Catalyst Deactivation

Effect of pore diffusion on catalyst deactivation

- For a pellet, *pore diffusion may strongly influence the progress of catalyst decay*

- In case of **parallel deactivation** $(A \rightarrow R \; ; A \rightarrow P \downarrow)$, the reactant is either distributed evenly throughout the pellet $(\phi < 0.4, \eta \approx 1)$ or maybe found close to the exterior surface $(\phi > 4, \eta < 1)$

  The poison is also deposited in a similar manner – uniformly for no pore diffusion resistance (***uniform poisoning***) or at the exterior, near the pore mouth for strong pore diffusion resistance

  For very strong diffusional resistance, a thin shell at the outside the pellet becomes poisoned, this shell thickens with time and the *deactivation front moves inside* and we have the ***shell model for poisoning***

- For **series deactivation** $(A \rightarrow R \rightarrow P \downarrow)$, in the regime of strong pore resistance, the concentration of the product R is higher within the pellet than at the exterior

  As the product R is the source of poison, the latter deposits in higher concentrations within the pellet interior. Hence there is *poisoning from inside-out* for series deactivation

- For **side by side deactivation** $(A \rightarrow R \ ; P \rightarrow P \downarrow)$, the rate at which the poison from the feed reacts with the surface determines where it deposits, no matter what the concentration of the reactants and products may be

  For small poison rate constant, the poison penetrates the pellet uniformly and deactivates all elements of the catalyst surface in the same way

  For large poisoning rate constants, poisoning occurs at the pellet exterior, as soon as the poison reaches the surface

- **Progress of deactivation** occurs in different ways depending on the **type of decay reaction occurring** and the **value of pore diffusion factor**

- For **parallel** and **series poisoning**, the **Thiele modulus (ϕ) for the main reaction is the pertinent pore diffusion parameter**

- For **side by side reactions**, the **Thiele modulus for deactivation (ϕ_d) is the prime parameter**

- **Non-isothermal effects** within the pellets may also cause **variation in deactivation with location**, especially when deactivation is caused by surface modifications due to high temperatures

How pore diffusion resistance distorts the kinetics of reactions with deactivating catalysts

- Consider the following rate schemes for reactions on spherical particles,

$$-r_A = kC_A a\eta$$

$$-\frac{da}{dt} = k_d a^d$$

- For **no deactivation** (with and without pore diffusion resistance), these rates become,

$$-r_A = kC_A \eta$$

$$a = 1$$

where $\eta = 1$ (for no diffusion resistance) and

$$\eta = \frac{1}{\phi} \, , \quad \phi = L\sqrt{\frac{k\rho_p}{D_{e.A}}} \quad \text{(for strong pore diffusion resistance)}$$

- With **deactivation** (with and without pore diffusion resistance), these rates become,
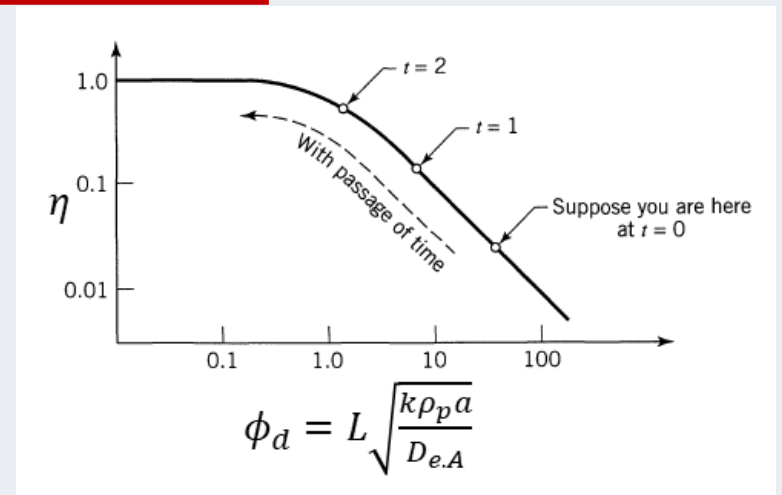
$$-r_A = kC_A \eta a$$

$$-\frac{da}{dt} = k_d a^d$$

where $\eta = 1$ (for no diffusion resistance) and

$$\eta = \frac{1}{\phi_d} \, , \qquad \phi_d = L\sqrt{\frac{k\rho_p a}{D_{e.A}}} = \phi\sqrt{a} \quad \text{(for strong pore diffusion resistance)}$$

