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A Review of Mass Transfer Controlling the Reaction Rate in Heterogeneous Catalytic Systems

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1. Introduction

Mass transfer limitations play an important role on the rate of reaction; the rate of conversion and product formation, including in the catalytic systems. In a homogeneous catalytic reaction in which all substances (reactant(s), product(s), and catalyst) are in the same phase, the effect of mass transfer between phases is mostly negligible. In a heterogeneous catalytic reaction; however, the catalyst is usually in a different phase from the reactant(s). Commonly the catalyst is in the solid phase embedded in the reacting species which usually are in the liquid or gaseous phase. Consequently, the reaction rate is principally relied on the mass transfer or diffusion between these phases.

A lot of efforts have been made, due to the important roles of mass transfer effects on the reaction rate. The main purpose for this chapter is to apply the basic restriction of mass transfer on the heterogeneous catalytic reaction. The illustrations based on the literature reviews in the heterogeneous catalytic processes are conducted for elucidation.

Since the reaction catalyzed by solid catalysts occurs when the reactant molecules come in contact with the active sites, which are usually located inside the catalyst pores. In other words, the catalytic reaction is taken place after the reactant molecules diffuse through the fluid layer surrounding the catalyst particles (external diffusion or film diffusion), then through the pore with in the particle (internal diffusion). The internal diffusion of the molecules competes with the reaction; at the same time, the external mass transfer is dependent on the stagnant film thickness and the activity on the outer layer. Hence, the diffusion of molecules is not only hindered by the other molecules, but also by the physical hindrances. The classical seven steps for a catalytic reaction (Fig. 1), i.e. (1) diffusion of the reactants from the bulk phase (boundary layer) to the external surface of the catalyst pellet (film diffusion or interphase diffusion), (2) diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface; the point where the chemical transformation occurs, (pore diffusion or intraparticle diffusion), (3) adsorption of reactants on the inner catalytic surface, (4) reaction at specific active sites on the catalyst surface, (5) desorption of the products from the inner surface, (6) diffusion of the products from the interior of the pellet to the pore mouth at the external surface, and (7) diffusion of the products from the external pellet surface to the bulk fluid (interphase diffusion), are generally used as the key for explanation.

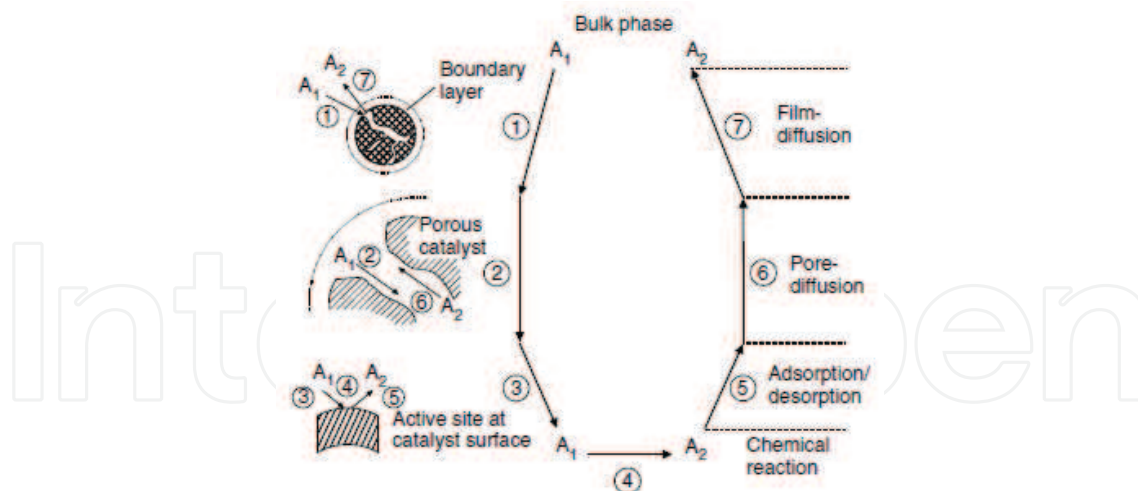


Fig. 1. Individual steps of a simple, heterogeneous catalytic fluid–solid reaction $A_1 \rightarrow A_2$ carried out on a porous catalyst (Dittmeyer & Emig, 2008)

The adsorption, surface reaction, and desorption are sequential steps. However, when a chemical reaction occurs on a surface, the rate of mass transfer to the reactive surface (intraparticle diffusion) is in steady state and equal to the rate of the reaction.

If diffusion or mass transfer steps (steps 1, 2, 6, and 7) are very fast, there is no resistance for the mass transfer from the bulk to the particle surface and from the particle surface to the active site in the pore. The concentration around the catalyst sites is supposed to be the same as that of the bulk one. Under these conditions, the mass transferring steps do not affect the reaction rate. The rate of reaction can be calculated from the reaction mechanism assuming that the concentration at the catalyst site is the same as that of the bulk.

If diffusion from the bulk to the catalyst surface is slow, e.g. the reactants are in the gas phase while the catalyst is in the solid phase, then the external mass transfer resistance is high and becomes an important factor with respect to the overall reaction rate. Nevertheless, the external mass transfer resistance is strongly depended on the flow conditions, e.g. temperature, pressure, and superficial velocity, in the reactor and the particle size of the catalyst (Fogler, 2006a). Varying these parameters can help to reduce the external mass transfer resistance.

In case of the internal diffusion effects are significant and there is no external mass transfer resistance then the concentration profile would vary across the catalyst pellet.

In this chapter, the influences of the mass transfer, i.e. external and internal diffusion, controlling the rate of heterogeneous catalysis reaction are focused. The important factors for mass transfer such as the flow rate conditions (temperature, pressure, and solvent) and the catalyst deactivation are discussed. The types of reactors effecting the enhancement of the mass transferring rate are also communicated. The objective is to summarize the main concepts and formulas for the rate of reaction, which identified to be limited by the mass transfer resistance.

