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Chemical Engineering Communications

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713454788>

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To cite this Article Choudhary, V.R. and Parande, M.G.(1979) 'STUDY OF DIFFUSION IN COPPER CHROMITE CATALYST UNDER REACTION CONDITIONS', *Chemical Engineering Communications*, 3: 1, 21 – 27

To link to this Article: DOI: 10.1080/00986447908935848

URL: <http://dx.doi.org/10.1080/00986447908935848>

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STUDY OF DIFFUSION IN COPPER CHROMITE CATALYST UNDER REACTION CONDITIONS

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(Received November 21, 1977; in final form February 2, 1978)*

INTRODUCTION

The knowledge of effective intraparticle diffusivities of reactants and products in porous catalysts is required for predicting the effects of intraparticle mass transfer on the reaction rate and also in the design of catalytic reactors. It is desirable to determine the effective diffusivity experimentally under actual reaction conditions or even during catalysis.

During the past twenty years, gas chromatographic techniques have been developed into very useful experimental tools for determining the physico-chemical properties (Choudhary and Doraiswamy, 1971) and transport properties (Choudhary, 1974) of solid catalysts and adsorbents. Apart from the simplicity and rapidity with which the required data are obtained, an attractive feature of this technique is that most of the studies can be made on a large and representative sample of the solid catalyst under the operating conditions of the catalyst. Recently Choudhary and Menon (1976) studied the effective diffusivity of hydrocarbons in commercial Pt-alumina reforming catalyst at temperatures which approach those used in the catalytic process using a gas chromatographic technique based on the plate theory.

The present investigation is concerned with the determination of the effective diffusivities of nitrobenzene and aniline in copper chromite catalyst (which is used for the reduction of nitrobenzene to aniline at 200-300°C and at atmospheric pressure) under reaction conditions using the gas chromatographic pulse broadening technique based on the plate theory.

EXPERIMENTAL

The chromatographic data were obtained by using an AIMIL-NCL dual column gas chromatograph with a thermal conductivity detector (TCD). Hydrogen (which is one of the reactants for the reduction of nitrobenzene to aniline) was used as a carrier gas at atmospheric pressure in order to simulate the reaction conditions.

The catalyst (copper chromite: $\text{CuO-CuCr}_2\text{O}_4$) has the following properties: Surface area, 54.2 m^2/g ; particle porosity, 0.634; and average pore radius, 108 Å. A chromatographic column was prepared by packing 0.113 mm diameter catalyst particles in a 6 mm

† NCL Communication No. 2093.

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diameter stainless steel tube. The length of the packed column was 68.4 cm and the void and solid fractions were 0.52 and 0.48, respectively.

The nitrobenzene and aniline were BDH Analar grade. The hydrogen was ultra high purity (UHP) grade.

The catalyst in the chromatographic column was reduced by passing hydrogen through at 310°C for about 24 h. Subsequently the catalyst was kept in a hydrogen atmosphere. The chromatographic data were obtained by injecting 3 μ l of the liquid sample and measuring the retention time and the height equivalent to a theoretical plate (HETP) of the effluent pulse as a function of carrier gas velocity at different temperatures. The interval between two successive injections was kept constant (at 20 min) throughout the experiment. The carrier interstitial gas velocity was varied from 96 to 373 cm/sec and the temperature from 224°C to 307°C. The inlet pressure of the catalyst column was about 22 mm Hg above the outlet (atmospheric) pressure. The reproducibility of the catalyst surface after a passage of the pulse over it was checked from time to time.

The extent of the reaction occurring during the passage of the nitrobenzene pulse through the catalyst column at the experimental conditions was found to be negligibly small.

RESULTS AND DISCUSSION

The values of the mass transfer term (C) in the Van Deemter equation (Van Deemter *et al.*, 1956) were evaluated from the slopes of linear plots of HETP vs interstitial gas velocity at high carrier gas flow rates according to the equation, $H = A + Cv$. The error in the determination of HETP was of the order of 3–6%, and hence the final values of the effective diffusivity are also expected to have an error of the same order. An average of 3–4 values of HETP was used. The measurements of HETP based on the catalyst alone are not as reliable as those obtained by comparison of results for the catalyst and for a truly nonporous pellet bed of the same dimensions (Trimm and Corrie, 1972). However, this was not done in the present study due to the lack of time and also because nonporous particles of the same dimensions as those of the catalyst were not available. The distribution coefficients (K) were obtained by using the expression (Eberly, 1969):

$$K = 1/[\epsilon + (t_R - t_d)\nu F_1/F_2L] \quad (1)$$

and the apparent adsorption equilibrium constants (K_n) from the relation (Eberly and Spencer, 1961):

$$K_n = (t_R - t_d)\nu F_1/L \quad (2)$$

The values of C , K and K_n are presented in Table I. It can be seen from the results that the coefficients C and K_n decrease with temperature while the distribution coefficient K increases with temperature.

