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Liquid-Phase Oxidation of Diethanolamine on a Pd-Al_2O_3 Catalyst. II.[1,2] The Effect of Mass Transfer on the Global Rate of Reaction

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The oxidation of diethanolamine to N-(2-hydroxyethyl)glycine in alkaline solution was carried out over a Pd–Al_2O_3 catalyst in a liquid-full reactor, and the effect of mass transfer on the global rate of reaction was studied. Data were taken at 40 °C and atmospheric pressure. Experiments were first done to determine the order of reaction with respect to oxygen, which was found to be 0.64 for an assumed tortuosity factor of 3.4 for the catalyst particles. Under the reaction conditions used, the effective mass transfer area between liquid and porous catalyst was found to be less than the outer surface area of the particles. With 0.5% Pd–Al_2O_3 catalyst, the global rate of reaction was mainly controlled by liquid-solid and intraparticle mass transfers, and the reaction was considered to be completed inside the deactivated outer shell, as the core of the particle still retained high catalyst activity.

Keywords——liquid-phase oxidation; diethanolamine; palladium on aluminum oxide catalyst; deactivation of catalyst; packed-bed reactor; liquid-full reactor; liquid-solid mass transfer; effective mass transfer area; intraparticle mass transfer

Packed-bed reactors in which gas and liquid phases flow through the catalyst particles are often chosen for the operation of three-phase reactions, such as catalytic oxidation and hydrogenation reactions. One of the principal advantages is that they may be easily operated and controlled as needed. However, because of the low solubility and low diffusivity of gases in liquid, the global rates of reaction in such reactors are often controlled by gas-liquid, liquid-solid and intraparticle mass transfers. Hence, correlations of rate coefficients for the several steps involved in the overall process are important. Mass transfer from gas to liquid has been studied extensively, and many reviews are available.[3] A number of correlations of liquid–solid mass transfer coefficients have been cited in the literature.[3–7] The correlations are based on either dissolution of nonporous particles or reaction with a nonporous solid. It was reported that the mass transfer rates from liquid to porous particles were less than those estimated from the correlations.[8,9]

The oxidation of diethanolamine to N-(2-hydroxyethyl)glycine on Pd–Al_2O_3 catalyst is fast and selective at temperatures and pressures near ambient,[1,10] and the kinetics has already been studied.[1] Thus, the reaction was chosen to determine the mass transfer coefficients from liquid to porous solid and to compare the results with those obtained from correlations. An aqueous solution of diethanolamine and sodium hydroxide saturated with a mixture of oxygen and nitrogen was introduced into the packed-bed of Pd–Al_2O_3 catalyst. This type of reactor, the liquid-full reactor, is suitable for studying liquid–solid mass transfer. Another objective was to study the effect of intraparticle mass transfer on the global rate of reaction.

Experimental

Chemicals——The chemicals used were the same as those described in the previous paper.[1]

Catalyst Preparation——Evacuated alumina particles (2—4 mm) were soaked in an aqueous hydrogen chloride solution of palladium chloride for 8 hours. The solution was evaporated off, and after thorough drying, the particles were reduced at 400 °C for 4 hours in a Pyrex glass tube through which hydrogen was flowing. After crushing and sieving, particles with average sizes of 0.055 cm (28 to 32 mesh) and 0.110 cm (14 to 16 mesh) were chosen for the reaction studies. Uniform dispersion of the palladium was visually confirmed throughout the particles. Catalysts of two activities, containing 0.05wt% and 0.5 wt% Pd, were prepared. The physical properties of the catalysts are shown in Table I.

TABLE I. Physical Properties of Catalysts

Surface area, m^2/g	150[a]
Pore volume, cm^3/g	0.53[a]
Solid phase density, ρ_S, g/cm^3	3.40[b]
Particle density, ρ_P, g/cm^3	1.21[c]
Bulk density, ρ_B, g/cm^3	0.72[b]
Porosity of particles, ε_P	0.644[c]
Void fraction of bed, ε_B	0.405[c]

a) From Sumitomo Chemical Ind., Ltd.
b) Measured.
c) Calculated.

