

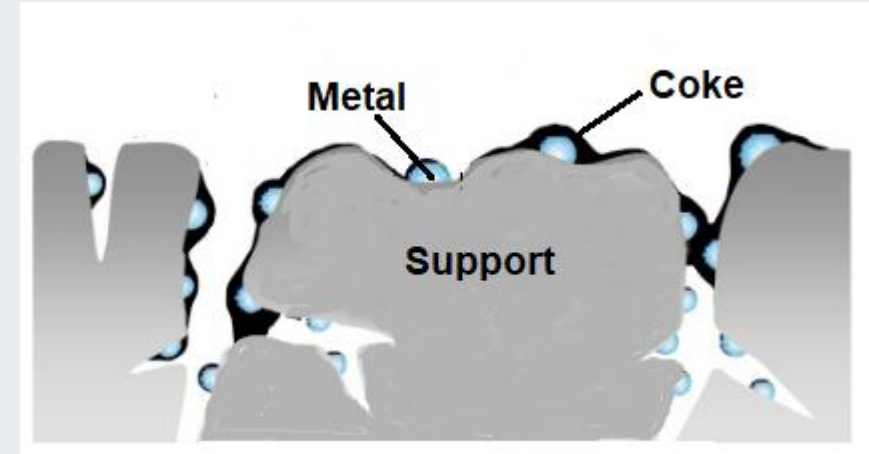
# Catalyst Deactivation

Book: *Chemical Reaction Engineering*, O. Levenspiel, 3<sup>rd</sup> Edition, Wiley and Sons (Chapter 21)  
*Chemical Engineering Kinetics*, J. M. Smith, (Chapter 11), 2<sup>nd</sup> and 3<sup>rd</sup> Edition

- In all the previous chapters, the activity of the catalyst remained constant throughout the catalyst's life – the total concentration of the active sites ( $C_t$ ) accessible for the reaction does not change with time
- This is, however, not true and the activity usually decreases as the catalyst is used
- This loss in activity and/or selectivity of the catalyst over time is known as **catalyst deactivation**
- Catalyst deactivation is a continuing problem in industrial catalytic processes. Costs to industry for catalyst replacement and process shutdown total billions of dollars per year
- Time scales for catalyst deactivation vary considerably – for example, in the case of cracking catalysts, catalyst lifespan may be in the order of seconds, while in ammonia synthesis the iron catalyst may last for 5–10 years
- Catalyst deactivation occurs essentially by **four different mechanisms**
  - (1) **Fouling**
  - (2) **Poisoning**
  - (3) **Thermal degradation/Sintering**
  - (4) **Vapour compound formation accompanied by transport**

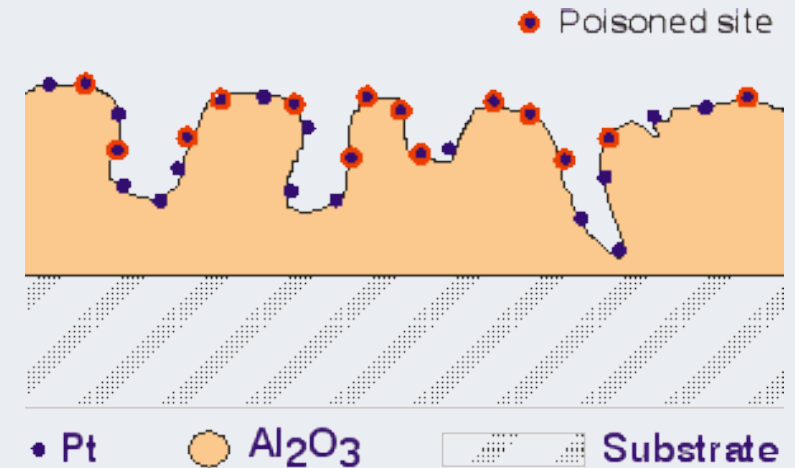
## (1) Fouling

- This process of deactivation is rapid and is caused by **physical blocking of the active sites on the surface**
  - This type of deactivation occurs when a substance (usually carbonaceous material or coke) is deposited on the catalytic surface and in catalyst pores
  - The sites are covered by deposition without any reaction – deactivation is ***mechanical*** in nature
  - Most catalysts have a tendency to form coke when dealing with hydrocarbons above 400°C. This can be reduced by running at high pressures (2000 – 3000 kPa) and hydrogen rich atmosphere
  - Removal of deposited solids is often termed as regeneration
  - Carbon deposition during catalytic cracking is a common example of fouling
- $$C_{10}H_{12} \rightarrow C_5H_{12} + C_4H_{10} + C \downarrow$$
- **Regeneration** may be done by burning off the carbon