The effective pore diffusion coefficients can be estimated from the C term using the following relationships:

TABLE I
Results of diffusion measurements

System	Temperature (°C)	$C \times 10^3$ (sec)	$K \times 10^3$	K_n	$D_k \times 10^3$ (cm ² /sec)	$(D_{II}/K) \times 10^3$ (cm ² /sec)	$(D_p/K) \times 10^3$ (cm ² /sec)	$D_r \times 10^3$ (cm ² /sec)	$D_e \times 10^3$ (cm ² /sec)
Nitrobenzene	224	41.4	9.0	51.3	21.1	16.9	19.3	17.6	17.9
	244	36.1	11.0	43.2	21.5	19.4	22.1	20.1	20.5
	272	32.9	19.8	23.9	22.1	21.2	24.2	22.1	22.5
	300	27.1	26.3	17.9	22.7	25.8	29.5	26.8	27.4
Aniline	227	109.0	10.5	45.7	24.3	6.4	7.3	6.7	6.9
	257	83.1	13.1	36.2	25.1	8.4	9.6	8.8	8.9
	277	53.8	17.4	27.3	25.6	13.0	14.8	13.5	13.8
	307	16.9	59.3	7.8	26.2	36.9	35.3	27.0	33.1

D_e is an average of the values of D_{II}/K , D_p/K and D_r .

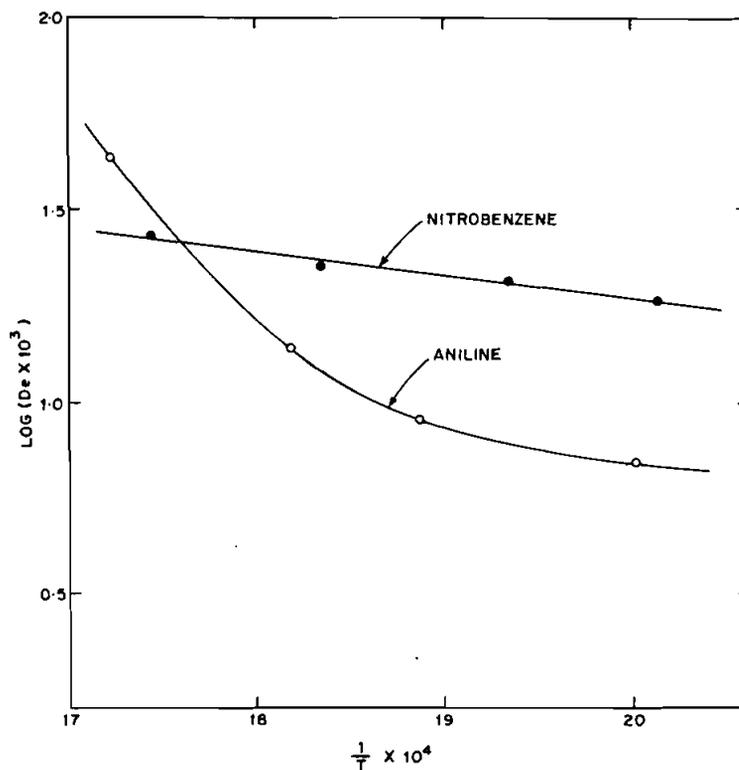


FIGURE 1 Temperature dependence of effective diffusivity.

$$C = \frac{F_1 d_p^2 K}{2\pi^2 F_2 D_{II} (1 + K F_1 / F_2)^2} \quad (3)$$

where D_{II} is the diffusivity in the porous solid,

$$C = \frac{\epsilon' (1 + K_n)^2 d_p^2}{30 [1 + \epsilon' (1 + K_n)]^2 D_r} \quad (4)$$

where D_r is the radial diffusion coefficient, and

$$C = \frac{F_1 F_2 [1 + (1 - \epsilon)/\epsilon K] d_p^2}{30 [1 + F_2 (1 - \epsilon)/\epsilon K]^2 D_p} \quad (5)$$

where D_p is the diffusivity in the solid phase. Equation (3) was the original expression (neglecting the external diffusion in the packed column) suggested by Van Deemter *et al.* (1956) for the case of an ion-exchange resin. Equation (4) was derived by Grubner *et al.* (1966) from the more exact theory (moment theory) of gas-solid chromatography, while

Eq. (5) was obtained from the relation derived by Hawkes (1972) using the Giddings theory of non-equilibrium chromatography (Giddings, 1965). In the case of the present study, $K \ll 1$ or $K_n \gg 1$ (see Table I). These inequalities are satisfied in all cases except for aniline at 307°C. Equations (3), (4) and (5) can then be simplified as:

$$C = \left[\frac{1}{2\pi^2} \right] \frac{F_1}{F_2} \frac{d_p^2}{(D_{II}/K)} \quad (6)$$

$$C = \left[\frac{1}{30\epsilon} \right] \frac{F_1}{F_2} \frac{d_p^2}{D_r} \quad (7)$$

$$C = \left[\frac{\epsilon}{30(1-\epsilon)} \right] \frac{F_1}{F_2} \frac{d_p^2}{(D_p/K)} \quad (8)$$