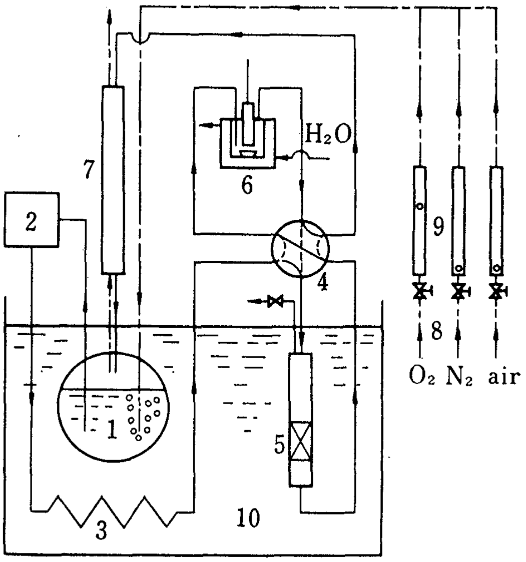

Fig. 1. Schematic Diagram of the Reactor Apparatus

1, absorber; 2, quantitative pump; 3, preheater; 4, six-way valve; 5, liquid-full reactor; 6, oxygen analyzer; 7, packed-bed (glass beads); 8, needle valve; 9, rotameter; 10, constant temperature bath.
- - -→-, gas flow line; ——→—, liquid flow line.

Apparatus and Operating Procedure——Fig. 1 shows a schematic diagram of the apparatus used. In an absorber 1, the aqueous solution of diethanolamine and sodium hydroxide was saturated with oxygen or a mixture of oxygen and nitrogen by continuous bubbling. The solution was recycled through the absorber after each pass through the liquid-full reactor 5. The reactor and the absorber were contained in a constant temperature bath 10 so that the reaction and absorption temperatures were equal. A series of runs was initiated by charging the absorber with 1 liter of the aqueous solution containing diethanolamine and sodium hydroxide (0.1 mol each) and terminated when conversion reached about 3%. Hence, the concentrations were essentially uniform throughout the reactor and were assumed to be uniform during runs. Simple calculations based on the average global rate of reaction indicated that one batch of the mixed solution could be used for about 50 hours. The auxiliary parts of the apparatus provided for measuring the oxygen concen-

TABLE II. Operating Conditions

Palladium content, wt%	0.05, 0.5
Catalyst particle size, d_P, cm	0.055[a] (0.05% Pd and 0.5% Pd), 0.110[b] (0.5% Pd)
Mass of catalyst in reactor, m, g	0.20 (0.5% Pd, $d_P=0.055$), 0.30 (0.5% Pd, $d_P=0.110$), 3.0 (0.05% Pd)
Concentration of diethanolamine, mol/cm^3	1.0×10^{-4}
Concentration of NaOH, mol/cm^3	1.0×10^{-4}
Concentration of O_2 in liquid entering the catalyst bed, C_{in}, mol/cm^3	$1.09\times10^{-7}-7.48\times10^{-7}$
Liquid feed rate, Q_L, cm^3/s	0.065—0.227 ($d_P=0.055$), 0.110—0.226 ($d_P=0.110$)
Reaction temperature, °C	40.0
Total pressure, atm	1.0

a) 28 to 32 mesh. b) 14 to 16 mesh.

tration in the liquid, measuring the flow rates of gases, and preheating and pumping the feed streams, as shown in Fig. 1.

The glass reactor was 0.96 cm i.d. and 25 cm long. The liquid was introduced into the top of the reactor. The catalyst bed was supported by a stainless steel screen, placed near the bottom of the reactor.

The effluent from the reactor was introduced into the top of a packed-bed 7 (3 cm i.d. and 20 cm long) with 3—4 mm glass beads. In this column the liquid was brought into contact with the gas stream from the absorber in a countercurrent mode, so that most of the oxygen consumed in the liquid-full reactor was supplied from the flowing gas to the liquid. The liquid was then recycled to the absorber. The gas, after passing through the packed-bed, was discharged. Operating conditions are shown in Table II.

