be calculated from experimental conditions in which the catalyst weight W and aniline flow rate F_A are given.

The curves obtained are shown in solid lines in Fig. 7 and it is found that theoretical curves generally coincide with experimental values.

DISCUSSION

The overall reaction for the process is bimolecular in aniline as follows:



However, as shown in Fig. 1, the process was first order in aniline. It was already

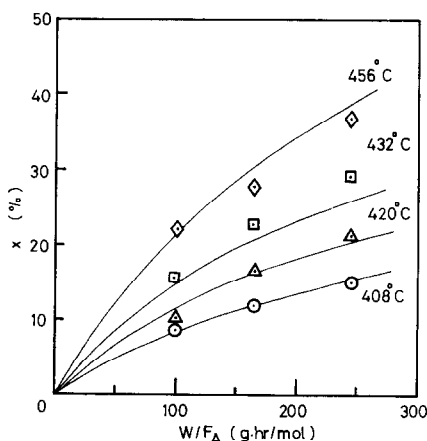
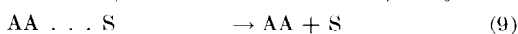
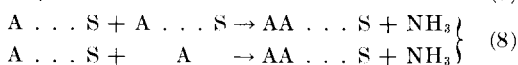
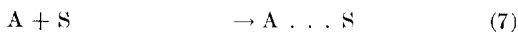


Fig. 7. Theoretical curves from the integrated form of the rate equation.

shown that the diffusional process was not a rate-determining step under the reaction conditions (9). Therefore, the following mechanism was selected as the most probable one:



where A and AA represent aniline and DPA, respectively, and S are active sites on the catalysts.

The process of adsorption of aniline to the sites is represented by step (7), while step (8) is the surface reaction of both adsorbed aniline, according to Langmuir-Hinshelwood mechanism, or of the adsorbed aniline with gaseous aniline, according to the Rideal mechanism. Step (9) is the desorption process of the adsorbed DPA.

The rate equation (1) can be exclusively derived from the case in which the aniline adsorption step (7) controls the rate. If step (8) is a rate-determining one, it cannot explain the rate equation (1), because the reaction rate would be the second order in aniline vapor pressure.

Since the adsorption term of the product was included in the denominator of the rate equation (1), it was also ruled out that the desorption step of DPA was rate determining.

In the previous report (9), the catalytic activity of three kinds of "solid acid catalyst," namely alumina, silica-alumina, and Y type molecular sieve were compared and the following activity order was obtained: γ -alumina > silica-alumina > Y type molecular sieve.

It was deduced that the activity order was not dependent on the kind of acid, amount of acid or acid strength, but on the geometric distribution of acid sites on alumina.

Hirota *et al.* (12) observed the NMR spectra of methylamine over alumina and they concluded the amine was bonded to alumina via the nitrogen atom. From the ir measurements in our other report (8), it was found that the Lewis acidity of alumina was strengthened by HCl treatment. Tak-

ing account of these observations, it seems that the aniline is adsorbed on the alumina catalyst by giving the free electron pair of the nitrogen to the Lewis acid sites. This phenomena has been well established for HCl-Al₂O₃ catalysts by ir studies (8).

Therefore, it should be concluded that the catalytic activity of the HCl-Al₂O₃ catalyst is due to the increase of Lewis acidity in addition to the geometric distribution of acid sites on the catalyst.

From the analysis of the results carried out by Hoelscher *et al.* using alumina catalyst, one can obtain a rather higher value of 25 kcal/mole for the apparent activation energy. Wakao *et al.* (13) also obtained an apparent activation energy of 26.2 kcal/mole using γ -alumina under similar reaction conditions.

These values are about twice that obtained in the present work. It should be noted that the catalytic activity for the reaction is greatly improved by HCl treatment of alumina. Taking into account that the adsorption process is the rate-determining step in this reaction, it seems that aniline is much more easily adsorbed on HCl-treated alumina than alumina catalyst itself, so that the activation energy is lowered by HCl treatment of the catalyst. From the results obtained by Beeck (14) in which an activation energy was related to a heat of adsorption, the adsorption state of aniline on HCl-Al₂O₃ catalyst could be more stable than the state on Al₂O₃.

In order to obtain more information about the change of sites of alumina by HCl-treatment, rough estimates are attempted as follows.

If the initial rate of alumina and HCl-treated alumina are, respectively, $r_0(1)$ and $r_0(2)$ under the same reaction conditions, the following equation is obtained, assuming the same reaction order:

$$\frac{r_0(2)}{r_0(1)} = \frac{A_2}{A_1} \exp\left(-\frac{E_2 - E_1}{RT}\right), \quad (10)$$

where A_1, A_2 : preexponential factor in alumina and HCl-Al₂O₃, respectively; E_1, E_2 : activation energy of alumina and HCl-Al₂O₃, respectively.

The ratio of the initial reaction rates on both alumina catalysts was 2.0 under the following conditions: reaction temp., 480°C; initial pressure of aniline, 0.305 atm, and S.V., 1540 hr⁻¹.

If one assumes that $E_1 = 25.0$ kcal/mole, one can obtain the numerical value $A_2/A_1 = 8 \times 10^{-4}$.

Therefore, it follows that the active sites on the HCl-Al₂O₃ are decreased about one thousandth of the original alumina.

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