2. Influences of external mass transfer

When a chemical reaction occurs on an active surface, the rates of intraparticle diffusion and chemical reaction are in steady state and simultaneously take place. For a given component "A", the reaction rate can be defined as:

$$r_A = k_{cA} (x_A^b - x_A^s) \quad (1)$$

where r_A (mol L⁻² t⁻¹) is the reaction rate of the component "A", k_{cA} (mol L⁻² t⁻¹) is the mass transfer coefficient in a binary system, x_A^b is the mole fraction of species "A" in gas bulk, and x_A^s is the mole fraction of species "A" in equilibrium with adsorbed "A" (Löffler & Schmidt, 1977).

In order to measure r_A , the value of $(x_A^b - x_A^s)$ must be small. In other words, the mass transfer resistance must be small compared to the surface reaction resistance which can be neglected. Löffler & Schmidt (1975) illustrated that in order to determine the reaction rates with only 10% error due to mass transfer, the Damköhler number (Da) should be less than 0.1. For a first order reaction, Da can be calculated with:

$$Da = \frac{r_A / k_c}{\left(x_A^b - \frac{r_A}{k_c}\right)} \quad (2)$$

The value of Da is varied between zero and infinity (the higher value of r_A/k_c than x_A^b is physically impossible). In a system in which Da is higher than 3, the reaction becomes mass transfer controlled. And the rate measured under these conditions should represent a measurement of k_c . Using the heat and mass transfer analogy and the correlation presented by Kyte et al. (1953) with elimination of the insensitive term, the mass transfer coefficient for the natural convection to horizontal wires becomes:

$$k_c \sim T^{0.5} D_w^{-1} \quad (3)$$

where T and D_w represent in temperature (K) and wire diameter (cm), respectively. When the temperature difference between gas and catalyst is small, the forced convection is the main mechanism for mass transfer. The mass transfer coefficient " k_c " presented by Bird et al. (2002) can be calculated as:

$$k_c \sim v^{0.3} T^{0.5} D_w^{-0.7} P^{-0.3} \quad (4)$$

where v is the gas velocity and P is the pressure.

The mass transfer coefficient, k_c , can be calculated by the correlations of the experimental data (Satterfield, 1970 as cited in Forni, 1999), between the Sherwood ($Sh = k_c D_p / D_{AB}$), Schmidt ($Sc = \mu / (\rho D_{AB})$), and Reynolds ($Re = D_p \rho u_s / \mu$) numbers. Wherein, " k_c " is the mass transfer coefficient for the system in which the reactant is the liquid phase (for the mass coefficient of a gaseous reactant " k_g ", it can be calculated from the relationship of $k_g = k_c / RT$). " D_p " (cm) is the diameter of the catalyst particle. " D_{AB} " (cm² s⁻¹) is the diffusion coefficient or diffusivity of component "A" in component "B". " ρ " (g cm⁻³) and " μ " (Pa s) are the density and viscosity of the fluid, respectively. " u_s " (cm s⁻¹) is the superficial flow rate of the fluid referred to the overall cross section of the catalyst bed, which is calculated in the absence of the catalyst. These correlations are in the terms of the Colburn " J " factor (i.e. J_D) as a function of the Reynolds number:

$$J_D = \frac{Sh}{Re Sc^{1/3}} \quad (5)$$

J_D is a function of the Reynolds number. For the gaseous reactants whereby $3 < Re < 2000$ and the interparticle void fraction (ϵ) of the bed of the particles $0.416 < \epsilon < 0.788$, J_D can be calculated as:

$$J_D \epsilon = 0.357 Re^{-0.359} \quad (6)$$

For the liquid reactants by which $55 < Re < 1500$ and $0.35 < \epsilon < 0.75$:

$$J_D \epsilon = 0.25 Re^{-0.31} \quad (7)$$

and for the liquid reactants with $0.0016 < Re < 55$

$$J_D \epsilon = 1.09 Re^{-0.67} \quad (8)$$

For a heterogeneously catalysed reaction, the reactants can be in the different phases (gas and liquid); in other words, comprising of the binary diffusion, the pressure of the gaseous reactant(s) influences the reaction rate as in the term of D_{AB} . By means of the solubility of gaseous reactant(s) in the liquid phase affects a higher reaction rate then improves the conversion.

Additionally, a higher reaction temperature influences the sorption processes on the catalyst surface, subsequently influences the reaction rate. The equations for predicting the gas, liquid, and solid diffusivities as the function of temperature and pressure are given in Table 1. It should be noted that the Knudsen, liquid, and solid diffusivities are independent of the total pressure.

| Phase | Order of Magnitude ($\text{cm}^2 \text{s}^{-1}$) | Temperature and Pressure Dependences ^a | Eq. |
|-----------|---|--|------|
| Gas | | | |
| - Bulk | 10^{-1} | $D_{AB}(T_2, P_2) = D_{AB}(T_1, P_1) \frac{P_1}{P_2} \left(\frac{T_2}{T_1} \right)^{1/2}$ | (9) |
| - Knudsen | 10^{-2} | $D_A(T_2) = D_A(T_1) \left(\frac{T_2}{T_1} \right)^{1/2}$ | (10) |
| Liquid | 10^{-5} | $D_{AB}(T_2) = D_{AB}(T_1) \frac{\mu_1}{\mu_2} \left(\frac{T_2}{T_1} \right)^{1/2}$ | (11) |
| Solid | 10^{-9} | $D_{AB}(T_2) = D_{AB}(T_1) \exp \left[\frac{E_D}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \right]$ | (12) |

^a μ_1 and μ_2 are liquid viscosities at temperatures T_1 and T_2 , respectively; E_D is the diffusion activation energy

Table 1. Diffusivity relationships for gases, liquid, and solid (Fuller et al. 1966; Reddy & Doraiswamy, 1967; Perry & Green, 1999, as cited in Fogler, 2006a)

For a binary mixture, the single diffusivity D_{AB} can be evaluated from the experimental data related to the Schmidt number. However, most practical reactions involve multicomponent mixtures, of which rigorous handling is more complicated. Since the flux of a given chemical

species “ j ” (N_j) is driven not only by its own concentration gradient, but also by those of all the other species. For ideal gas mixtures, the kinetic theory leads to the Maxwell-Stefan equation as demonstrated in Eq. (13) (Maxwell, 1866; Stefan, 1871, as cited in Froment & Bischoff, 1979):

$$N_j = - \sum_{k=1}^{N-1} C_t D_{jk} \nabla y_k + y_j \sum_{k=1}^N N_k, \quad j = 1, 2, \dots, N-1 \quad (13)$$

in which the last term accounts for bulk flow of the mixture. The exact form of D_{jk} depends on the system under study. The technique for solving the equation is done by using matrix methods.

