BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN　VOL. 39　2527—2531 (1966)

The Catalytic Hydrogenation of Aniline in Fluidized Beds[1]

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(Received January 11, 1966)

The hydrogenation of aniline in fluidized beds was studied. As a result of the experiments, the following conclusions were obtained: 1) The reaction rate of the catalytic hydrogenation of aniline in the temperature range between 150°C and 180°C was approximately first-order with respect to hydrogen. In the case of a large molar ratio of hydrogen to aniline, however, the reaction rate became zeroth-order with respect to aniline. 2) A good agreement was obtained between the conversion by the fluidized-bed experiment and the values calculated on the model of the contact-time distribution for low degrees of conversion. For high degrees of conversion, the deviation of the values calculated using this model from the experimental value was found to be about 10%. It was suggested that this model can well be applied to predicting the conversion for zeroth-order reaction within the limits of uncertainty given above.

Studies of the catalytic hydrogenation of aniline have previously been reported by the present authors. In this paper, the study of the hydrogenation of aniline in fluidized beds will be reported. The fluidization technique has been widely used in the chemical industry. The quantitative design of a fluidized bed reactor is, however, complicated by the gas by-passing the reaction zone via bubbles and channelling, with the result that the conversions obtained in fluidized beds are often lower than those in fixed bed at the same space velocity. Consequently, many modified reactor models have been proposed to represent the behavior of the gas flows in the fluidized bed. The experimental results of fluidized-bed runs will be analyzed in this paper in terms of the contact-time distribution model reported before.[2)]

Experimental

The Preparation of Catalysts.—*20% Cobalt-alumina.*—Powdered alumina was added to a solution of cobalt nitrate. The slurry was stirred for some time, and to it was then slowly added at 20°C a quantity of dissolved ammonium carbonate in a slight excess. The mixture was then heated and kept at 60—70°C for 5 hr. After being filtered and washed, the precipitate was dried at 100°C and calcined at 500°C for 2 hr. At this reaction temperature, the catalyst powder could be fluidized satisfactorily.[3)]

Rate Constant Measurements.—The reaction rate constant was measured by a flow-type fixed bed in a Pyrex reactor (1.8 cm. ID and 80 cm. long). The reactor was immersed in a fluidized thermal bath in order to maintain the desired reaction temperature. The temperature was controlled automatically within a range of 1.0—1.5°C. About 5—10 g. of a cobalt-alumina catalyst was placed on a porous glass disk, and a thin glass thermowell was inserted from the top of the reactor. The heat of the reaction for this process was about 40 kcal./mol. Then, under the experimental conditions, a temperature gradient in the longitudinal direction of the catalyst bed was obtained. The mean temperature was estimated from the temperature distribution curves. The activity of the catalyst became almost constant after 2 hr.; the variation in the catalyst activity with reaction time was almost negligible for 30 hr. No effects of the different particle size of the catalyst on the reaction rate was observed. After the steady state of the catalyst's activity was reached, the reaction rate was estimated by the integral method.

Fluidized-bed Equipment.—The equipment used for the fluidization experiments consisted of a glass tube 90 cm. long and 5 cm. ID. Its lower part had a porous glass plate and was connected to a conical section for preheating. The temperature of the reactor was controlled by an external electric furnace. The equipment was surrounded with heating wires and was insulated with asbestos. The temperatures within the bed were measured by chromel-alumel thermocouples in glass wells located at the axis and on the inside of the reactor wall. The temperature distribution of the bed was occasionally checked by moving the thermocouples vertically throughout the bed. The observed difference in temperature between top and bottom was not more than 1 to 1.5°C.

The Measurement of the Contact-time Distribution Functions.—A method described before[2)] was used in the investigation of the contact-time distribution function in the fluidized bed. Propane was used as the adsorbent, and argon, as an inert gas.

Gas Analysis.—Samples were analyzed by gas chromatography. Separations were made by a 3 m. coulmn of polyethyleneglycol 20000 on polytetrafluoroethylene, with hydrogen as the carrier gas. The temperature of the column was 180°C.