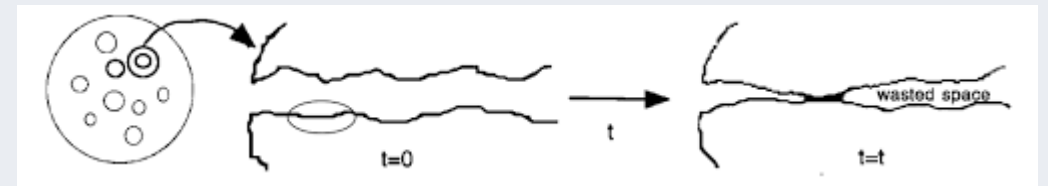
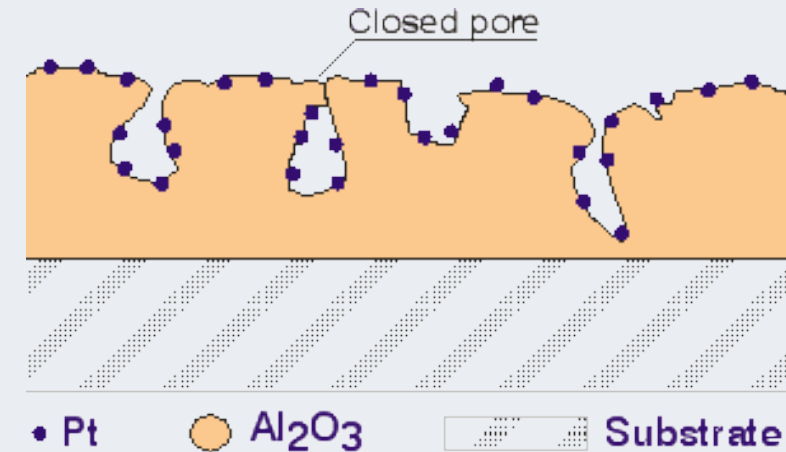
## (2) Poisoning

- Deactivation by this mechanism occurs when the **poisoning molecules become irreversibly chemisorbed on the active site**
- This reduces the number of active sites available for the main reaction
- This type of deactivation is **chemical** in nature and is a slower mode of deactivation
- The poison molecule may be a reactant and/or a product in the main reaction or may be an impurity in the feed stream
- The poisons may be selective (most active sites are poisoned first) or non-selective (any site may be poisoned first)
- Example: Sulphur is a notorious poison
- Restoration of the activity of such catalysts if possible is called **reactivation**



### (3) Thermal degradation/Sintering

- Sintering or aging is the loss of catalytic activity due to **loss of active surface area** resulting from prolonged exposure to high temperatures
- The active surface is lost either by **crystal agglomeration** and **growth of the metals deposited on the support** (crystallites migrate over the surface and form larger crystallites leading to lower dispersion) or by **narrowing and closing of the pores** in the catalyst pellet
- Change in the surface structure may also occur due to surface recrystallization or formation or elimination of surface defects (active sites)
- Thermal degradation also involves the **transformation of the catalytic phase** (by reaction of fluid, support, or promoter with catalytic phase) **to a non-catalytic, inactive phase**
- Example: Nickel on alumina support gets converted to Ni aluminate at high temperature, Ni aluminate is not a catalyst



## (4) Loss of catalytic active phase by vapour transport

- This type of deactivation involves the **reaction of gas with catalyst phase to produce volatile compound**
- Such reactions may occur at moderate temperatures also
- For example, there is a loss of catalytic metal species due to formation of volatile metal compounds
- *Ni, Fe* forms  $Ni(CO)_4$  and  $Fe(CO)_5$  between 0 – 300°C
- *Ru, Pb* forms  $RuO_3$  (25°C) and  $PbO$  (> 850°C)

Loss of catalytic material **may also occur by mechanical failure** which includes:

- (a) Crushing of granular material or pellets due to load
- (b) Attrition (size reduction) and/or breakup of catalyst granules or pellets to produce fines especially in fluid or slurry beds
- (c) Erosion of catalyst particles or monolith coatings at high fluid velocities

# Type of decay reactions

Decay or deactivation can occur in four ways –

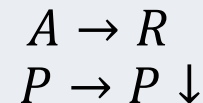
- **Parallel deactivation:** The reactant may produce a side product which deposits on and deactivates the surface