In an empirical binary mixture of ideal gases, the diffusivity can be expressed in terms of the chemical potential gradient (μ_i) (Krishna & Wesselingh, 1997). Under isothermal conditions with a constant pressure of a species “ i ”, referred to the Maxwell-Stefan equation, the diffusivity “ D ” can be derived from:

$$-\frac{y_1}{RT} \nabla_{T,P} \mu_1 = \frac{y_2 N_1 - y_1 N_2}{C_t D} \quad (14)$$

where y_1 and y_2 are the mole fractions of the species “1” and “2”, C_t is total molar concentration of the fluid mixture (mol m^{-3}), and D is defined as the Maxwell-Stefan diffusivity ($\text{m}^2 \text{s}^{-1}$).

For a non-ideal fluid mixture, the component activity coefficients are introduced to express the left member of Eq. (14) as:

$$-\frac{y_1}{RT} \nabla_{T,P} \mu_1 = \left(1 + y_1 \frac{\partial \ln \gamma_1}{\partial y_1} \right) \nabla x_1 = \Gamma \nabla y_1 \quad (15)$$

where γ_1 is the activity coefficient of species “1” (dimensionless) and Γ is the thermodynamic correction factor portraying the non-ideal behavior. Combining of Eq. (14) and (15) after introducing $y_2 = (1 - y_1)$, Eq. (16) is obtained:

$$N_1 - y_1 N_t = C_t D \Gamma \nabla y_1 \quad (16)$$

For highly non-ideal mixtures, the thermodynamic factor Γ strongly depends on the mixture composition and vanishes in the region of the critical point.

For gaseous mixtures at low to moderate pressures and for thermodynamically ideal liquid mixtures, the thermodynamic factor Γ is equal to 1 and the Maxwell-Stefan diffusivity is independent of composition.

For highly non-ideal liquid mixtures, the thermodynamic factor Γ strongly depends on the composition of the mixture. An empirical formula for the composition dependence is:

$$D = (D_{(x_1 \rightarrow 1)})^{x_1} (D_{(x_1 \rightarrow 0)})^{(1-x_1)} \quad (17)$$

where the bracketed terms are the infinite dilution values of the Maxwell-Stefan diffusivity at either ends of the composition range and x_1 is the liquid mole fraction of the species “1”. The mechanistic picture developed for the diffusion in a two-component system can be extended to the general multicomponent cases, analogous to Eq. (14) as:

$$-\frac{y_i}{RT} \nabla_T \mu_i = \sum_{\substack{j=1 \\ j \neq i}}^n \frac{y_j N_i - y_i N_j}{C_t D_{ij}} = \sum_{\substack{j=1 \\ j \neq i}}^n \frac{y_j J_i - y_i J_j}{C_t D_{ij}}, \quad i = 1, 2, \dots, n \quad (18)$$

where the second equality holds irrespective of the reference velocity frame chosen for the diffusion process.

The examples for the heterogeneous catalysis which are strongly limited by the external mass transfer are the oxidation of alkanes (C₂ - C₄) (Hiam et al., 1968 as cited in Löffler & Schmidt, 1977) and ammonia decomposition (Löffler & Schmidt, 1976)

3. Influences of internal mass transfer

In a heterogeneously catalysed reaction, the mass transfer of the reactants first takes place from the bulk fluid to the external surface of the pellet (Fogler, 2006b). The reactants then diffuse from the external surface into and through the pores within the pellet to the catalytic surface of the pores, in which the reaction occurs. Generally, the overall reaction rate is affected by the external surface diffusion only for the low temperature process (Thomas & Thomas, 1997). Under high temperature conditions, a total pressure difference across the pore usually presents, generating a forced flow in pores. Depending on the catalyst pore size, three diffusion modes can be observed (Forni, 1999). When the pore diameter d_p is much larger than the mean free path " λ " of the diffusing molecules, the diffusion takes place in the usual way as observed outside the pores (bulk or molecular diffusion). When $d_p \approx \lambda$, the diffusing molecules hit the pore walls more frequently than the other molecules (Knudsen diffusion). In addition, in the microporous solids, such as zeolites, the pore diameter of which is close to the size of the reactant molecule. Thus, the reactant molecules can only diffuse in the pores by remaining constantly in contact with the pore walls (surface or configurational diffusion).

According to the mole balance for diffusion and reaction inside the catalyst pellet as described by Fick's law, the internal diffusion rate " N_A " (mol cm⁻² s⁻¹) is defined as:

$$N_A = -D_e \left(\frac{\partial C_A}{\partial z} \right) \quad (19)$$

where C_A is the number of moles of component "A" per unit of the open pore volume, z is the diffusion coordinate, with the effective diffusion coefficient (diffusivity) D_e (cm² s⁻¹) is given by:

$$\frac{1}{D_e} = \frac{1}{D_{b,e}} + \frac{1}{D_{k,e}} \quad (20)$$

where $D_{b,e}$ and $D_{k,e}$ are the effective diffusion coefficients for bulk and Knudsen diffusions, respectively. $D_{b,e}$ and $D_{k,e}$ can be calculated using the equations as demonstrated by Satterfield (1970) as:

$$D_{b,e} = \frac{D_b \theta}{\tau} \quad (21)$$

$$D_{k,e} = 1.94 \times 10^4 \frac{\theta^2}{\tau S_g \rho_p} \sqrt{\frac{T}{M}} \quad (22)$$

where D_b ($\text{cm}^2 \text{ s}^{-1}$) is the bulk diffusion coefficient, θ is the internal void fraction of the solid particle, τ is the tortuosity factor of the pores, S_g ($\text{cm}^2 \text{ g}^{-1}$) is the specific surface area of the catalyst, ρ_p (g cm^{-3}) is the particle density, T (K) is the reaction temperature, and M (g mol^{-1}) is the molecular mass of the diffusing species.

