Kinetics of heterogeneous catalysis: Diffusion control

Kinetics of heterogeneous catalysis: diffusion controlling – mechanism of diffusion – Effect of pore size on activity and selectivity

Introduction

For a catalytic reaction certain physical steps are necessary before the chemical reaction. The mass and heat transport processes are very important in heterogeneous catalysis. Often these physical processes which precede the actual chemical reaction will determine the outcome of a process. The significant steps in a catalytic reaction can be given as

a. Transport of reactants from bulk phase to the catalyst surface (macroscopic diffusion)
b. Diffusion of the reactants through the catalyst pore to the interior of the pellet (microscopic diffusion)
c. Adsorption of reactants at the adsorption site (interior of catalyst pellet)
d. Surface (chemical) reaction to form products
e. Desorption of products from the reaction site (interior of catalyst pellet)
f. Diffusion of the products through the catalyst pore to the exterior of the pellet (microscopic diffusion)
g. Transport of products from catalyst surface to the bulk phase (macroscopic diffusion)

The macroscopic diffusion processes are very rare to become rate limiting. The microscopic diffusion processes often interfere with the chemical kinetics and usually becomes rate limiting step. The following section deals with microscopic diffusion control of catalytic reactions.

Mechanisms of mass transfer through pores

The diffusion of reactants and products inside the pores happens mainly by three mechanisms a) Knudsen diffusion b) Bulk diffusion and c) Forced flow.

Knudsen diffusion occurs when the mean free path is large in comparison with the pore diameter. This happens at low gas density. The amount of gas flowing through the capillary decreases with the length. This is because molecules after sticking the surface leave randomly independent of the direction in which they hit. At high pressures or with larger pores, collisions with gas molecules will be much frequent than collisions with the wall. This happens with high pressures and large pore diameter. Forced flow happens when a pressure difference is maintained in a pore. If mean free path is large compared to pore diameter, forced flow is identical with Knudsen diffusion and if mean free path is small it is identical with bulk diffusion.

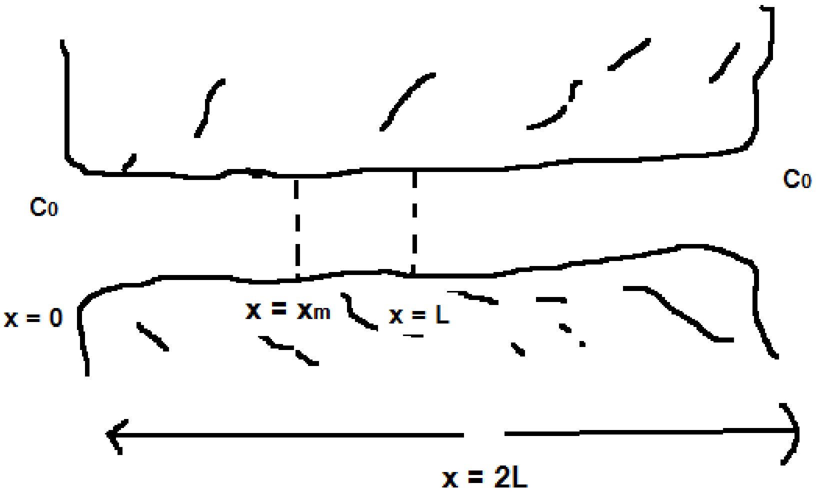
Catalyst Effectiveness factor and /Thiele dimensionless parameter h

The difference between the flow rates in and out must be equal to the rate of disappearance of reactant, and hence must be equal to the reaction rate. Mathematically this can be expressed by the equation

$$V_A(in) - V_A(out) = \int kC_{An}dS$$

Where VA(in) and Va (out) are inward and outward flow of reactants.

Consider a cylindrical pore in a catalyst (open at both ends) with radius ‘r’ and length ‘2L’. The reaction we are considering in this case is



A → qB; where q is the number of moles of B formed per mole of A reacted. At each mouth the concentration of A is C0 which can be called as the bulk concentration. Thus total pressure is same at both ends and reactants reach the inside of pores only by diffusion. The plane at x= L divides the pore in to two halves. We need to consider only one half of the pore i.e. from x = 0 to x = L; where x is the distance from the pore mouth. As the A molecules gets reacted by the time it reaches x = L; the plane is considered to be a dead end and no flow occurs through the plane.