- From rate of deactivation equations, $a = exp(-k_d t)$ for $d = 1$

$$a = [1 + (d-1)k_d t]^{1/1-d} \quad \text{for } d \neq 1$$

- Thus, in the regime of strong pore diffusion resistance, activity, $\boldsymbol{a}$ decreases with time causing ϕ_d to decrease
- Since $\boldsymbol{\phi_d}$ decreases, $\boldsymbol{\eta}$ rises with time
- However, $\boldsymbol{a}$ decreases faster than $\boldsymbol{\eta}$ rises, so the reaction rate decreases with time

$$\phi_d = L\sqrt{\frac{k\rho_p a}{D_{e.A}}}$$

Performance equation in the regime of strong pore diffusional resistance

Let us consider the following rate form

$$-r_A = kC_A a\eta \qquad \text{and} \qquad -\frac{da}{dt} = k_d a$$

For batch solid, plug flow of liquid (constant flow) with simple first order system,

(a) In case of no resistance to pore diffusion

For no deactivation, $\quad ln\frac{C_{Ao}}{C_A} = k\tau \quad$ and $\quad a = 1$

With deactivation, $\quad ln\frac{C_{Ao}}{C_A} = k\tau e^{-k_d t} \quad$ since $\quad a = e^{-k_d t}$

**(b) With strong resistance to pore diffusion**

For no deactivation, $\quad ln\frac{C_{Ao}}{C_A} = \eta k\tau = \frac{k\tau}{\phi}$

With deactivation, $\quad ln\frac{C_{Ao}}{C_A} = \eta k\tau a = \frac{k\tau a}{\phi_d}$

Now $\phi_d = \phi\sqrt{a}, \qquad ln\frac{C_{Ao}}{C_A} = \frac{k\tau a}{\phi\sqrt{a}} = \frac{k\tau\sqrt{a}}{\phi} = \frac{k\tau}{\phi}[exp(-k_d t)]^{1/2} \qquad$ since $\quad a = e^{-k_d t}$

$$ln\frac{C_{Ao}}{C_A} = \frac{k\tau}{\phi}exp\left(\frac{-k_d t}{2}\right)$$

- The figure shows how reactor performance decreases with time in the presence of deactivation and pore diffusional resistance

- In the exit, C_A rises with time and conversion decreases with time

- For 1st order systems, the conversion **decreases more slowly in the presence of strong pore diffusional resistance than in the diffusion free regime** – this applies to all reactor types

- Equation similar to the one discussed can be developed for other reaction orders and deactivation orders