- **Series deactivation:** The reaction product may decompose or react further to produce a material which then deposits on and deactivates the surface



- **Side by side deactivation:** An impurity in the feed may deposit on the surface and deactivate it



- **Independent deactivation:** Catalyst decay is caused by structural modifications or sintering of the catalyst surface due to exposure to extreme conditions

- Independent deactivation is dependent on the time that the catalyst spends in the high temperature environment and is unaffected by materials in the gas stream
- For parallel, series and side by side deactivation, the deposition depends on the concentration of the reactant, product or some other substance in the feed

Since the distribution of these substances varies with position in the pellet, the location of deactivation will depend on which decay reaction is occurring

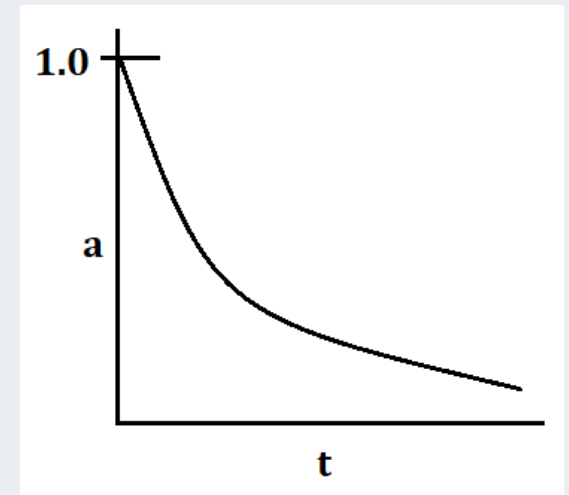
## Intrinsic deactivation kinetics

The activity of a catalyst pellet at any time  $t$  is defined as,

$$a = \frac{\text{rate of reaction at time } t}{\text{rate of reaction at time } t = 0}$$

$$a(t) = \frac{-r_A(t)}{-r_A(t = 0)}$$

$$\text{at } t = 0, a = 1$$





- In analysing reactions over decaying catalysts, reactions are divided into ***separable kinetics*** and ***non-separable kinetics***
- In ***separable kinetics***, the rate law and the activity are separate

$$\text{Rate}(-r_A) = a(\text{past history})(-r_A)(\text{fresh catalyst present condition})$$

$$r_{int} = f_1(C, T) \cdot a$$

$$-\frac{da}{dt} = f_2(C, T)a^d \quad d = \text{deactivation order}$$

Catalyst decay and reaction kinetics can be studied separately

- For ***non-separable kinetics***, the reaction rate depends on both past history and fresh catalyst condition,

$$\text{Rate}(-r_A) = (-r_A)(\text{past history, fresh catalyst present condition})$$

Catalyst decay and reaction kinetics cannot be studied separately

This will not be considered further

For  $n$ th order kinetics,

(Reaction time) =  $f_1$ (main stream temperature).  $f_2$ (main stream conc).  $f_3$ (present activity of cat pellet)

$$-r_A = \left( k_o e^{-E/RT} \right) (C_A^n)(a)$$

(Deactivation rate) =  $f_4$ (main stream temperature).  $f_5$ (main stream conc).  $f_6$ (present state of cat pellet)

$$-\frac{da}{dt} = \left( k_{do} e^{-E_d/RT} \right) (C_i^m)(a^d)$$

For different decay reactions,

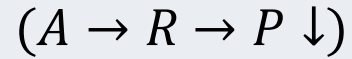
For **Parallel deactivation**,

( $A \rightarrow R ; A \rightarrow P \downarrow$ )

$$-r_A = k C_A^n a$$

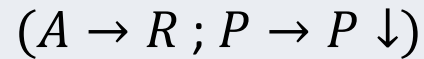
$$-\frac{da}{dt} = k_d C_A^m a^d$$

For **Series deactivation**,



$$-r_A = kC_A^n a \qquad -\frac{da}{dt} = k_d C_R^m a^d$$

For **Side by side deactivation**,



$$-r_A = kC_A^n a \qquad -\frac{da}{dt} = k_d C_P^m a^d$$

For **Independent deactivation**,

*(concentration independent)*

$$-r_A = kC_A^n a \qquad -\frac{da}{dt} = k_d a^d$$

If the reaction is,



$$-\frac{da}{dt} = k_d (C_A + C_R)^m a^d$$