The rate of reaction is equal to the flow rate of reactant into the half pore. Considering the equation 1;The rate of reaction is

$$2\pi r k = \int_{x=0}^{x=L} C_A^n(x)\,dx$$

V(out) will be zero as there in no flow at x = L. Thus our task is to find V(in). If our pore is a very long one (L large) then at some value of *x,* say ***x*,** all reactant diffusing through the pore will have had so many collisions with the pore wall that it will have reacted to product, and beyond this point C_A will be substantially zero. x_m is thus defined as the maximum depth that the reaction can penetrate into a pore. We can find a rough value of x_m**,** as follows. If we consider only diffusive flow of reactant into the pore then the flow through the pore mouth is:

$$V_A(in)_{(at\, x=0)} = \pi r^2 D\left(dC_A/dx\right)_{x=0}$$

$\rightarrow$ ①

$$\pi r^2 D\left(\frac{dC_A}{dx}\right)_{x=0} = 2\pi r k \int_{x=0}^{x=L} C_A^n(x)\,dx$$

Now we are going to some assumptions: If we assume *CA* has the value *Co* at *x* = 0 and falls to.0 zero at some value of *x*, *x* = *xm*, then the average gradient of *CA* over this region is *(dC/dx)* (average) = Co/xm. The rough average value of CA can be approximated to ½ C0. The actual reaction rate can be approximated as the useful area of the pore wall multiplied by the rate constant and the average value of the concentration to the power of order (n).

Thus
'actual rate' = $2\pi r x_m$ (useful area) x k (rate constant) x $(C_0/2)^n$ (average value of concentration)

$$=2\pi r x_m k (C_0/2)^n$$

Substituting these values in (4)

$$\pi r^2 D \frac{C_0}{x_m} = 2\pi r x_m k \frac{C_0^n}{2} \quad \text{--------(5)}$$

upon solving for x_m

$$x_m = (2)^{n/2}\sqrt{\frac{rD}{2kC_0^{n-1}}} \quad \text{.........(6)}$$

Substituting this value in either side of (5) we get the reaction rate in the half pore as

$$\text{Rate} = \frac{\pi r}{2^{n/2}}\sqrt{2rkDC_0^{n+1}} \quad \text{......(7)}$$

Thus rate on a catalyst pore is not proportional to rake constant but to square root of rate constant. Now if the pore was completely available for the reaction; there won't be any decrease in concentration and the rate would be

$$\text{Rate} = 2\pi r L k C_0^n \quad \textbf{..........(8)}$$

Dividing (7) by ((8) we get the effectiveness factor which is the fraction of available surface. This factor Effectiveness factor 'f' is very important in catalysis and can be defined as the ratio of the observed rate to the rate which would be observed if the surface were completely available.

$$f = \frac{1}{2^{r/2}} \sqrt{\frac{rD}{2kC_0^{n-1}}} \frac{1}{L}$$

…(9)

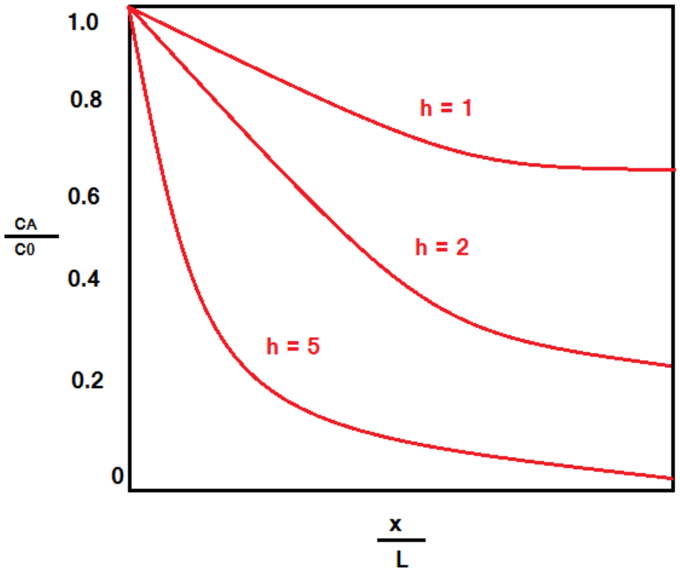
Here we can adopt a dimensionless quantity called as Thiele parameter 'h' as

$$h = L\sqrt{\frac{2kC_0^{n-1}}{rD}}$$

……..(10)

The Thiele parameter if directly proportional to length of the pore and inversely proportional to the square root of the radius.

Whenever the reaction is fast (diffusion slow), only a part of the catalyst will be used.



The decrease in concentration of reactant as function of 'h' (varying pore sizes). Note that for h =5 (very small pore radii); the concentration of reactant drastically decreases at the entrance of the pore.