The concentrations of oxygen in liquid entering and leaving the reactor were measured with a Beckman-Toshiba model 777 Oxygen Analyzer 6, and recorded. The oxygen sensor of the instrument was placed in a water-jacketed vessel in which the liquid was continuously stirred.

The mass of catalyst packed in the reactor satisfied the requirement of differential operation, that the conversion of oxygen per pass should be low. The average concentration of oxygen in the bulk liquid of the catalyst bed, C_B [mol/cm^3], was calculated as

$$C_B = C_{in}(1-x/2) \tag{1}$$

where C_{in} [mol/cm^3] is the concentration of oxygen in the liquid entering the reactor and x [—] is the conversion of oxygen per pass.

The global rate of reaction, R_V [mol/(cm^3 of catalyst)(s)], was calculated as follows

$$R_V = \frac{Q_L C_{in} x}{(m/\rho_P)} \tag{2}$$

where Q_L [cm^3/s] is the liquid feed rate, m [g] is the mass of the catalyst in the reactor and ρ_P [g/cm^3] is the catalyst particle density.

Results and Discussion

Reaction Order with Respect to Oxygen

It is well known that the slurry reactors are usually used to determine the order of reaction, since in slurry reactors the reaction mixture with fine powdered catalyst is vigorously stirred, so that both interphase and intraparticle mass transfer resistances are less significant and can be neglected. As described in the previous paper,[1] however, experiments employing the slurry reactor were not successful in determining the order of reaction with respect to oxygen, because of the rapid decrease in catalyst activity at the very beginning of the reaction. In this study, by using less active catalyst particles (0.05% Pd–Al_2O_3), the dependence of the intrinsic rate of reaction on the concentration of oxygen in the liquid was investigated.

The global rates of reaction are plotted as a function of reaction time in Fig. 2. At intervals of 1 to 1.5 hours C_{in} was varied. Five points connected by the dotted line are R_Vs for $C_{in}=1.97\times10^{-7}$. A rapid decrease in R_V was observed on passing the liquid of $C_{in}=7.84\times10^{-7}$ during a period of 1.6 to 3 hours. Qualitatively, this observation is in agreement with the previous result for powdered catalyst, that the initial activity of catalyst is inversely proportional to the concentration of oxygen in the liquid.[1] After 4 hours the further decrease in R_V was observed to be insignificant even on passing liquid of $C_{in}=1.09\times10^{-7}$, 4.30×10^{-7} or 7.84×10^{-7}. Thus, R_V for each concentration of oxygen in the liquid was corrected on the basis of the value for $C_{in}=1.97\times10^{-7}$ at 6 hours. A linear relationship for the decrease in R_V was assumed between the adjacent values of R_V for $C_{in}=1.97\times10^{-7}$, represented by the dotted line in Fig. 2. By multiplying the measured R_V by the ratio of the values of solid and dotted lines at the corresponding reaction time, the corrected R_V was obtained. The corrected values are shown in the figure.

Under the experimental conditions used, the limiting reactant was oxygen, since the concentrations of diethanolamine and sodium hydroxide were more than 100 times larger than the concentration of oxygen in the liquid.

The global rate of reaction can be expressed in terms of the mass transfer rate of limiting reactant to the catalyst particles;