Grubner (1968) has justified the use of the simplified expression (Eq. 7) when $K_n > 15$. Equations (6) to (8) are similar except for the terms given in the square brackets. The values of effective intraparticle diffusion coefficients were estimated from the mass transfer term (C) using Eqs. (6) to (8). For the case of aniline at 307°C, Eqs. (3) to (5) were used. The results are presented in Table I along with the Knudsen diffusion coefficient (D_k) obtained from the relationship (Satterfield, 1970):

$$D_k = 9700r_p\sqrt{(T/M)} \quad (9)$$

The temperature dependence of the effective diffusion coefficients when expressed by the Arrhenius relationship (Figure 1) was found to be linear, with ΔE equal to 2.93 kcal/gmol. In the case of aniline, however, the Arrhenius plot is non-linear and there is a marked increase in the dependence of effective diffusivity on temperature above 257°C. The temperature dependence of the effective intraparticle diffusivity of nitrobenzene is expressed by the relation:

$$D_e = 0.343 \exp(-2930/RT) \quad (10)$$

The values of the mean free path calculated from the relation based on the kinetic theory of gases (Glasstone, 1948) for nitrobenzene (431 Å at 200°C and 523 Å at 300°C) are greater than the average pore diameter (216 Å) and hence the gas flow in the catalyst is controlled by Knudsen diffusion. It can be noted from the experimental results (Table I) that the values of D_e for aniline except at 307°C are smaller than those for nitrobenzene. Thus the values of D_e do not depend on the molecular weight alone as predicted by Knudsen diffusion.

Further, in the case of nitrobenzene, the activation energy for D_e ($\Delta E = 2.93$ kcal/gmol) is very high as compared to that for D_k ($\Delta E < 0.2$ kcal/gmol), while in the case of aniline there is a pronounced effect of temperature on D_e above 257°C (Figure 1). All these facts indicate pronounced effects of adsorption and surface diffusion on the overall flow in the catalyst. Such anomalous results have also been obtained by Trim and Corrie (1972) for the effective diffusivity of oxygen and butadiene in tin and antimony

oxide catalysts above a temperature of 400°C and were explained in terms of the surface diffusion model. As the surface mobility increases exponentially with temperature because of the weakening of the bonding between the surface and the absorbed molecules, it provides a good explanation for such effects.

Apart from the surface diffusion, the transient gas flow in the catalyst depends also on its retardation due to adsorption on the pore wall, which decreases with temperature. Thus the temperature dependence of the effective diffusivity is governed by the combined effect of adsorption and surface diffusion, which may vary from system to system. In the case of aniline, the influence of adsorption and surface diffusion seems to be very pronounced above 257°C, leading to a non-linear dependence of D_e on temperature, while in the case of nitrobenzene the effect leads to a linear dependence of D_e on temperature.

It can be seen from the results (Table I), that the values of D_{II}/K , D_p/K and D_r are comparable. Grubner *et al.* (1967, 1968) have thoroughly investigated the nature and the actual significance of the coefficient D_r in Eq. (4) or (7) and have established that D_r has the significance of the actual coefficient of effective diffusion. Hence the coefficients D_{II}/K and D_p/K have the significance of actual coefficients of effective diffusion.

CONCLUSION

The effective diffusivities of nitrobenzene and aniline in copper chromite catalyst have been determined under reaction condition (at temperatures of 224°C and 307°C and a pressure 1 atm) using the gas chromatographic pulse broadening method based on the plate theory. The results show the pronounced effect of adsorption and surface diffusion on the catalyst diffusivity.

ACKNOWLEDGEMENT

The authors wish to thank Dr. L.K. Doraiswamy, Director, National Chemical Laboratory, Poona for his encouragement throughout the investigation.

NOMENCLATURE

C	Mass transfer term in the Van Deemter equation
D_e	Effective diffusivity of catalyst (cm ² /sec)
D_{II}	Diffusivity in the porous solid (cm ² /sec)
D_k	Knudsen diffusion coefficient (cm ² /sec)
D_r	Radial diffusion coefficient (cm ² /sec)
d_p	Average particle diameter (cm)
F_1	Void fraction in packing

F_2	Solid fraction in packing ($1 - F_1$)
H	Height equivalent to a theoretical plate (cm) $H = (L/16)(W/t_R)^2$
K	Distribution coefficient
K_n	Apparent adsorption equilibrium constant
L	Length of the packed column (cm)
M	Molecular weight
T	Temperature ($^{\circ}\text{K}$)
t_R	Retention time of the absorbate (sec)
t_d	Retention time of the non-absorbate (sec)
v	Interstitial carrier gas velocity (cm/sec)
W	Peak width at base line (sec)

Greek Symbols

ΔE	Apparent activation energy for diffusion (kcal/gmol)
ϵ	Porosity of the catalyst
ϵ'	$\epsilon(F_1/F_2)$

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