Kinetics of the Catalytic Vapor Phase Reduction of Nitrobenzene[*]

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Summary: *The kinetics of the catalytic vapor phase reduction of nitrobenzene to aniline over copper-magnesia catalyst in the temperature range from 175°C to 220°C was studied using a differential reactor. The rate of reaction was measured at atmospheric pressure with a high mole ratio of hydrogen to nitrobenzene. From the analysis of the experimental data, it was concluded that the rate-controlling step was the adsorption process of hydrogen on the copper-magnesia catalyst surface. According to the Langmuir-Hinshelwood mechanism, the final rate equation r for the vapor phase reduction of nitrobenzene on copper-magnesia catalyst in the temperature range from 175°C to 220°C was obtained as follows;*

$$r = \frac{kP_H}{1 + K_N P_N + K_A P_A + K_W P_W}$$

where   k; rate constant

   P_H, P_N, P_A and P_W; partial pressure of hydrogen, nitrobenzene, aniline and water

   K_N, K_A and K_W; adsorption equilibrium constant of nitrobenzene, aniline and water

   This equation will be useful if it can be used to predict the rate over a wide range of reactions and hence, be suitable for reactor design.

1 Introduction

Aniline, which is a very important intermediate in fine chemistry, has been produced on a commercial scale primarily by the batch process for reducing nitrobenzene with iron.

In recent years, the vapor phase reduction of nitrobenzene over several metal supported catalysts, such as copper or nickel on a suitable carrier, has been widely studied using a fixed bed reactor. However, few reports on the kinetics of the catalytic reaction of nitrobenzene have been found.

In this study, the catalytic vapor phase hydrogenation was investigated. Many kinds of catalysts were tested and copper magnesia was found to be the best. Therefore, the kinetic study was done over this catalyst using a normal, flow type fixed bed reactor to obtain a rate equation which is suitable for reactor design.

2 Experimental

2.1 Catalyst Preparation

Sodium hydroxide solution (1N) was added to the mixture containing magnesium nitrate solution (1N) and copper nitrate solution (1N) in the ratio of 12 : 0.6 by volume, with stirring and at room temperature until a pH of 9.55 was reached.

The precipitate was filtered and washed until the blue color of diphenylamine solution, which was used to check the nitrate anion, was gone. The wet cake, after complete washing, was dried at 90~100°C and calcined at 500°C for 2 hr in an atmosphere of nitrogen.

The catalyst obtained by this procedure was analyzed by the usual iodine method. The copper content in the catalyst was 3.6 wt%. Before reaction, the catalyst (particle size 100~150 mesh) was reduced at 300°C for 2 hr with 200 ml/g·min of hydrogen in a fixed bed reactor.

2.2 Apparatus

The flow sheet for the experimental apparatus used is shown in **Fig. 1**. The reactor consisted of a glass tube 50 cm in length and 1.8 cm in diameter, and was heated by a fluidized thermal bath.

Hydrogen and nitrobenzene with the required mol ratio were introduced to the catalyst bed through the preheater which was filled with small Raschig rings located in the reactor. The gaseous products were collected in a condenser trap which was cooled with a mixture of dry ice and methanol. The catalysts were diluted with inert materials such as quartz sand to obtain the desired iso-

A ; Hydrogen cylinder   G ; Catalyst bed
B ; Deoxygen tube   H ; Fluidized thermal bath
C ; Drying tube   I ; Air compressor
D ; Flow meter   J ; Cold trap
E ; Feeder   K ; Thermocouple
F ; Reactor
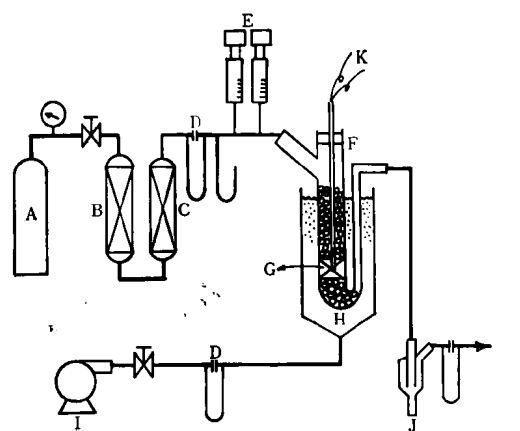
Fig. 1 Flow Sheet of Experimental Apparatus