In a multicomponent system, the Maxwell-Stefan equation is more generally used than the Fick's law for providing the diffusivity data. The interesting example is the application of the Maxwell-Stefan equation for diffusion in zeolites (Kapteijn et al., 2000). The extended approach to describe the surface diffusion of the adsorbed molecules for an n -components mixture is started with Eq. (23) (Krishna, 1990, 1993a, 1993b, as cited in Kapteijn et al., 2000):

$$-\nabla\mu_i = RT \sum_{\substack{j=1 \\ j \neq i}}^n \theta_j \frac{u_i - u_j}{D_{ij}^s} + RT \frac{u_i}{D_i^s}, \quad i = 1, 2, \dots, n \tag{23}$$

where $\nabla\mu_i$ is the force acting on the species "i" tending to move along the surface with a velocity u_i . The first term on the right-hand side reflects the friction exerted by adsorbate "j" on the surface motion of species "i", each moving with velocities u_j and u_i with respect to the surface, respectively. The second term reflects the friction between the species "i" and the surface. D_{ij}^s and D_i^s represent the Maxwell-Stefan surface diffusivities. The fractional surface occupancies are given by " θ_i ":

$$\theta_i = \frac{q_i}{q^{sat}} \tag{24}$$

where q_i represents the loadings of component "i" in zeolite and q^{sat} is referred to the saturation loading (molecules per unit cell or mol kg^{-1}).

Eq. (23) has been successfully applied to describe the transient uptake in zeolites, such as the single-component adsorption on MFI-type zeolites (silicalite-1 and ZSM-5 etc.), carbon molecular sieves, and in zeolitic membrane permeation.

For a first-order catalytic reaction, the reaction rate r_A ($\text{mol cm}^{-3} \text{ s}^{-1}$) referred to the unit volume of catalyst particle is given by:

$$r_A = k_s S_v C_A \tag{25}$$

where k_s (cm s^{-1}) is the reaction rate constant and S_v ($\text{cm}^2 \text{ cm}^{-3}$) is the surface area per unit particle volume. For a spherical catalyst pellet with a radius r_1 (cm) (Fig. 2), the profile of the reactant concentration as a function of radius can be calculated using a mass balance of which referred to the spherical shell thickness dr and r (Fogler, 2006b).

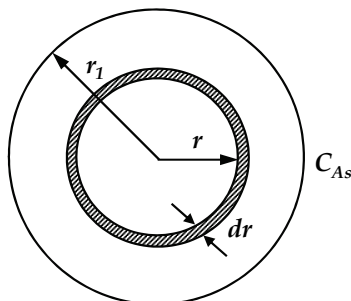


Fig. 2. Shell balance on a catalyst pellet

The integration is easily managed by introducing a dimensionless term known as Thiele modulus (Φ), Eq. (26).

$$\Phi = r_1 \sqrt{\frac{k_s S_v C_{As}^{v-1}}{D_e}} \quad (26)$$

where C_{As} is the reactant concentration at the external particle surface and v is the reaction order. The parameter Φ represents the ratio of reactivity over diffusivity of the reacting species. For first-order reactions, Φ is independent of reactant concentration. The result of the integration is implicit as:

$$C_A = \frac{C_{As}}{r \sinh \Phi} \sinh \left(\frac{r\Phi}{r_1} \right) \quad (27)$$

For a low value of Φ , the concentration everywhere inside the pore is high. In other words, the diffusion coefficient is very high as compared to the reaction rate. The concentration is uniform across the pore and almost equal to the surface concentration C_{As} . The reaction rate in comparison to the diffusion rate is very low. Hence, one can say that the surface reaction is the rate determining step for a reaction having a low value of Φ .

For a high value of Φ , the reaction rate is fast compared to the diffusion rate. The internal diffusion rate results in the distinctive concentration gradients. Therefore, the reaction rate is evaluated based on the concentration existing at each spatial position inside the pore, not at the surface.

In comparison the relationship between diffusion and reaction limitations, the internal effectiveness factor eta (η) is defined (Pushpavanam, 2009).

$$\eta = \frac{\text{actual reaction rate}}{\text{reaction rate assuming no diffusion resistance}} \quad (28)$$

The magnitude of the effectiveness factor is range from 0 to 1. For a first-order reaction, the effectiveness factor can be derived from:

$$\eta = \frac{-r_A}{-r_{As}} = \frac{-r_A \times \text{volume of catalyst particle}}{-r_{As} \times \text{volume of catalyst particle}} \quad (29)$$

For a spherical particle:

$$\frac{4}{3} \pi r_1^3 r_A = 4 \pi r_1^2 N_A = 4 \pi r_1^2 D_e \left(\frac{dC_A}{dr} \right)_{r=r_1} \quad (30)$$

Combination of Eq. (30) and (27) results in:

$$\frac{4}{3} \pi r_1^3 r_A = 4 \pi r_1^2 D_e \left[\frac{C_{As} \Phi}{r_1} \left(\frac{1}{\tanh \Phi} - \frac{1}{\Phi} \right) \right] \quad (31)$$

For the absence of any diffusion resistance:

$$\frac{4}{3}\pi r_1^3 r_{As} = \frac{4}{3}\pi r_1^2 C_{As} k_s S_v \tag{32}$$

Substitution of Eq. (31) and (22) in (29) results in:

$$\eta = \frac{3D_e\Phi}{r_1^2 k_s S_v} \left(\frac{1}{Tgh\Phi} - \frac{1}{\Phi} \right) \tag{33}$$

Using the definition of Φ in Eq. (26), then Eq. (30) becomes:

$$\eta = \frac{3}{\Phi} \left(\frac{1}{Tgh\Phi} - \frac{1}{\Phi} \right) \tag{34}$$

On the other hand:

$$\eta = \frac{3}{\Phi} (\Phi \coth \Phi - 1) \tag{35}$$

The dependence of η on Φ for the first-order reaction is shown in Fig. 3.