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[1)] E. Echigoya, H. Hagiwara and A. Sakurai; presented at the 31th Annual Meeting of Chemical Engineering in Japan, Tokyo, April, 1966.

[2)] M. Iwasaki, I. Furuoya, H. Sueyoshi, T. Shirasaki and E. Echigoya, *Chem. Eng.* (*Kagaku Kogaku*), **29**, 892 (1965).

[3)] E. Echigoya, H. Hagiwara and A. Sakurai, This Bulletin, in press.

Catalyst.—The cobalt catalyst used in the kinetic studies in both fixed and fluidized beds was the 150—200 Tyler mesh fraction of the catalyst. The bulk density of the catalyst containing 20 wt.% cobalt was 0.998—1.02 g./cc.; it was reduced for 2 hr. at 450°C.

Velocity at the Minimum Fluidization.—The minimum fluidization velocity, (U_{mf}) [cm./sec.] was taken as the value at which the pressure drop across the reactor vs. hydrogen flow curve showed a discontinuity. In cases where no sharp discontinuity occurred, the intersection of the two parts of the curve was selected as the value defining U_{mf}. The average value of U_{mf} over the experimental range used 160 to 200°C was 2 cm./sec.

Experimental Results and Discussion

Kinetic Data.—The rate equation for a catalytic reaction in a flow system may be written as:

$$W/F = y_0 \int_0^x \mathrm{d}x/r \qquad (1)$$

where W: the catalyst weight [g.]
F: the total molar feed of the reaction mixture [mol./hr.]
y_0: the mole fraction of aniline in the reaction mixture
x: the conversion
r: the reaction rate [mol./g. cat. hr.]

The hydrogenation of aniline followed approximately a first order reaction kinetics with respect to hydrogen in the 150°C—180°C temperature range, for which the equation is:

$$r = k_c C_{\mathrm{H}_2} = k\,(m-3x)/(1+m-3x) \qquad (2)$$

where k_c: the specific reaction rate
C_{H_2}: the concentration of hydrogen
k: $=k_c(\pi/RT)$ [mol./g. cat. hr.], π: the total pressure [atm.]
m: the molar ratio of hydrogen to aniline
R: the gas constant
T: the reaction temperature [°K]
x: the conversion

When Eq. 2 is substituted into Eq. 1 and integrated by assuming an idealized piston flow, the following equation is obtained:

$$1/k(m+1)\int_0^x (1+m-3x)\mathrm{d}x/(m-3x) = W/F$$

$$f(m,\ x) = (1/m+1)x$$

$$+\{1/(3(m+1))\}\ \ln\,[1/\{1-(3/m)x\}] = k(W/F) \quad (3)$$

The value of the rate equation found was as follows (Fig. 2):

Temp., °C		
160	1.35×10^{-3}	(mol./g. hr.)
170	1.9×10^{-3}	
180	2.4×10^{-3}	
190	2.75×10^{-3}	

The temperature dependence of the rate constants was evaluated from the Arrehenius plot over the temperature range from 150 to 180°C. An overall activation energy (E) of 12 kcal./mol. was calculated from the slope of the plot, log k vs. $1/T$. The kinetic data could be written also in the following simple form in the case of a large value of m.[4)]

$$k(W/F) = f(m,\ x) = Mx \qquad (M=1/m) \qquad (4)$$

The above equation shows that the reaction rate is zero order with respect to aniline.

Fluidized-bed Runs.—Fluidized-bed runs were made in a 2-inch-ID reactor over the temperature range between 150°C and 230°C. The results of a fluidized-bed run are shown in Table I, while a typical run is demonstrated in Fig. 3. The conversion data for the fluidized-bed were plotted as a function of the dimensionless number $k/(W/F)$. The dashed line represents the conversion in a fixed bed. All the data fall below the dashed line. An apparent rate constant, k', may be estimated from Eq. 5 for fluidized beds, but it depends on the catalyst activity, the gas-solid contact behavior,

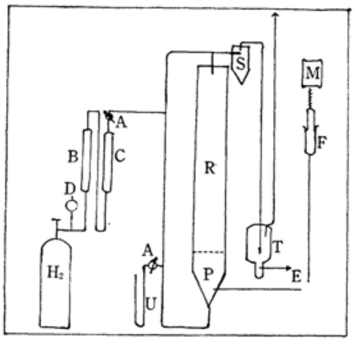

Fig. 1. Arrangement of experimental equipment.