$$R_V = k_S a_V (C_B - C_S) \tag{3}$$

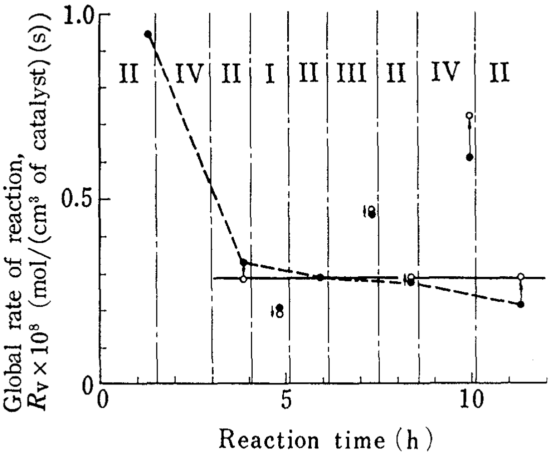

Fig. 2. Deactivation of the Catalyst

●, measured; ○, corrected.
Catalyst: 0.05% Pd–Al_2O_3, $d_P=0.055$ cm. $Q_L=0.227$ cm³/s. $C_{in}\times10^7$ (mol/cm³): I, 1.09; II, 1.97; III, 4.30; IV, 7.84.

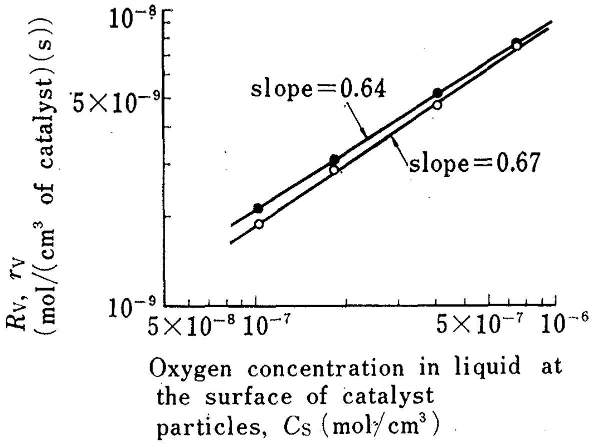

Fig. 3. Effect of Oxygen Concentration on the Rate of Reaction

○, R_V; ●, r_V.
Catalyst: 0.05% Pd–Al_2O_3, $d_P=0.055$ cm. $Q_L=0.227$ cm³/s.

where k_S [cm/s] is the liquid–solid mass transfer coefficient, a_V [1/cm] is the effective liquid-solid mass transfer area per unit volume of catalyst, and C_S [mol/cm³] is the concentration of oxygen in the liquid at the surface of the catalyst particles.

Many correlations for mass transfer factor, j_D [—], have been presented in the literature.[3–7] Dwivedi *et al.* reanalyzed the previous experimental data on fluid-solid mass transfer in a fixed bed, and developed the following correlation;[7]

$$\varepsilon_B j_D = \varepsilon_B \frac{k_S}{u_0} Sc^{2/3} = \frac{0.765}{Re_P^{0.82}} + \frac{0.365}{Re_P^{0.386}} \tag{4}$$

where ε_B [—] is the void fraction of the bed, u_0 [cm/s] is the superficial velocity of liquid, Sc $(=\mu_L/(D\rho_L))$ [—] is the Schmidt number, and Re_P $(=u_0 d_P \rho_L/\mu_L)$ [—] is the Reynolds number based on the particle diameter, d_P [cm]: D [cm²/s] is the molecular diffusivity of oxygen in the liquid, and ρ_L [g/cm³] and μ_L [g/(cm·s)] are the density and viscosity of the liquid, respectively. The liquid–solid mass transfer area was calculated by supposing that the particles are spherical, so that

$$a_V = 6/d_P \tag{5}$$

This is the area employed in the various correlations for j_D.

By using equations (4) and (5), C_S was calculated from equation (3). As shown in Fig. 3, R_V is apparently proportional to the 0.67 th power of C_S. Even at the lowest C_{in} $(=1.09\times10^{-7}$ mol/cm³), C_S was 97.1% of C_B calculated from equation (1); the largest mass transfer resistance was expected under this condition. Therefore, the liquid–solid mass transfer resistance was negligible. However, according to the criterion for the significance of intraparticle mass transfer resistance,[11] this resistance should not be neglected in determining the order of reaction with respect to oxygen.