Reaction temperature ;   190°C
$H_2/C_6H_5NO_2$ mole ratio ;   33
W/F ;   0.0303 (g-cat·hr/g-mol)

Fig. 2   Variation of Catalytic Activity with Reaction Time

thermal temperature distribution in the catalyst bed.

2.3 Analysis

The condensates collected during the desired reaction period were analyzed by gas chromatography. The conditions for this chromatographic analysis were as follows, silicon DC 550 on celite 545 in teflon pipe (2 m); temperature of thermal bath, 155°C; carrier gas, hydrogen; flow rate, 60 ml/min. In all experiments using the copper-magnesia catalyst, the condensed reaction products contained only aniline, water and unreacted nitrobenzene. No by-products such as hydroxylamine or azoxybenzene could be detected.
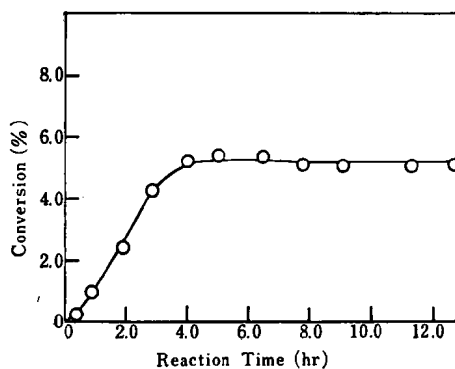
3 Results and Discussion

3.1 The Variation of Catalytic Activity with Reaction Time

When several runs in the absence of the catalyst were carried out in the temperature range from 160°C to 350°C, no reaction occurred. Therefore, the change of the catalyst activity against the reaction time was examined. The experimental result obtained is shown in **Fig. 2**. The catalytic activity increased with the reaction time up to about 4 hr. This phenomenon was strange, compared with usual catalytic experiments. However, the catalytic activity reached a constant value after about 4 hr and did not change for at least 10 hr.
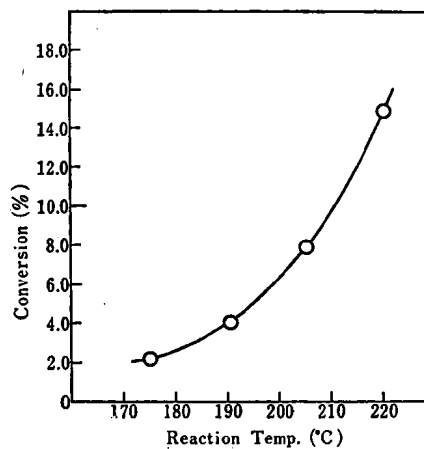
3.2 The Effects of Reaction Temperature and Mass Transfer

Fig. 3 illustrates that the catalytic activity

$H_2/C_6H_5NO_2$ mole ratio ;   33
W/F ;   0.0270 (g-cat·hr/g-mol)

Fig. 3   Dependancy of Catalytic Activity upon Reaction Temperature

increased consistently with the reaction temperature. To check the effect of mass transfer, the catalyst's weight and the total flow rate were varied at the same time so as to maintain constant contact time. The results obtained indicated no changes in conversion within the range of experimental conditions examined.