A	flow control valve	M	feed motor
B	oxygen eliminator	P	preheater
C	flow meter	R	reactor unit
D	pressure gauge	S	cyclone
E	analysis unit	U	mercury manometer
F	aniline feed syringe	T	trap

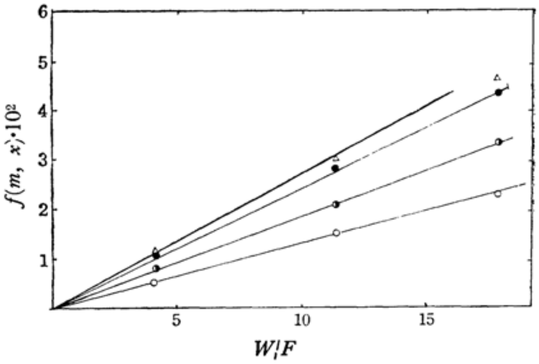

Fig. 2. Kinetics of hydrogenation of aniline with a fixed bed.

○ 160°C, ◑ 170°C, ● 180°C

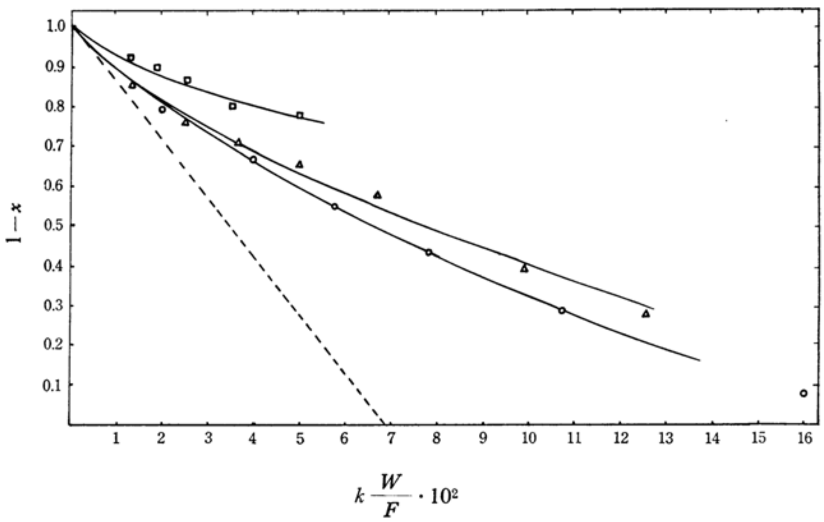

Fig. 3. The experimental data for fluidized bed (Reac. temp. 180°C).
U: ○ 3.34, △ 5.34, □ 10.69 cm./sec.

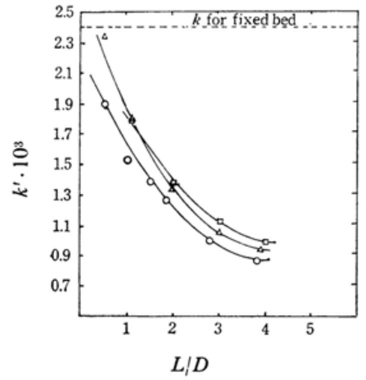

Fig. 4. Apparent rate constant as a function of L/D ratio and gas velocity for a fluidized bed.
k': rate constant (fluidized bed)
k: rate constant (fixed bed)
U: ○ 3.34, △ 5.34, □ 10.69 cm./sec.