When n represents the order of reaction with respect to oxygen, the global rate of reaction can be written as follows

$$R_V = k_V \eta C_S^n \tag{6}$$

where k_V is the intrinsic rate constant and η [—] is the effectiveness factor. For an nth order reaction, η can be expressed in terms of the Thiele modulus, ϕ [—][12]

$$\eta = \frac{3}{\phi}\left(\frac{1}{\tanh\phi} - \frac{1}{\phi}\right) \tag{7}$$

$$\phi = \left(\frac{n+1}{2}\right)^{1/2} r_S \left(\frac{k_V C_S^{\,n-1}}{D_e}\right)^{1/2} \tag{8}$$

where r_S [cm] is the particle radius and D_e [cm^2/s] is the effective diffusivity of oxygen in liquid-filled pores. The tortuosity factor, τ [—], can be expressed as

$$\tau = D\varepsilon_P/D_e \tag{9}$$

where ε_P [—] is the porosity of particles. From equation (6) the ratio of the effectiveness factors for two values of C_S (denoted by subscripts 1 and 2) may be written as

$$\zeta_{12} = \frac{\eta_1}{\eta_2} = \frac{(R_V)_1}{(R_V)_2}\left\{\frac{(C_S)_1}{(C_S)_2}\right\}^{-n} \tag{10}$$

When there are four data, there are six possible combinations of two data. Thus, six values of ζ_{obsd} for a known value of n can be obtained from the data. From equation (8)

$$\phi_i = \phi_1\left\{\frac{(C_S)_1}{(C_S)_i}\right\}^{(1-n)/2} \qquad (i=2,\ 3,\ 4) \tag{11}$$

Assigning a value to ϕ_1, ϕ_i can be calculated; then, applying equation (7), six values of ζ_{calcd} can be obtained. The optimum value for ϕ_1 can be estimated by minimizing $\Sigma(\zeta_{\text{obsd}}-\zeta_{\text{calcd}})^2$. With this ϕ_1, k_V and D_e can be calculated from equation (**10**).

Assigning any value to n, τ was calculated. The molecular diffusivity of oxygen in the liquid was assumed to be identical with that in water.[13] For $n=0.63$, 0.64 and 0.65, $\tau=4.6$, 3.4 and 2.1, respectively. Employing Pd–Al_2O_3 catalyst, values of $\tau=3.9$ ($\varepsilon_P=0.585$)[14] and $\tau=2.59$ ($\varepsilon_P=0.503$)[8] were observed for the diffusion of hydrogen in liquid-phase hydrogenation of α-methylstyrene, and $\tau=2.9$ ($\varepsilon_P=0.423$) was observed for the diffusion of oxygen in liquid-phase oxidation of ethanol.[15] Tortuosity factors of the order of 3 to 4 have been reported in a number of investigations when the pores were filled with gas.[16] Since a similar catalyst was used in our experiments, and since no serious error will be introduced, τ was assumed to be 3.4; then, for $n=0.64$, values of $k_V=6.3\times10^{-5}$ and $D_e=6.3\times10^{-6}$ [cm^2/s] were obtained. With these values of n and k_V, the intrinsic rates of reaction, r_V [mol/(cm^3 of catalyst) (s)], were calculated, and are plotted in Fig. 3. The difference between the two lines corresponds to the intraparticle mass transfer effect.

Mass Transfer Effect on the Global Rate of Reaction

Next, the active catalyst (0.5% Pd–Al_2O_3) was used. Before taking the rate data, the catalyst was treated with the reaction mixture saturated with oxygen for about 10 hours to achieve a nearly constant activity. Corrections similar to those made in the case of the less active catalyst were made on the rate data. As shown in Fig. 4, R_V increases with Q_L for both $C_{in}=7.84\times10^{-7}$ and 1.97×10^{-7}. This means that the liquid–solid mass transfer is significant. According to correlation (4) for k_S and equation (5) for a_V, C_S was calculated from equation (3). Then the value of k_V was estimated by the least-squares method for equations (6) to (8) for $n=0.64$. The calculated R_Vs with the resulting k_V do not agree with the experimental results. It was suspected that the order of reaction with respect to oxygen for this catalyst was different from that for the less active catalyst. Thus, the same calculations were made for $n=0$ and 1. The discrepancy is much larger, as shown in Fig. 4. It is concluded, therefore, that n is 0.64 and the disagreement is mainly due to inadequate estimation of the liquid–solid mass transfer rates.