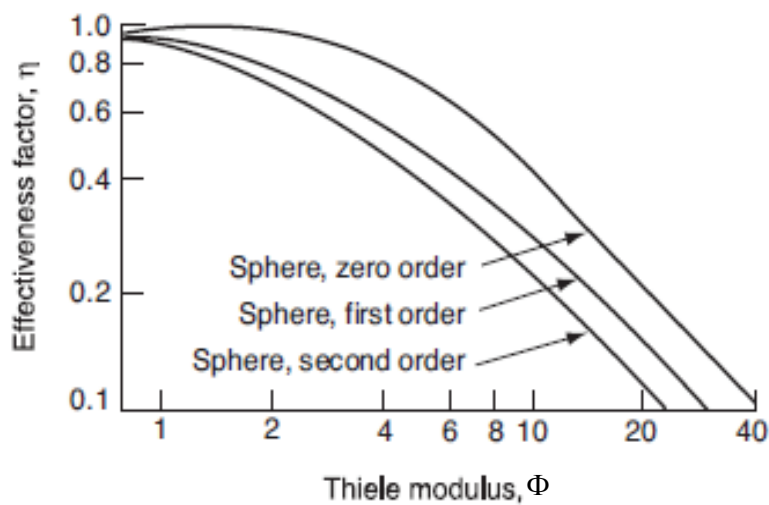


Fig. 3. Effectiveness (η) of a catalyst as a function of Thiele modulus (Φ) for the spherical particles (Fogler, 2006b)

In many circumstances, one is interested to identify the step, determining the reaction rate. The Weisz-Prater criterion (C_{WP}) is used to measure the rate of reaction in order to determine whether the internal diffusion is limiting the reaction. This criterion can be calculated with the following equation:

$$C_{WP} = \eta\Phi^2 = 3(\Phi \coth \Phi - 1) \tag{36}$$

For $C_{WP} \ll 1$, there is no diffusion limitation and consequently no concentration gradient exists within the pellet. However, for $C_{WP} \gg 1$, the reaction is tremendously limited by the internal diffusion.

4. Effect of the catalyst deactivation on mass transfer

The rate of heterogeneous catalytic reaction usually decreases with the time-on-stream due to the catalyst deactivation. The catalyst deactivation takes place by means of several reasons; for example, the products or by-products produced in the system plug the catalyst pores, subsequently, limit the mass transfer process from the external pore mouth to the internal catalyst surface. In some cases, the foreign molecules, such as coke, are formed under the reaction conditions, deposit on the active surface (fouling or poisoning), and then render the catalyst activity. The presence of an appropriate solvent can assist to prevent or reduce these deactivation problems.

Generally, there are three categories of deactivation mechanisms of which the loss of the catalytic activity is traditionally divided (Fogler, 2006c), i.e. sintering or aging, fouling or coking, and poisoning.

4.1 Deactivation by sintering (aging)

Deactivation by sintering is the loss of the catalytic activity due to the loss of the active surface area or of a crystal phase transformation resulting from a prolonged exposure to high temperature conditions. The active surface area may be lost either by crystal agglomeration and growth of the metals deposited on the support or by narrowing or closing of the pores inside the catalyst pellet. A change in the surface structure may also result from either surface recrystallization or the formation or elimination of surface defects (active sites). The reforming of alkanes over platinum on alumina is an example of catalyst deactivation as a result of sintering.

Deactivation by sintering, in some cases, is a function of the mainstream gas concentration. The most commonly used is the second order with respect to the present activity:

$$r_d = k_d a^2 = -\frac{da}{dt} \quad (37)$$

where a is the catalyst activity as the function of time, $a(t)$, and k_d is the constant for the sintering decay.

The amount of sintering is usually measured in the term of the active area of the catalyst, S_a :

$$S_a = \frac{S_{a0}}{1 + k_d t} \quad (38)$$

4.2 Deactivation by coking or fouling

Deactivation by coking or fouling is commonly involved in the reactions of hydrocarbons, such as catalytic reforming, hydrogenation, oxidation etc. The decay mechanism results from a carbonaceous (coke) material depositing on the surface of the catalyst. The amount of coke on the surface after a certain time can be found with the following empirical relationship (Voorhies, 1945 as cited in Fogler, 2006c):

$$C_C = At^n \quad (39)$$

where C_C is the concentration of carbon on the surface (g m^{-2}) while n and A are fouling parameters, which are the functions of feed rate. This expression can be used for a wide variety of catalysts and feed streams.

4.3 Deactivation by poisoning

Deactivation by this mechanism occurs when the poisoning molecules (P) become irreversibly chemisorbed on active sites (S), thereby reducing the number of sites available for the main reaction. The poisoning molecule can be a reactant and/or a product in the main reaction, or it may be an impurity in the feed stream. The reaction rate for poisoning is:

$$r_d = k_d' C_P^m a^q = 2 \frac{da}{dt} \quad (40)$$

where m and q are the reaction orders.

5. Effect of reactor types on mass transfer

As the result of the kinetics data obtained from the integral reactors under the conditions which limited by mass and heat transfer cannot be used for formulating the meaningful kinetic expressions. In other words, for any kinetic measurements, modeling, and the typical approaches to the reactor rate calculations, the mass transfer limitation is always assumed to be of less effect that can be negligible. An appropriate type of reactor characteristically helps to enhance the mass transferring rate of the system. Accordingly, the design of any reactor generally concerns on the need for eliminating heat and mass transfer effects or accounting them in the suitable manner.

Several types of reactors exist for the heterogeneous catalytic reactions. These include fixed bed reactors, tubular catalytic wall reactors, and fluidized bed reactors. However, for gas-liquid-solid reactions, the reactor types (e.g. trickle bed reactor or bubble column reactor) are usually developed for the specific reaction conditions (Levenspiel, 1999).