3.3 The Dependency of the Mole Fraction of Nitrobenzene Converted upon the Contact Time

As shown in **Fig. 4**, the relationship between the conversion of nitrobenzene and the contact time, up to about 10% conversion, can be expressed as a straight line which passes through the origin. The differential rate of reaction could therefore be simply calculated by the following expression;
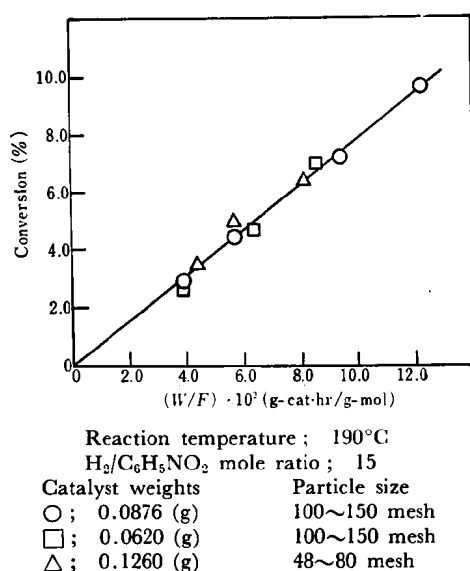
$$r = y_0 \frac{\Delta x}{\Delta W/F} \tag{1}$$

Fig. 4 Relationship between Contact Time and Conversion

Reaction temperature ; 190°C
$H_2/C_6H_5NO_2$ mole ratio ; 15

Catalyst weights	Particle size
O ; 0.0876 (g)	100~150 mesh
□ ; 0.0620 (g)	100~150 mesh
△ ; 0.1260 (g)	48~80 mesh

where

r; reaction rate (g-mol/g-cat·hr)

Δx; conversion in the differential reactor (—)

y_0; the mole fraction of nitrobenzene at the entrance of reactor (—)

ΔW; catalyst weight (g)

F; total flow rate (g-mol/hr)

In addition, **Fig. 4** proved that the catalyst particle size had no effect, and that the effect of pore diffusion was negligible.

3.4 The Analysis of the Reaction Rate

The initial rate data obtained are shown in **Table 1**. The chemical process, except mass transfer, in a fluid-solid catalytic system can be divided into the following three steps.

1. Adsorption of hydrogen or nitrobenzene on the catalyst surface.

2. A surface reaction between hydrogen and nitrobenzene on the catalyst surface.

3. Desorption of reaction products from the catalyst surface to the fluid.

All the mechanisms whose rate-controlling step were assumed to be step 2 or 3 were checked by comparing the initial rate data. But no rate equations could be correlated. Hence, the re-

maining step 1 was examined. This step may have two reaction mechanisms, *i.e.* adsorption of hydrogen and adsorption of nitrobenzene, on the same active sites, and the rate controlling step is either the adsorption of hydrogen (a), or the adsorption of nitrobenzene (b).

According to the Langmuir-Hinshelwood mechanism, the initial rate equation of reaction mechanism (a) is given as the following one;

$$r_0 = \frac{kP_H}{1 + K_N P_N} \tag{2}$$

In the same manner, the equation of mechanism (b) is;

$$r_0 = \frac{kP_N}{1 + K_H P_H} \tag{3}$$

where

r_0; initial reaction rate (g-mol/g-cat·hr)

k; reaction rate constant (g-mol/g-cat·hr·atm)

P_H and P_N; partial pressure of hydrogen and nitrobenzene, respectively (atm)

K_H and K_N; adsorption equilibrium constant of hydrogen and nitrobenzene, respectively (atm⁻¹)

As shown in **Fig. 5**, the results of case (2) was negative. Finally, the results of the case (1) showed that the experimental data can be well
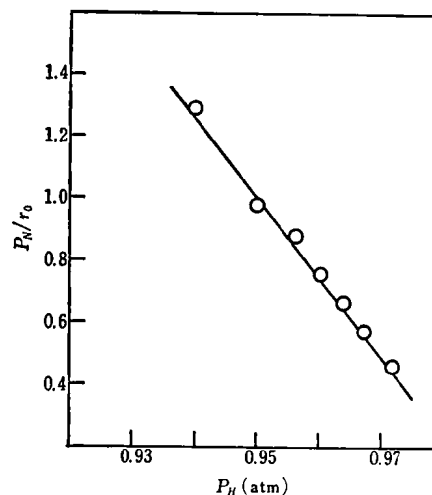
Reaction temperature ; 190°C