The mass transfer factor can be conveniently correlated to the power function of Re_P;

$$j_D = \beta Re_P^{-\alpha} \tag{12}$$

where α and β are the parameters. By using equation (12) instead of equation (4), similar calculations were made for arbitrary given values of α and β. In the calculation 19 data were

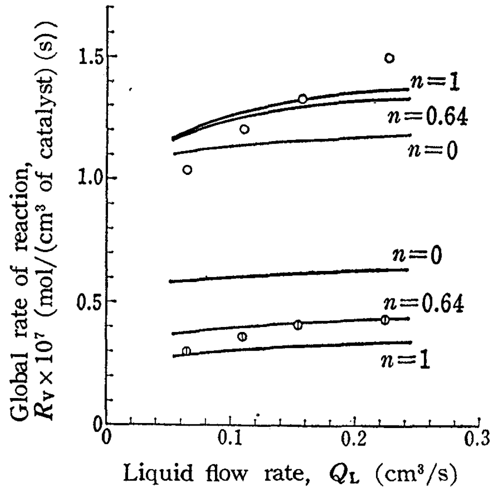

Fig. 4. Effect of Liquid Flow Rate on the Global Rate of Reaction

$C_{in}\times10^7$ (mol/cm^3): ○, 7.84; ⦶, 1.97.
Catalyst: S2, 0.5% Pd-Al_2O_3, d_P=0.055 cm.

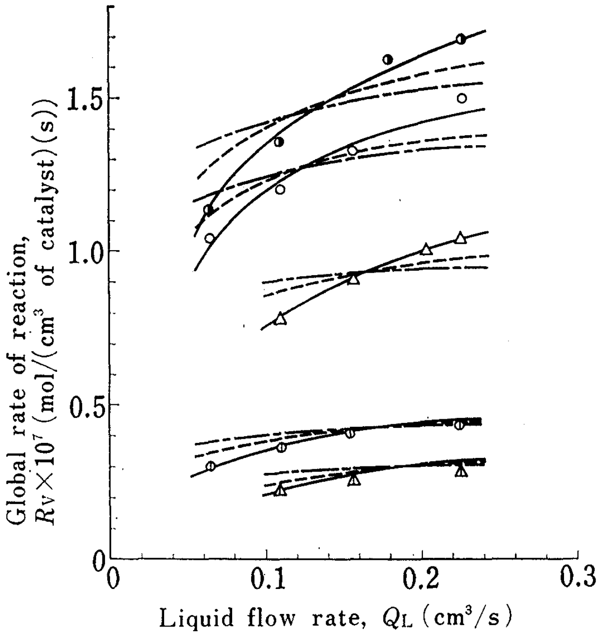

Fig. 5. Rate Data for 0.5% Pd–Al_2O_3 Catalyst

Catalyst, d_P(cm), $C_{in}\times10^7$(mol/cm^3): ◑, S1, 0.055, 7.84; ○, S2, 0.055, 7.84; ⦶, S2, 0.055, 1.97; △, L2, 0.110, 7.84; ⧊, L2, 0.110, 1.97.
———, predicted from equation (13);
- - - - -, predicted from the correlation of Evans *et al.*;
— — —, predicted from the correlation of Dwivedi *et al.*

used. The sum of squares of residuals was found to be minimum at $\alpha=0.38$ and $\beta=1.05$, and the following empirical equation was obtained;

$$j_D = 1.05Re_P^{-0.38} \tag{13}$$

The solid curves in Fig. 5 show the calculated R_V from equation (13) under various experimental conditions. The curves agree well with the experimental values. The dotted and chained curves are calculated from the correlations of Evans *et al.*[5] and Dwivedi *et al.*,[7] respectively.