Effect of pore size of activation energy and order of reaction

Recalling equation ..(7); For diffusion-controlled reactions rate is not proportional to rate constant k but to square root of rate constant. Activation energy will only be one half of the true activation energy.

Also we can infer that the kinetic order of the reaction will be (n+1)/2; where n is the true order of reaction. Thus, first order reactions will remain first order, but second order reactions will become 1.5 order and zero order reactions will become 0.5 order.

Effect of pore size on catalyst activity and selectivity

Type I. Reactions (Parallel reaction of two reactants)

Type 1 selectivity can be defined by the reaction scheme

$$A \overset{k1}{\rightarrow} B + C$$
$$X \overset{k2}{\rightarrow} Y + Z$$

Molecules A and X react on the same catalyst with varying rate constants k1 and k2.
The rate equations can be given as

$$-\frac{dA}{dt} = k1[A]$$
$$-\frac{dX}{dt} = k2\ [X]$$

If the rate of first reaction is faster; more of A would have converted to products in a given time. Selectivity will be more for faster reaction.
If the catalyst has large pores; Thiele parameter h will be small, diffusion will be fast and the overall reaction will be controlled by rate of chemical reaction.
Selectivity S

$$S = \frac{k_A}{k_X} (for\ h \ll 1)$$

Under such circumstances the selectivity will be just the ratio of rate constants. But if diffusion is slow the 'h' values becomes large and the selectivity changes,

$$S = \sqrt{\frac{k_A D_X}{k_X D_A}} (\text{for h } >> 1)$$

Where DA and DX are diffusion constants of A and X. The selectivity will change if one of the reactions is fast. Only a small fraction of the catalyst is available for the faster reaction; while the whole catalyst surface is accessible by the slower reaction. Thus, small pores in a catalyst will weaken the type 1 selectivity by retarding the rate of faster reaction.

Type II. Reactions (Parallel reactions of single reactant)

Type II selectivity can be defined by the reaction scheme

$$C \overset{k_2}{\leftarrow} \mathrm{A} \overset{k_1}{\rightarrow} B$$

An example of this type of reaction is dehydrogenation of cyclohexanol to cyclohexanone and dehydration of cyclohexanol to cyclohexene on mixed oxide catalysts.
If two competing reactions are of same order the catalysts pore structure will not affect Type II selectivity. This is because at each point in the catalyst pore the two reactions will proceed at the

same rate k1/k2, independent of the concentration of A. Hence the yield of desired product will be k1/(k1+k2).

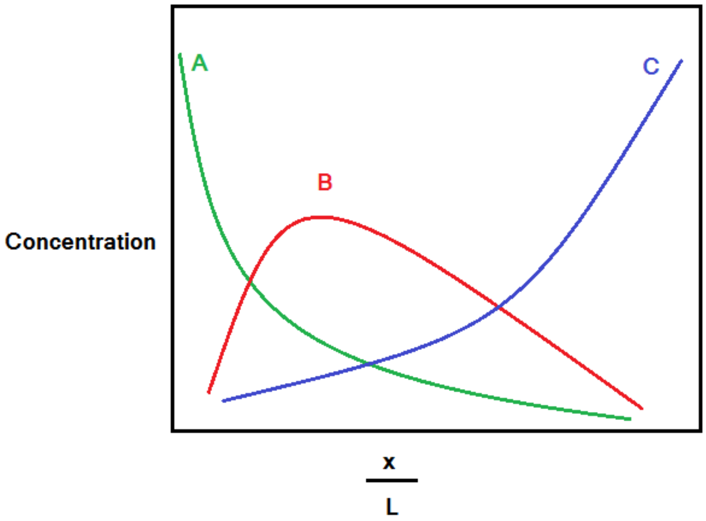
If reactants are of different kinetic orders; then selectivity depends on the pore size. For the reaction with higher order the decrease in concentration will be fast and hence its rate will be lower. If the reaction $A \rightarrow B$ were first order with respect to ***A***, and if the reaction $A \rightarrow C$ were second order, then the lower concentration of ***A*** existing in the catalyst interior will cause the rate of the second order reaction to fall markedly, thus favoring $A \rightarrow B$ at the expense of $A \rightarrow C$**.** In this case a catalyst with small pores should give better yields of ***B*** than a catalyst with larger pores. It follows that a practical rule for Type I1 selectivity is that: if operating a reactor at low pressures of reactant gives better yields than higher pressures, then catalysts with small pores should further improve the yields of the desired product. On the other hand, if high pressure operation gives improved selective yields, then catalysts with small pores should be avoided.