Fig. 5 Verification of Langmuir Equation (3)

Table 1 Experimental Data of the Initial Reaction Rates at 190°C

Cat. W (g)	F_N (mol/hr)	F_H (mol/hr)	P_H (atm)	P_N (atm)	Conv.	r_0(exp)×10²	r_0 (cal)×10²
0.08	9.78×10⁻²	3.23	0.9706	0.0294	0.045	5.51	5.74
0.08	9.78×10⁻²	2.94	0.9677	0.0323	0.044	5.40	5.64
0.08	9.78×10⁻²	2.64	0.9643	0.0357	0.043	5.24	5.53
0.08	9.78×10⁻²	2.35	0.9600	0.0400	0.042	5.14	5.42
0.08	9.78×10⁻²	2.06	0.9545	0.0455	0.040	4.98	5.26
0.08	9.78×10⁻²	1.76	0.9474	0.0526	0.039	4.83	5.08
0.08	9.78×10⁻²	1.47	0.9374	0.0625	0.039	4.74	4.83

correlated by the rate equation (2).

The general rate equation containing a reverse reaction term and the adsorption term of reaction products is presented as the following one.

$$r = \frac{\overrightarrow{k}P_H - \overleftarrow{k}K_H \sqrt[3]{\dfrac{P_A P_W^2}{KP_N}}}{1 + K_H \sqrt[3]{\dfrac{P_A P_W^2}{KP_N}} + K_N P_N + K_A P_A + K_W P_W} \qquad (4)$$

where

$\overrightarrow{k}$; rate constant of the forward reaction (g-mol/g-cat·hr·atm)

$\overleftarrow{k}$; rate constant of the backward reaction (g-mol/g-cat·hr)

P_A and P_W; partial pressure of aniline and water (atm)

K_A and K_W; adsorption equilibrium constant of aniline and water (atm^{-1})

K; chemical equilibrium of reaction (atm^{-1})

The values of K calculated from the termodynamic constants are much greater than unity. In addition, P_A and P_W are less than unity, because the rate equation is initial. Therefore, Eq. (4) can be reduced to Eq. (2) written before. To check Eq. (2) by the experimental data, Eq. (2) is transformed to the following equation.

$$\frac{P_H}{r_0} = \frac{1}{K} + \frac{K_N}{K} P_N \qquad (5)$$

As shown in **Fig. 6**, a linear relationship was obtained between P_H/r_0 and P_N. From the reciprocal of the intercept, the value of K can be obtained directly and the value of the slope divided by K gives K_N. The calculated values of K and K_N are shown in **Table 2**. Of course, the adsorption equilibrium constants K_N are possitive and decrease as the temperature becomes high.

Fig. 7 gives the activation energy of 5.4 kcal/mol and the heat of adsorption of nitrobenzene
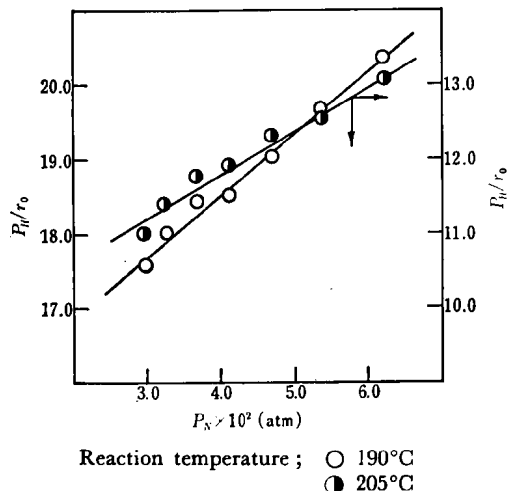
Table 2 The Values of the Rate Constant and Adsorption Equilibrium Constants