The plots according to equation (13) and some available correlations based on mass transfer data (in the absence of reaction) are shown in Fig. 6. Our j_D is about 0.7 times that of Evans *et al.*[5] and about 0.25 times that of Hobson *et al.*[6] This discrepancy is too large to be explained by the uncertainties in D or other physical properties.

The difference between the mass transfer correlations and our j_D values is most likely due to differences in the effective surface areas for mass transfer. The correlations are based on the dissolution of solid particles (for example, the dissolution of benzoic acid into water). In these systems, the external surface area calculated from equation (5) may be taken as the effective surface area. In contrast, when the reaction occurs predominantly inside the pores of a catalyst particle, the mass transfer is constrained to a region close to the pore openings on the outer surface of the particle. Hence, the effective surface area for mass transfer could be considerably less than the area calculated from equation (5). A similar explanation has been proposed for mass transfer effects in disproportionation reactions[17] and a hydrogenation reaction.[8] In addition, mass transfer behavior inside the semi-stagnant liquid zone at the particle contact points may be considered to explain the difference in the effective surface area. In the dissolution system, the liquid in this zone is nearly saturated with the dissolved substance, so that the interfacial area between the flowing liquid and the semi-stagnant liquid is effective for mass transfer. On the other hand, in the reaction system, the low liquid renewal zone may not contribute appreciably to the average rate of mass transfer because of the low

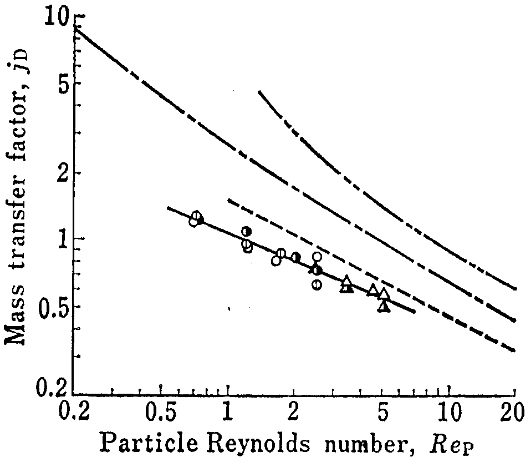

Fig. 6. Mass Transfer Factor *vs.* Particle Reynolds Number

Keys: as in Fig. 5.

————, equation (13);
– – – – –, Evans *et al.*;
— — — —, Dwivedi *et al.*;
— - — - —, Hobson *et al.*

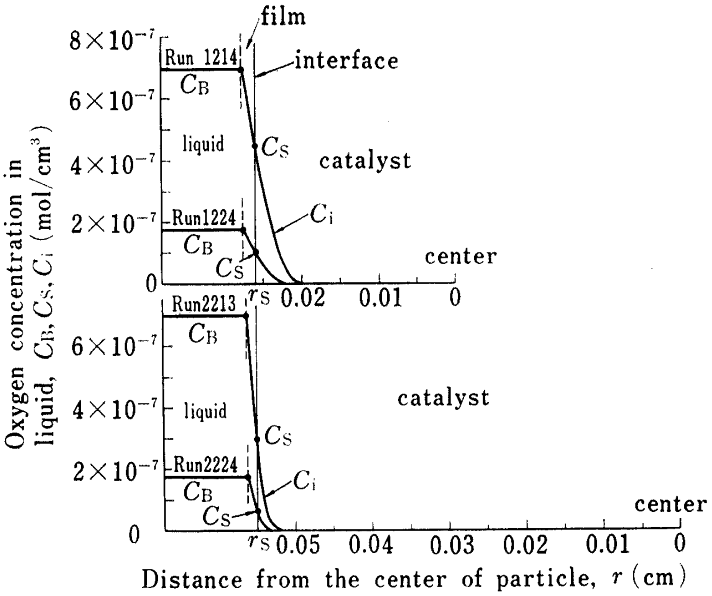

Fig. 7. Profiles of Oxygen Concentration in the Liquid

diffusivity of oxygen in the liquid, so that the effective surface area in contact with them is more and more underestimated as the rate of reaction increases. A similar explanation has been made for the effectively wetted area in trickle-bed reactors.[18] More studies are needed on porous catalysts in order to provide a complete explanation for the difference in j_D.