- For second order reactions and mixed flow conditions
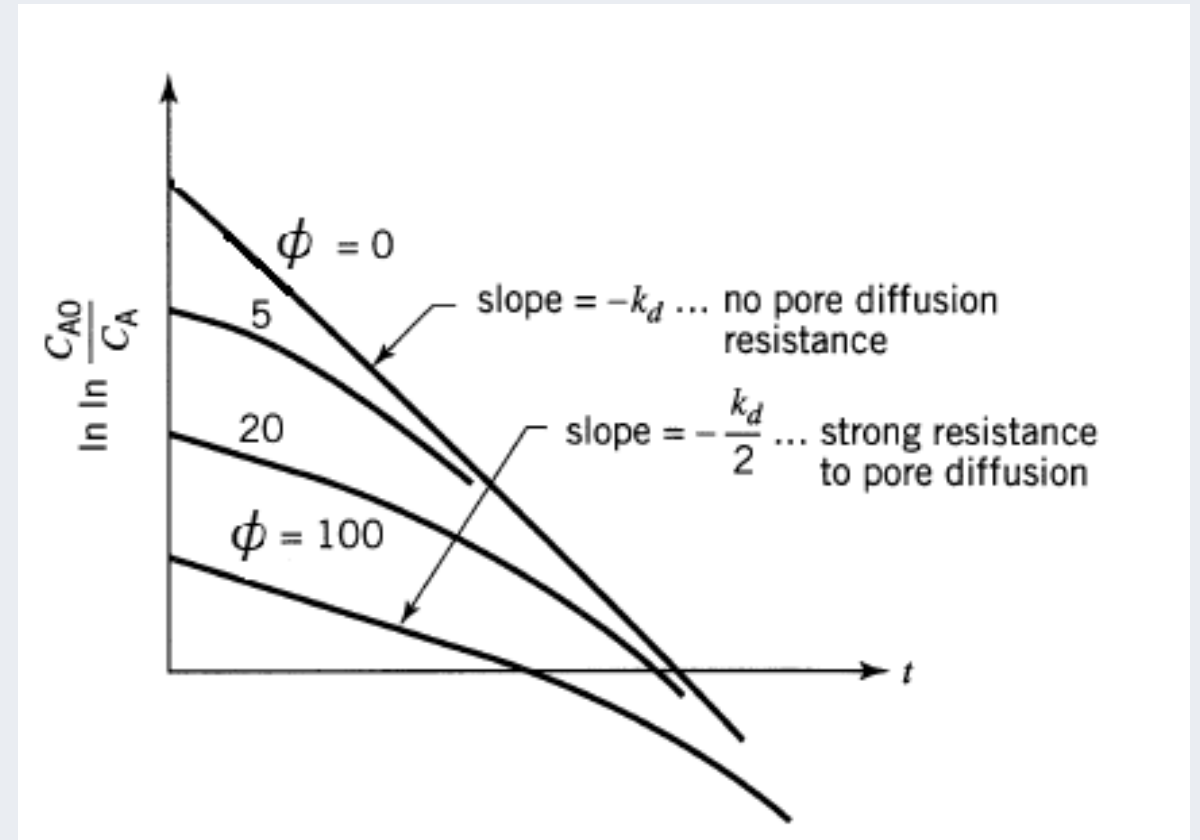
$$\tau = \frac{C_{Ao} - C_A}{kC_A^2 a\eta} \quad \text{with} \quad a = e^{-k_d t} \quad \text{and} \quad \phi = L\sqrt{\frac{3k\rho_p C_{Ao}}{2D_{e.A}}}$$

Rates for poisoned porous catalysts

- The interaction of the intra-pellet diffusion on the rate of the main and poisoning reactions can lead to a **variety of relations between activity and extent of poisoning**

- The following discussion will be for <u>parallel and independent poisoning</u>

Uniform poisoning

- This happens when rate of adsorption (or reaction) which poisons the catalytic sites is slow with respect to intra-pellet diffusion (rate of poisoning slow compared to its transport)

- The surface is deactivated uniformly throughout the pellet

- If α = fraction of surface poisoned   and $k(1-\alpha)$ = rate constant of main reaction

- As   Rate $\propto$ Concentration of active sites, for a first order system

$$\boxed{Rate\ per\ pellet\ =\ r_p = \eta k(1-\alpha)C_{As}}$$

(i)   When diffusion resistance for the main reaction is low (low ϕ), then $\boxed{\eta \to 1 \ \ and\ r_p = k(1-\alpha)C_{As}}$

Now, $a = \dfrac{poisoned\ rate}{unpoisoned\ rate} = \dfrac{k(1-\alpha)C_{As}}{kC_{As}}$

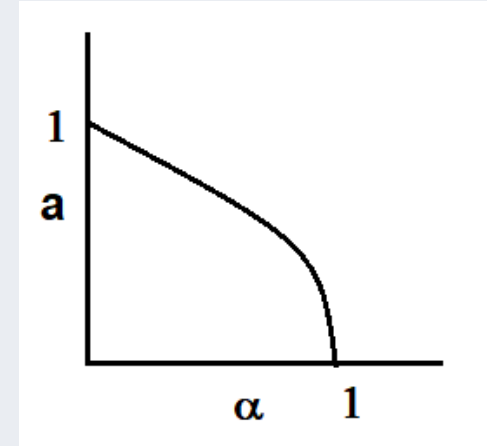$\therefore$ $\boxed{a = (1-\alpha)}$
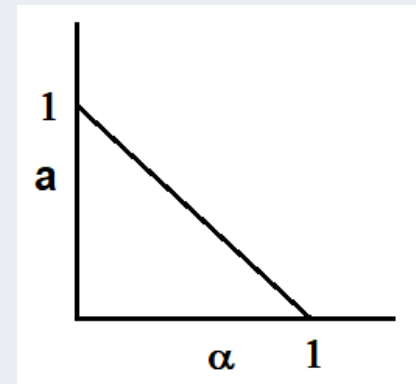
(ii)   For large intra-pellet diffusion resistance ($\phi>5$) , then $\boxed{\eta = \frac{1}{\phi}}$ and