Type III. Reactions (Consecutive reactions)

Type II selectivity can be defined by the reaction scheme

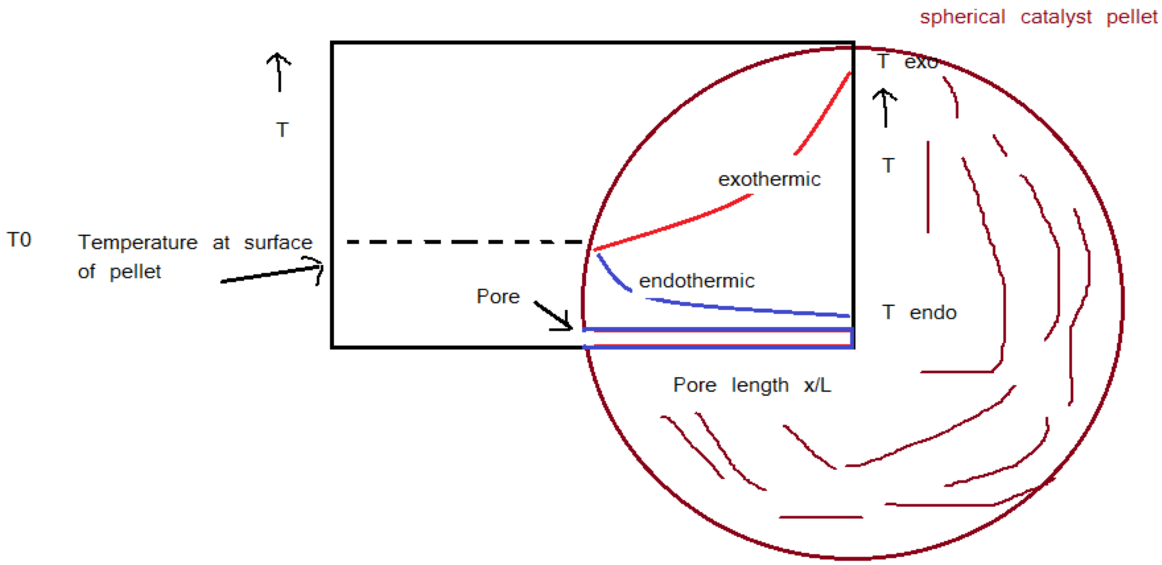
$$\mathrm{A} \overset{k_1}{\rightarrow} B \overset{k_2}{\rightarrow} C$$

Where B is the desired product. Many partial oxidation reactions come under this category. In the absence any diffusional limitations; a good selectivity will be observed if k1>>k2.