The concentration of oxygen in liquid-filled pores, C_l [mol/cm^3], can be calculated by solving numerically the mass balance equation (14);

$$\frac{d^2C_l}{dr^2}+\frac{2}{r}\frac{dC_l}{dr}=\frac{k_VC_l^{0.64}}{D_e} \tag{14}$$

with boundary conditions;

$$r=r_S;\ C_l=C_S \tag{15}$$

$$r=r_S;\ \frac{dC_l}{dr}=\frac{r_SR_V}{3D_e} \tag{16}$$

where r [cm] is the distance from the center of a particle. The concentration profiles for four examples are shown in Fig. 7. For both small and large particles, C_l approaches zero at a point very close to the outer surface.

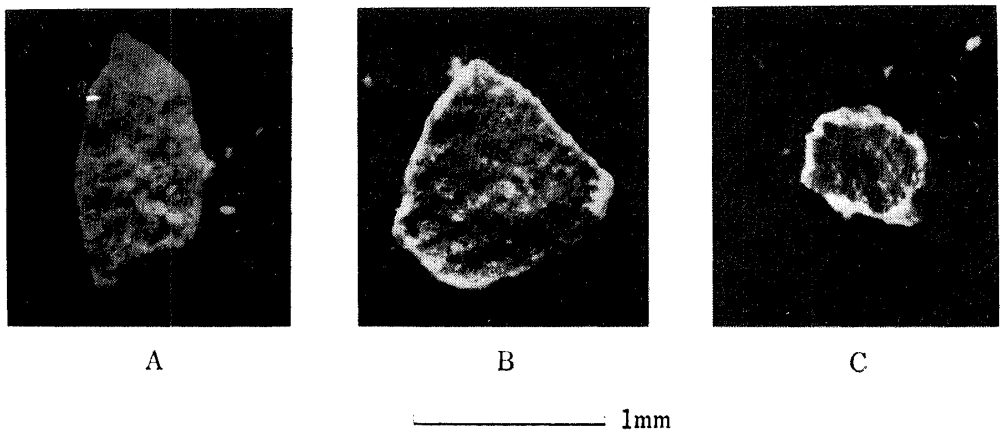

Fig. 8. Sections of Catalyst Partiales

A: fresh($d_P=0.110$ cm). B: 40 hours used($d_P=0.055$ cm). C: 40 hours used($d_P=0.110$ cm).

Fig. 8 shows sections of fresh and about 40-hour-used catalyst particles (0.5% Pd–Al_2O_3). The used particles have a whitish outer shell about 0.01 cm in thickness. It was observed in the previous work that when the powdered catalyst was treated with the solution saturated with oxygen, it turned a whitish color with a rapid decrease in activity.1) From this observation and by comparing the thickness of the outer shell with the concentration profile shown in Fig. 7, it may be concluded that the oxidation of diethanolamine is completed inside the outer shell while the core still retains high activity, and that the coloration corresponds to deactivation of the Pd–Al_2O_3 catalyst, though the colored substance has not yet been identified.

Conclusion

For the liquid-phase oxidation of diethanolamine on Pd–Al_2O_3 catalyst, the order of reaction with respect to oxygen was found to be 0.64. The global rate of reaction could be well explained by assuming the tortuosity factor of the particles to be 3.4. The mass transfer factors in a liquid-full reactor were about 0.25 to 0.7 times as large as those obtained from the correlations based on mass transfer experiments with nonporous particles. It may be postulated that the difference is due to less effective surface area for mass transfer. As Pd was very active for the oxidation of diethanolamine, the global rate of reaction was mainly controlled by both liquid–solid and intraparticle mass transfers of oxygen. This indicates that a catalyst having Pd only at the outer part of the particle is sufficient when the reaction is carried out in a packed-bed reactor operating under ambient pressure. However, the decrease in the catalyst activity with reaction time shows that a more stable catalyst is still required.

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