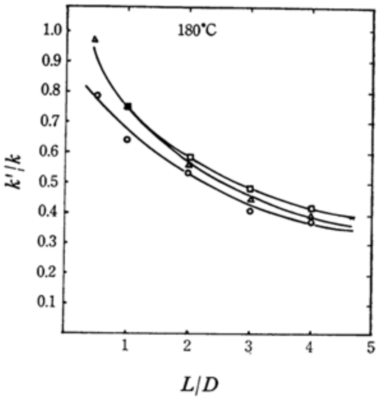

Fig. 4′ k'/k as a function of L/D ratio and gas velocity for the fluidized bed.
k': rate constant (fluidized bed)
k: rate constant (fixed bed)
U: ○ 3.34, △ 5.34, □ 10.69 cm./sec.

and the temperature.

$$k' = (F/W)Mx \tag{5}$$

When the catalyst activity and the temperature are held constant, k'/k is a measure of the efficiency of the fluidized bed as a device for the gas-solid contact. The fixed bed value is also shown in Fig. 4 for the sake of comparison. The value of k' appears to decrease rapidly with an increase in the bed height and to decrease slightly with a decrease in the gas velocity. At a lower temperature (for example, 160°C), the effects of these parameters on k' were not very large.

The Application of the Contact-time Distribution Model.—Fluidized beds have been characterized by the distribution of residence time. The use of a residence-time distribution $E(\varphi)$ is, however, restricted to homogeneous reactions of the first-order. It seems desirable, therefore, to define a contact-time or reaction-time W/F in connection with heterogeneous reactions. For the zeroth-order reaction, the mean fraction of reactant remaining at the exit of the bed is given below in terms of the contact time:[4]

$$1-x = \int_0^{\theta_{\mathrm{lim}}} (1-K\theta)C(\theta)\mathrm{d}\theta \tag{6}$$

where $K=(k/M)(W/F)$, $\theta_{\mathrm{lim}}=(W/F)_{\mathrm{lim}}/(W/F)$; W/F: the mean contact time [hr. g./mol.]; $(W/F)_{\mathrm{lim}}$: the contact time when x attains to

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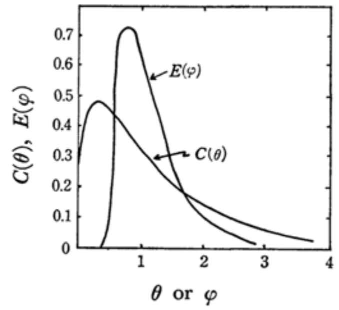
[4] E. Echigoya, K. Toyoda and K. Morikawa, presented at the 30th Annual Meeting of Chemical Engineering in Japan, Osaka, April, 1965.

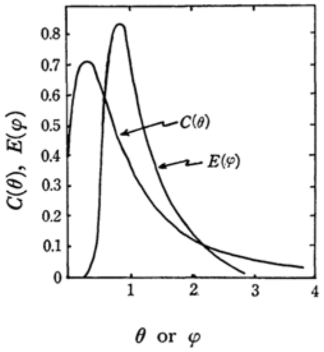
TABLE I. EXPERIMENTAL RESULTS IN THE FLUIDIZED BED

	W/F [g. hr./mol.]	U cm./sec.	Conversion % Reaction temp. 160°C	170°C	180°C	190°C	200°C	210°C	220
49 g.	8.3	3.34	15.5	20.0	23.6	24.5	23.0	22.5	18
	5.2	5.34	8.7	12.4	17.9	17.5	15.6	16.2	15
	2.6	10.69	5.1	5.7	7.8	8.2	8.2	8.0	
98 g.	16.6	3.34	27.5	34.0	37.5	38.4	374	33.0	27
	10.4	5.34	17.8	23.6	23.1	23.0	26.5	23.2	20
	5.1	10.69	8.9	12.4	14.6	15.0	13.8	11.7	7
145 g.	24.6	3.34	34.8	45.1	51.7	51.0	48	40.5	32
	15.4	5.34	23.1	30.4	34.7	35.7	35.0	31.4	25
	7.6	10.69	11.4	15.2	17.7	18.4	17.5	13.0	7
194 g.	32.9	3.34	40.0	54.5	63	62.5	57	47.7	36
	20.6	5.34	27.2	36.0	42	42.1	40.3	37.1	34
	10.1	10.69	13.6	17.0	21.5	22.4	20.4	17.2	11
266 g.	45.2	3.34	42.5	57.4	68	66.5	61.0	52.2	38
	28.3	5.34	32.3	40.8	46.5	46.0	42.5	39.5	35
	13.9	10.69	16.5	21.1	24.6	25.5	24.0	21.6	17
395 g.	67.1	3.34	67	82.3	90	85.1	75.0	66.4	49
	42.0	5.34	44	53.8	60.0	57.5	50.4	43.1	34
	20.6	10.69	22.6	27.4	31	30.6	28.2	24.6	19
496 g.	53.0	5.34	54.0	65.2	71	67.3		51.5	