The continuous flow-through reactors/plug flow reactor (tubular and column) are widely used for the heterogeneous systems. The tubular reactors permit a vigorous heat exchange in the reaction zone and ensure a uniform residence time for all particles in the flow. Whereas, the column reactors are structurally less suited for vigorous heat exchange and therefore are used in those cases where an addition (or removal) of heat to the reaction zone is either unnecessary or is carried out on a limited scale. In column reactors, it is very important to have a uniform distribution of flow through the cross section of the column. In such a case, the flow-through reactors are usually equipped with the circulation loops for recycling any substances which are unreacted.

The reactors in which the diffusional effect can be precisely predicted are the tubular flow or plug-flow reactor (PFR). These reactors are sometimes filled with the solid packing (packed-bed reactor, PBR), in order to accelerate the mass transfer between phases and reduce the variation in residence time of the reactant particles. In multiphase catalytic reaction, PBR is regularly used as a model reactor. The PBR can be operated either with a continuous gas or in a distributed liquid phase (trickle operation; in which the catalyst is stationary, so called trickle-bed reactor (TBR)) or with a distributed gas and a continuous liquid phase (bubble operation; in which the catalyst is suspended in the liquid phase) flowing through a packed bed of the catalyst, so called fixed-bed like reactor (FBR). The directions of gas and liquid flows in the system, i.e. cocurrent downflow, cocurrent upflow, and countercurrent flow (Fig. 4 (A) - (C)), are considered as one of the most important factors.

An alternative reactor type is the slurry reactor, a vessel in which the gaseous reactant is dispersed into a liquid phase containing the suspended solid catalyst. At high ratio of fluid-

feed flow rate to the reactor diameter, the gas-liquid-solid reactor is often termed an ebullating-bed (a high solid concentration type of fluidized bed reactor in which catalyst particles are held in suspension by the upward movement of the liquid reactant and gas flow), Fig. 4 (D), or bubble column reactor, as a low solid concentration, Fig. 4 (E).

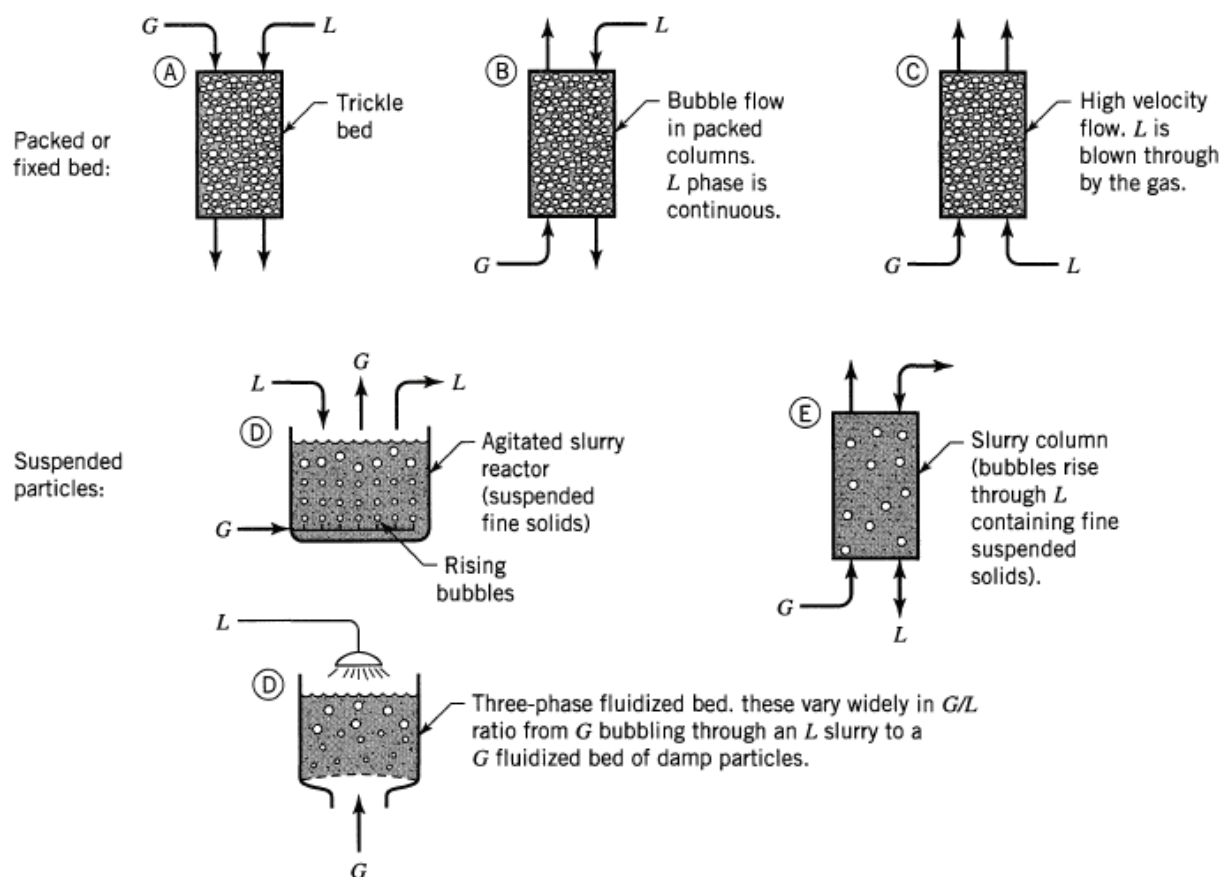


Fig. 4. Various types of reactors with direction of gas (G) and liquid (L) flows for the reactions catalyzed by the solid catalysts (Levenspiel, 1999)

Some special chemical reactor types are fluidized (Fig. 5. (A)) and moving (Fig. 5 (B)) bed reactors, which have characteristics that set them apart from the other reactors. The advantages of these reactors include the possibility of a continuous intake of fresh solid phase and removal of depleted solid phase, a high rate of heat exchange, the lack of dependence of the speed of the fluidizing agent (gas, vapour, or liquid), and a wide range of properties of solid particles (including suspensions and pastes) and fluidizing agents. However, the use of reactors with fluidized and moving beds is limited. This is because they do not ensure a uniform residence time of the particles of the two phases in the beds, and do not preserve the solid-phase properties. In addition, they require the powerful recovery equipment for fines.