$$r_p = \frac{3}{R}\sqrt{\frac{D_e}{k(1-\alpha)\rho_p}}\,k(1-\alpha)C_{As}$$

$$\boxed{r_p = \frac{3}{R}\sqrt{\frac{D_e k(1-\alpha)}{\rho_p}}\,C_{As}}$$

Now, $a = \dfrac{poisoned\ rate}{unpoisoned\ rate} = \dfrac{\frac{3}{R}\sqrt{\frac{D_e k(1-\alpha)}{\rho_p}}C_{As}}{\frac{3}{R}\sqrt{\frac{D_e k}{\rho_p}}C_{As}} = \sqrt{(1-\alpha)}$

∴ $\boxed{a = \sqrt{(1-\alpha)}}$

Effect of poisoning on the rate of the main reaction is less than the linear effect

This happens in the case of a *slow poisoning reaction* and a *fast main reaction* (large ϕ)

This is also known as ***anti-selective poisoning***

- Now, the relationship between the effect of poisoning (a) in terms of the fraction (α) of the catalytic surface that has been poisoned has been determined

- As a practical problem, however, it is essential to determine how *activity (a) is related to time (t)*

$$\boxed{a \rightarrow \alpha \rightarrow t}$$

- This helps to determine how the rate of the main reaction decreases with time

Variation of α with t

Rate of deposition of poison is first order in C_p and in the fraction $(1 - \alpha)$ of unpoisoned surface

$$\boxed{\frac{dn}{dt} = k_p C_p (1 - \alpha)}$$

where n = adsorbed phase concentration of poison

C_p = fluid phase concentration of poison

If monomolecular adsorption is assumed, n is proportional to α

$$\boxed{\alpha = \frac{n}{n_o}}$$

where n_o = adsorbed phase concentration corresponding to complete deactivation (corresponding to monolayer coverage)

$$\therefore \quad \boxed{\frac{d\alpha}{dt} = \frac{k_p C_p}{n_o}(1-\alpha)}$$

Integrating
$$\int_0^\alpha \frac{d\alpha}{1-\alpha} = \frac{k_p C_p}{n_o}\int_0^t dt$$

$$-\ln(1-\alpha) = \frac{k_p C_p}{n_o}t$$

$$\boxed{(1-\alpha) = exp\left[-\frac{k_p C_p}{n_o}t\right]} \qquad \Rightarrow \qquad \boldsymbol{\alpha = f(t)}$$

Now, $\quad Rate\ per\ pellet\ = r_p = \eta k(1-\alpha)C_{As}$

- For low ϕ, $\quad \eta \approx 1$ $\qquad \boxed{r_p = k\ exp\left[-\frac{k_p C_p}{n_o}t\right]C_{As}} \qquad \Rightarrow \qquad \boldsymbol{r_p = f(t)}$

- For high ϕ, $\quad \eta = \frac{1}{\phi}$ $\qquad r_p = \frac{3}{R}\sqrt{\frac{D_e}{k(1-\alpha)\rho_p}}k(1-\alpha)C_{As} = \frac{3}{R}\sqrt{\frac{D_e k(1-\alpha)}{\rho_p}}C_{As}$

$$\boxed{r_p = \frac{3}{R}\sqrt{\frac{D_e k\ exp\left[-\frac{k_p C_p}{n_o}t\right]}{\rho_p}}C_{As}} \qquad \Rightarrow \qquad \boldsymbol{r_p = f(t)}$$

For <u>series poisoning cases</u>, the <u>equations relating a and α and α and t are coupled</u>. They become partial differential equations and their simultaneous solution becomes more complex when intraparticle diffusion is involved