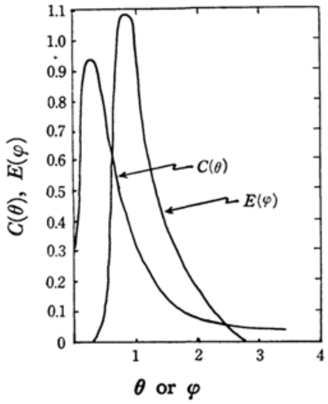


$L/D=3$, $U=3.5$ cm./sec.

1 [hr. g./mol.] $C(\theta)$: contact time distribution function (see lit. 2) [mol./hr. g.]. This equation was normalized with respect to W/F, the average contact time. $C(\theta)$ could be estimated by the input (pulse) response technique. Some examples of the curves of $C(\theta)$ are shown in Fig. 5. The distribution of residence time for an inert gas (obtained by an input-response technique) is superimposed on the contact-time distribution plots in Fig. 5. The conversion curve calculated by Eq. 6 is compared with the experimental values in Fig. 6. From the comparison, a good agreement between the calculated conversion on the model and the experimentally-determined conversion was obtained for low degrees of conversion. However, for high degrees of conversion, the calculated value was a little low compared with that of the experimental conversion. From these data, it may be concluded that the $C(\theta)$ curve can give enough information for predicting the conversion in the zeroth-order reaction.



$L/T=5$, $U=5.5$ cm./sec.



$L/D=3$, $U=10.5$ cm./sec.

Fig. 5. Contact time distribution $C(\theta)$ and sidence time distribution $E(\varphi)$.

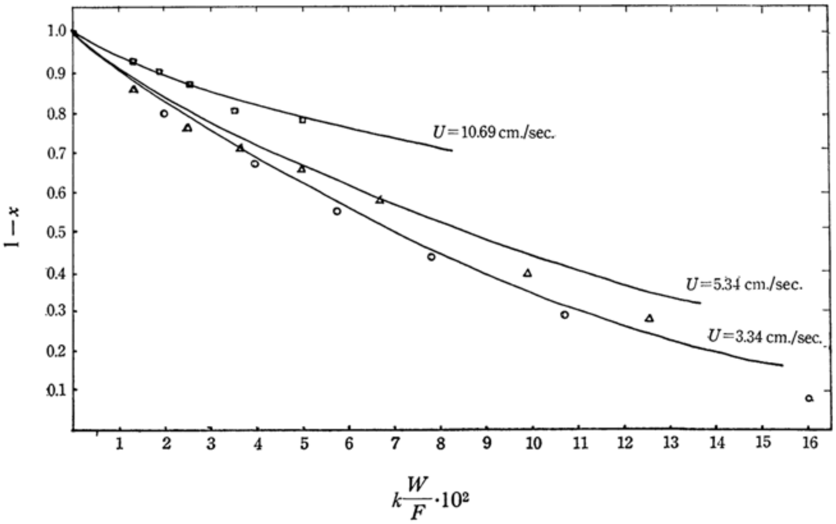


Fig. 6. The calculated values from the contact time distribution (180°C) model (full lines).

○, △, □……experimental points

Summary

1) The catalytic hydrogenation of aniline to cyclohexylamine over a cobalt alumina catalyst was carried out in the fluidized bed under the following conditions; the temperature range: 160—220°C, W/F: [g. hr./mol.] 2.6—67.

2) The reaction rate was found to be of the zeroth-order with respect to aniline in the case of a large molar ratio of hydrogen to aniline, using the fixed bed.

3) It was found that the contact-time distribution model could be usefully applied to predicting the conversion for the zeroth-order reaction in the fluidized bed within limits of 10%.

The authors wish to thank Professor Kiyoshi Morikawa for his useful discussion and constant guidance.