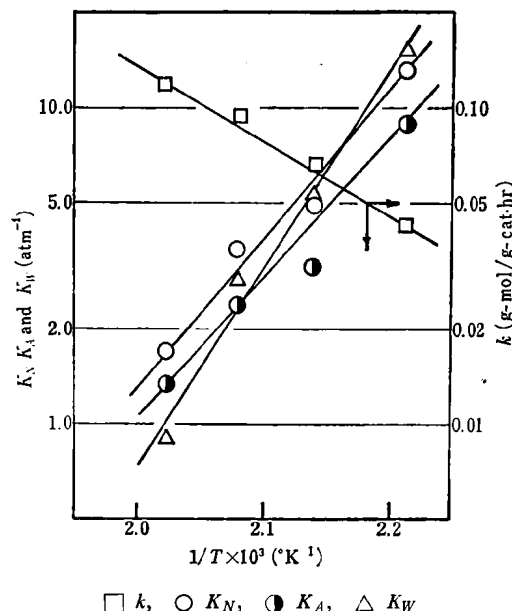|	175°C	190°C	205°C	220°C	E or Q kcal/mol
k	0.045	0.068	0.098	0.12	5.4
K_N	13.3	5.1	3.8	1.7	13.0
K_A	9.0	3.7	2.3	1.3	12.0
K_W	14.8	5.3	2.8	0.89	15.5

□ k, ○ K_N, ◑ K_A, △ K_W

Fig. 7   Temperature Dependency of Rate Constant and Adsorption Equilibrium Constants of Nitrobenzene, Aniline and Water

is 13.0 kcal/mol.

3.5 The Rate Equation with the Partial Pressures of Aniline and Water

The Langmuir rate equation containing the partial pressure of aniline may be written as follows;

$$r_0' = \frac{kP_H}{1 + K_N P_N + K_A P_A} \qquad (6)$$

Eq. (6) can be transformed into Eq. (7).

$$Z = \frac{kP_H}{r_0'} - 1 - K_N P_N = K_A P_A \qquad (7)$$

In the same manner, the modified rate equation with the partial pressures of aniline and water can be written as follows;

$$r_0'' = \frac{kP_H}{1 + K_N P_N + K_A P_A + K_W P_W} \qquad (8)$$

$$Z' = \frac{kP_H}{r_0''} - 1 - K_N P_N - K_A P_A = K_W P_W \qquad (9)$$

where r_0' or r_0''; initial reaction rate with aniline partial pressure or with both aniline and water partial pressure. As shown in **Fig. 8** and **Fig. 9**, the adsorption equilibrium constants of aniline and water, K_A and K_W can be calculated. **Fig. 7**
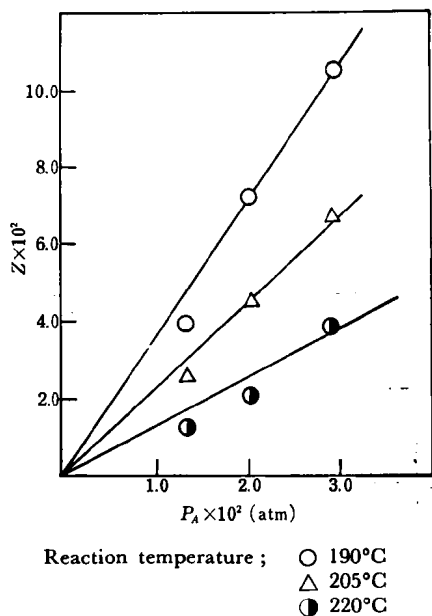

Reaction temperature ; ○ 190°C
                         ◑ 205°C

Fig. 6   Verification of Langmuir Equation (2)