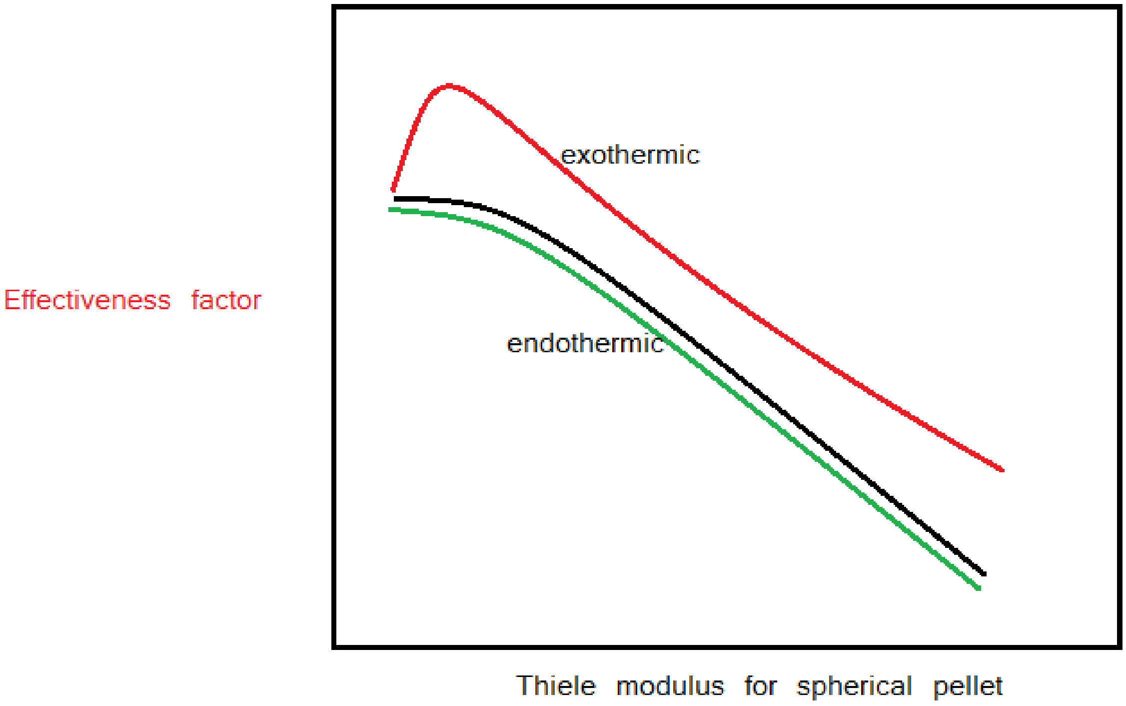


The reactant ***A*** will diffuse into the pore structure where it will be reacted to the unstable intermediate *B.* An unstable molecule *B* formed within a pore must make many random collisions with the pore walls before it escapes out of a pore mouth into the gas phase. Thus while trying to “find its way out” of the pore structure, the intermediate *B* has a high probability of degenerating into the undesired product C. We can thus expect catalysts with small pores to give poorer yields of an unstable intermediate than will the same material prepared in a nonporous condition.

Effect of heat transfer on catalyst activity and selectivity



For exothermic reactions the centre of the pellet will be at a higher temperature. As the reaction proceeds to the inside of pore exothermic reactions liberate thermal energy. Rate of reactions increases as temperature increases and thus, there will be a steep rise in temperature. On the contrary; for endothermic reactions consumes heat energy and there will be a decline in temperature and also on the rate of reaction. Effectiveness factor for endothermic reactions will always be less than one. For highly exothermic reactions; effectiveness factor may achieve values greater than 1.



Question 1:

1. In a research laboratory, a hydrogenation catalyst was developed to hydrogenate olefins to alkanes. However, the reaction mixture contains some valuable aromatics. If the olefin hydrogenation is much faster than aromatic hydrogenation; the ideal catalyst for the process should possess

Options

a) small pore radii and large pellet size b) large pore radii and small pellet size c) small pore radii and small pellet size d) large pore radii and large pellet size

feedback

wright answer- Your answer is right

wrong answer- Your answer is wrong. The rate of olefin hydrogenation decreases fast on the catalyst interior; where as aromatic hydrogenation gains momentum. Selectivity for alkanes will decrease.

Question 2:

1. A catalyst was developed to convert ethanol to acetaldehyde; which follows a second order reaction. However, there is a side reaction in which ethanol dehydrogenates in to ethene which is a first order reaction. Upon commercialization the catalyst should have

Options

a) small pore radii and large pellet size b) large pore radii and small pellet size c) small pore radii and small pellet size d) large pore radii and large pellet size

feedback

wright answer- Your answer is right

wrong answer- Your answer is wrong. Here the desired reaction is second order; and as the concentration of ethanol is lowered the rate of dehydrogenation will be affected and hence yield of acetaldehyde will be lowered. Catalyst with large pore radii and small pellet size will be beneficial as there will not be any diffusional limitation.

Question 3:

1. A catalyst researcher is trying to optimize a hydrogenation catalyst to convert acetylene to ethane. The ethane is to be used in perfumery; so ethene should be avoided. The final catalyst should have

Options

a) small pore radii and large pellet size b) large pore radii and small pellet size c) small pore radii and small pellet size d) large pore radii and large pellet size

feedback

wright answer- Your answer is right

wrong answer- Your answer is wrong. Here the desired reaction is ethane; which is the last product. The smaller the radii of the catalyst pore; ethene will be forced to convert to ethane.

Question 4:

1. Dimensionless parameter for temperature sensitivity of catalyst pellet ‘β’ is defined as $\beta = \frac{T - T_0}{T_0}$; where T is the temperature at the centre of the catalyst pellet; and T0 is the temperature at the catalyst surface. Which of the following is correct

Options
a) β is positive for exothermic reaction and negative for endothermic reaction b) β is positive for endothermic reaction and negative for exothermic reaction c) β is positive for both exothermic and endothermic reaction d) β is negative for both exothermic endothermic reaction

wright answer- Your answer is right
wrong answer- Your answer is wrong. Exothermic reaction releases heat

Major Contribution by: Ahlborn Wheeler (Catalytic Scientist)

References:

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2. The Theory of Adsorption and Catalysis: Academic Press, 1978: *Alfred Clark*