5.1 Slurry reactor

The three phase (gas and liquid as the reactants with solid as the catalyst) catalytic slurry reactors are commonly used in industry for a wide variety of processes, such as oxidation, hydrogenation, carbonylation, and pollution control (Ramachandran & Chaudhari, 1980). A

number of steps such as gas-liquid mass transfer, liquid-solid mass transfer, intraparticle diffusion, and chemical reaction are involved for the reaction. A useful concept for analyzing these kind of heterogeneous catalysis reactions is the overall effectiveness factor (Ω) which incorporated the effects of all transport resistances (internal and external).

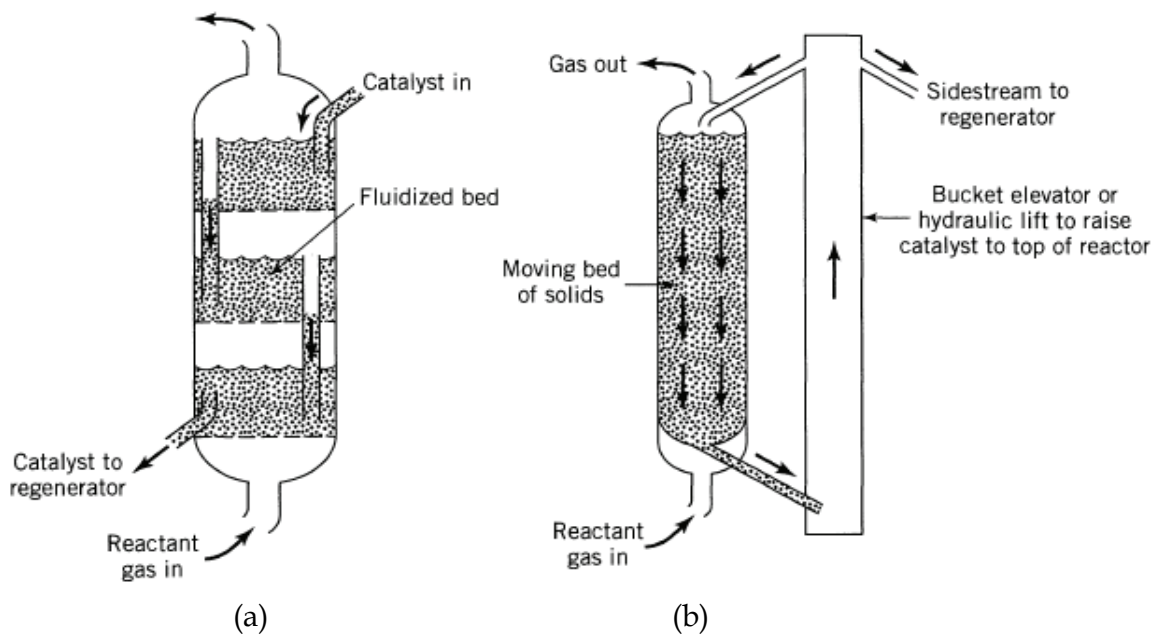


Fig. 5. Fluidized-bed (a) and moving-bed (b) reactors (Levenspiel, 1999)

For the first-order reaction in which a gas phase containing reactant “A” is continuously bubbled through the agitated slurry (a semibatch reactor), the overall effectiveness factor for a slurry reactor is defined as (Fogler, 2006b):

$$\Omega = \frac{\text{actual overall rate of reaction}}{\text{reaction rate if entire surface area is exposed to the bulk concentration}} \quad (41)$$

The actual overall rate of the reaction can be expressed in terms of the rate per unit volume, r_A , the rate per unit mass, r'_A , and the rate per unit surface area, r''_A , which are related by the equation:

$$-r_A = -r'_A \rho_b = -r''_A S_a \rho_b \quad (42)$$

The overall rate of reaction in terms of the bulk concentration C_{Ab} is:

$$-r_A = \Omega(-r''_{Ab}) = \Omega k_1 C_{Ab} \quad (43)$$

The rates of reaction based on surface and bulk concentrations are related by:

$$-r_A = \Omega(-r''_{Ab}) = \eta(-r''_{As}) \quad (44)$$

where:

$$-r''_{As} = k_1 C_{As} \quad (45)$$

$$-r_{Ab}'' = k_1'' C_{Ab} \quad (46)$$

with the effectiveness " η " can be calculated as Eq. (35).

5.2 Fixed-bed reactor

For external mass transfer-limited reactions in a PBR, the rate of reaction at any points in the bed is (Fogler, 2006b):

$$-r_A' = k_c a_c C_A \quad (47)$$

where the correlation for the mass transfer coefficient k_c is directly proportional to the flow rate and inversely proportional to the particle diameter (D_p). The factor a_c ($\text{m}^2 \text{m}^{-3}$) is the external surface area of the catalyst per volume and defined as:

$$a_c = \frac{6(1 - \Phi)}{d_p} \quad (48)$$

Consequently, for the external mass transfer-limited reactions, the reaction rate is inversely proportional to the particle diameter.

For reactions which are controlled by the internal diffusion, the rate of reaction varies inversely with the particle diameter and exhibits exponential temperature dependence; however, it is independent on the velocity.

The multiphase catalytic PBR operated with the trickle operation (TBR) are widely used in the petroleum and petrochemical industry, especially, when processing with the heavy petroleum fraction, such as in hydrocracking, hydrodesulphurization, hydrogenation, etc. In a TBR, different flow regimes can exist, depending on the physical properties of the gas and liquid phases, the flow rates, and the nature and size of the catalyst packing (Lemcoff et al., 1988). The retention of liquid in the packed-bed or liquid hold up is an important parameter in the performance of a TBR. The partial catalyst wetting is a common phenomenon found in TBR (Satterfield, 1975, as cited in Sakornwimon & Sylvester, 1982). This may result from a poor liquid distribution caused by a faulty design of the liquid distributor or from an inadequate ratio between reactor and particle diameter. The fraction of the external surface of a particle wetted by the liquid or external wetting efficiency, has an important effect on the rate of reaction in a TBR.