Reaction temperature ;   O 190°C
                         △ 205°C
                         ◐ 220°C

Fig. 8   Verification of Modified Langmuir Equation
(7)

Reaction temperature ;   △ 175°C
                         O 190°C
                         ◑ 205°C
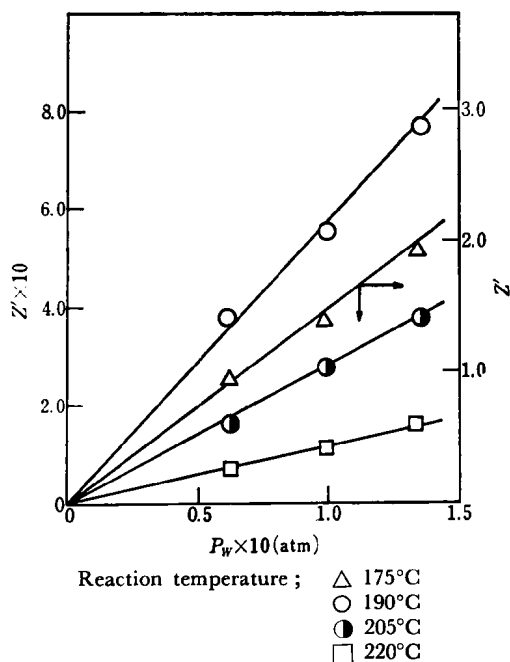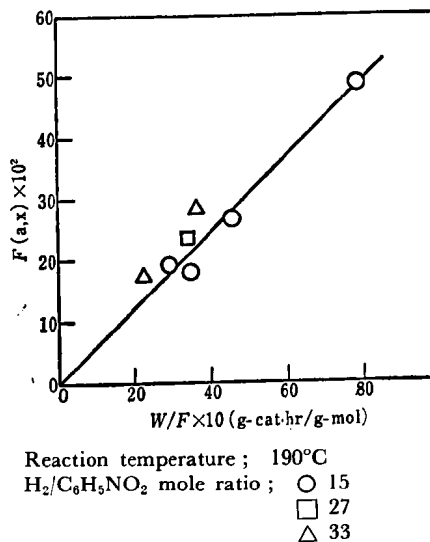   □ 220°C

Fig. 9   Verification of Modified Langmuir Equation
(9)

indicates that the heats of adsorption of aniline and water were 12.0 kcal-mol, and 15.5 kcal/mol respectively. As a final result, the rate equation for the vapor phase reduction of nitrobenzene on copper-magnesia catalyst was determined to be as follows;

$$r = \frac{kP_H}{1 + K_N P_N + K_A P_A + K_W P_W}$$ (10)

The average deviation of the proposed rate equation from the experimental data is about

Reaction temperature ;   190°C
$H_2/C_6H_5NO_2$ mole ratio ;   O 15
                                 □ 27
                                 △ 33

The solid line is the calculated values.

Fig. 10   Relationship between Contact Time and
F(a, x)

10%.

3.6   A Verification of the Rate Equation Obtained by the Differential Reactor

Eq. (10) written as a function of the conversion x instead of the partial pressure is substituted into the following equation;

$$W/F = y_0 \int \frac{dx}{r}$$ (11)

By the arrangement of intergrated form, the relationship between W/F and x was obtained as follows;

$$k\ W/F = \frac{1}{a+1}\left[\left(\frac{1+K_N-K_A-2K_W}{3}\right)x + \frac{1}{9}\right.$$

$$\left. \{2a+3+(3-a)K_N + aK_A + 2aK_W\}\ln\frac{a}{a-3x}\right]$$

$$= F(a, x)$$ (12)

where a is the mole ratio of hydrogen to nitrobenzene. Up to a conversion of about sixty percent, the correlation of Eq. (12) with the experimental data was well verified as shown in **Fig. 10**.

The rate equation obtained here will be useful to predict the conversion for reactor design.

References

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