For the interphase mass transfer, the evaluation is generally considered at the equilibrium conditions (Lu et al., 1984, as cited in Lemcoff et al., 1988).

For the intraphase mass transfer, in case of partial internal wetting, the gaseous reactant will partly diffuse into the dry pores. Therefore, it affects the diffusion of gas and solute in liquid within the catalyst pores. The total molar flux of a component (N_j) in a porous media can be described in terms of diffusion (N_j^D) and viscous fluxes (N_j^V) in the gas phase, and of a surface flux (N_j^σ) at the gas-solid interface:

$$N_j = N_j^D + N_j^V + N_j^\sigma \quad (49)$$

The total diffusion flux, N_j^D , involves both the molecular and Knudsen diffusion (Mason et al., 1967; Feng & Stewart, 1973, as cited in Lemcoff et al., 1988), whilst, the viscous flux, N_j^V , can be described in terms of the Darcy law:

$$N_j^v = -x_j \frac{B_0 C}{\mu} \nabla P \tag{50}$$

where B_0 is the viscous permeability of the porous media. The surface diffusion is commonly represented by the Fick's law equation:

$$N_j^\sigma = -D_j^\sigma \nabla C_j^\sigma \tag{51}$$

where C_j^σ is the surface concentration of species "j".

When the molecular size becomes comparable to that of the pore, the rate of solute diffusion in liquids within porous media is reduced. Thus, diffusion is related to an exclusion phenomenon and a hydrodynamic drag effect. Then the total molar flux is suggested with the use of Fick's law equation:

$$N_j = -D_{e,j}^L \nabla C_j + x_j N \tag{52}$$

where $D_{e,j}^L$ represents the effectiveness coefficient, x_j is the molar fraction and N is the molar flux of the component "j".

$D_{e,j}^L$ is given by:

$$D_{e,j}^L = D_{b,j}^L \varepsilon K_p \frac{K_r}{\tau} \tag{53}$$

where $D_{b,j}^L$ is the bulk diffusivity in free solution, ε is the particle porosity, K_p is the equilibrium partition coefficient and K_r is the fractional reduction of diffusivity resulting from the proximity of the pore wall.

At equilibrium:

$$K_p = (1 - \lambda)^2 \tag{54}$$

where λ is the ratio of molecular diameter to pore diameter. When the solvent molecule is also comparable:

$$K_p = \frac{(1 - \lambda_{solute})^2}{(1 - \lambda_{solvent})^2} \tag{55}$$

The parameter K_r is the function of the solute diameter, $K_r = K_r(\lambda)$, which correlated to:

$$\log K_r = -2.0\lambda \tag{53}$$

The overall effectiveness factor for the partially wetted catalyst pellet (η_0) is presented in several literatures; however, they all are related to the relationship of the following equation (Lemcoff et al., 1988):

$$\eta_0 = f\eta_w + (1 - f)\eta_d \tag{56}$$

where η_w and η_d are the overall effectiveness factors for a pellet completely covered by liquid and gas, respectively, and f is the external wetting efficiency. The solutions of this

effectiveness factor depend on the limiting phase (gas or liquid) and completion of wetting in the catalyst pellet, which the more detail are documented elsewhere (as cited in Lemcoff et al., 1988; Sakornwimon & Sylvester, 1982).

6. Conclusion

In a gas-liquid reaction catalysed by a porous-solid catalyst, one of the most important key parameters which influence the catalyst activity and selectivity is the mass transfer between the multiphases. The reactants which are typically in the gaseous and liquid phase diffuse through the boundary layer (external diffusion), then through the catalyst pore mouths into the internal catalytic surface (internal diffusion). After adsorption on the active surface, the reaction occurs on the specific active sites. Subsequently, the formed products desorb and diffuse to the catalyst pore mouths and finally to the bulk phase.

Numerous reactions are limited by the step of external or internal diffusion. The reaction depends on the parameters involving the diffusion coefficient between gas and liquid phase (D_{AB}), the size of the catalyst particle, the pore size diameter, the diffusive surface area, the physical properties (density and viscosity) of the fluids, and the flow conditions (temperature, pressure, and flow rate) of the gas and liquid reactants. The relationships of these parameters are analogous between heat and mass transfer, which can be written as in the dimensionless terms, e.g. Sherwood, Schmidt, and Reynolds numbers. However, these correlated equations are limit in explanation for the multicomponent mixtures; as a result, the Maxwell-Stefan equation is more widely used. Subsequently, the mass transfer factors, e.g. molar flux and effectiveness factors can be determined.

The rate of catalytic reaction regularly decreases with time, due to catalyst deactivation. This deactivation occurs because of three main mechanisms: sintering, fouling, and poisoning. Different deactivation mechanisms affect catalytic rate in different ways.

Different flow characteristics in different reactor types influence the mass transfer between different phases. Hence, for a selection and invention the catalytic reactor, besides the factors, i.e. ensuring a given yield include the volume, flow rate, heat-exchange surface, rate of catalyst substitution, and various structural parameters (particularly in the case of high-pressure reactors), the obligatory need involves the use of experimental data on the kinetics of reactions, catalytic poisoning, and the rates of heat and mass transfer (particularly the effectiveness factor).

For reactions involving gaseous, liquid, and solid (as the catalyst) phases, a high interface area can be achieved by dispersing one of the reactants as in the TBR or bubble operation reactor. The partial catalyst wetting is a common phenomenon found in TBR, which is an important effect on the rate of catalytic reaction. In order to calculate the overall effectiveness factor, the important step is to consider the phase of reactant which limits the catalyst wetting.

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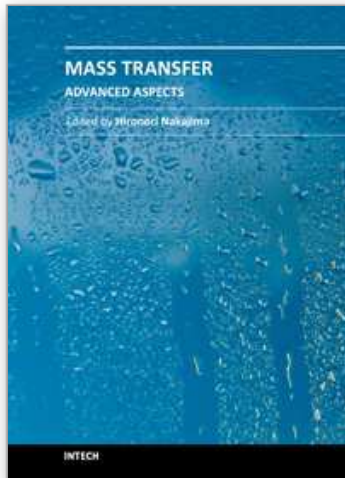
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