Catalysis

Catalyst deactivation

Deactivation of catalyst is a loss of catalyst activity with time due to three main reasons: sintering, fouling and poisoning.

(1) Sintering

Sintering is closing or narrowing of the catalyst pores due to crystal growth that takes place inside the catalyst particle due to accidental or long period of exposure at high temperature. This will decrease the surface area of the catalyst. Also, the catalyst atoms move across the surface and agglomerate. This leads to permanent damage

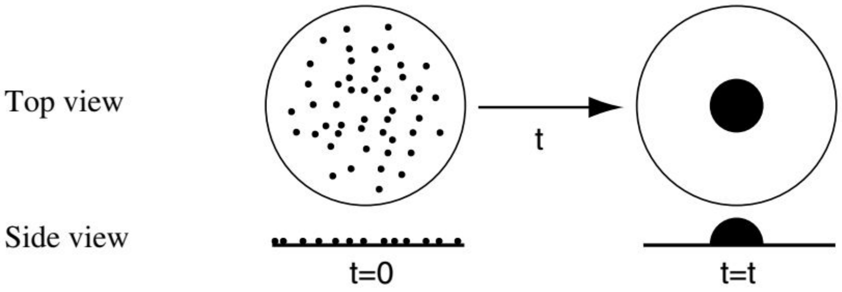
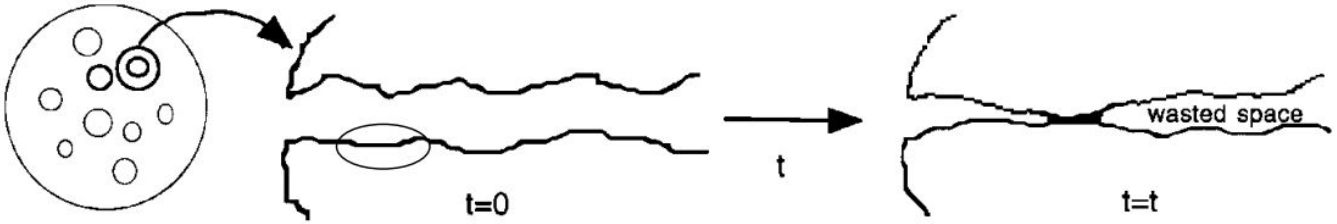


Figure 10-24 Decay by sintering: agglomeration of deposited metal sites; loss of reactive surface area.



Decay by sintering: pore closure; loss of reactive surface area.

Deactivation by sintering may in some cases be a function of the mainstream gas concentration. Although other forms of the sintering decay rate laws exist, one of the most commonly used decay laws is second order with respect to the present activity

$$r_d = k_d a^2 = -\frac{da}{dt}$$

Integrating, with $a = 1$ at time $t = 0$, yields

$$a(t) = \frac{1}{1 + k_d t}$$

The amount of sintering is usually measured in terms of the active surface area of the catalyst S_a

$$S_a = \frac{S_{a0}}{1 + k_d t}$$

The sintering decay constant, k_d, follows the Arrhenius equation

$$k_d = k_d(T_0)\ \exp\left[\frac{E_d}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$

For the first-order reaction $\mathrm{A} \longrightarrow \mathrm{B}$ The mole balance in batch reactor $N_{A0} = \frac{dX_d}{dt} = -r'_A W$

where X_d is the conversion of A when the catalyst is decaying.

Reaction-Rate Law $-r'_A = k' a(t)\, C_A$ and for second-order decay by sintering: $\boxed{a(t) = \frac{1}{1+k_d t}}$

Stoichiometry $C_A = C_{A0}(1 - X_d) = \frac{N_{A0}}{V}\,(1 - X_d)$

Combining gives us $\frac{dX_d}{dt} = k'(1-X_d)a\frac{W}{V}$

Let $k = k'W/V$. Substituting for catalyst activity a, we have $\frac{dX_d}{dt} = k(1-X_d)a = k\frac{(1-X_d)}{(1+k_d t)}$

Separating variables and integrating yields

$$\int_0^X \frac{dX_d}{1-X_d} = k\int_0^t \frac{dt}{1+k_d t} \quad \Longrightarrow \quad \ln\frac{1}{1-X_d} = \frac{k}{k_d}\ln(1+k_d t)$$

Solving for the conversion X_d at any time t, we find that

$$X_d = 1 - \frac{1}{(1+k_d t)^{k/k_d}}$$

the analytical solution **without decay**

$$\boxed{\ln\frac{1}{1-X} = kt}$$

2. Fouling

Fouling or cocking occurs at the surface of the catalyst as a results of long term reaction of the organics on the surface of the catalyst which lead to decomposition of carbon particles inside the catalyst pores. This leads to temporary damage

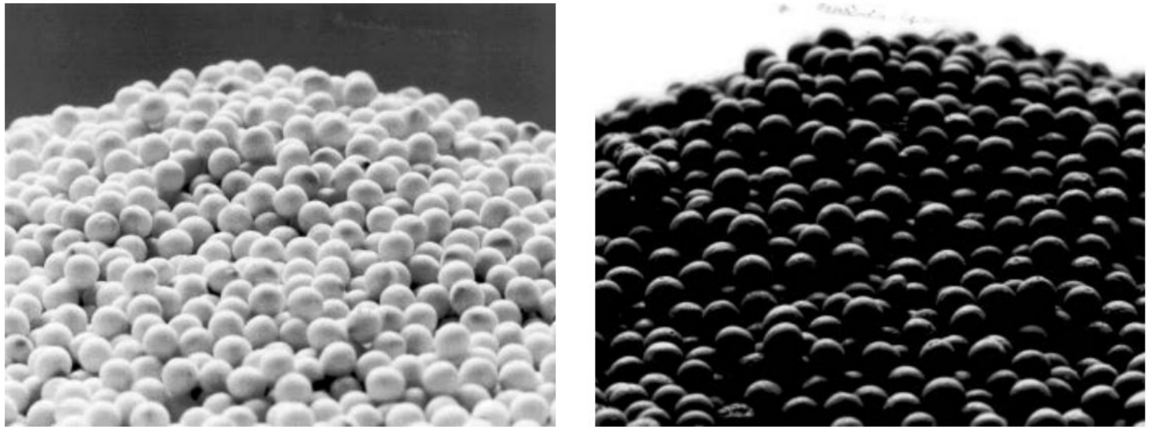

(a) Fresh catalyst (b) Spent catalyst

Figure 10-26 Decay by coking. (Photos courtesy of Engelhard catalyst, copyright by Michael Gaffney Photographer, Mendham, NJ.)

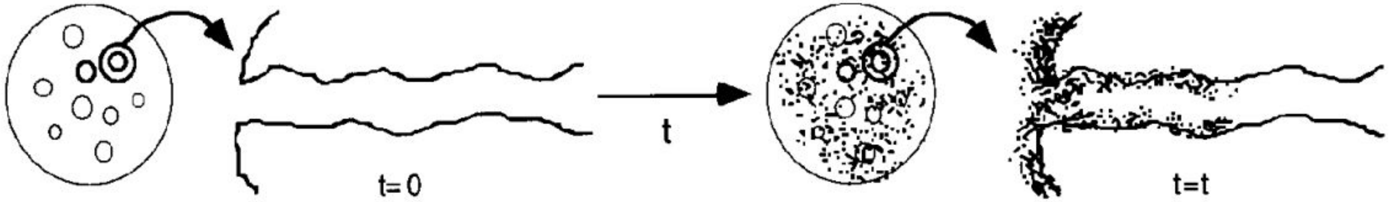


Figure 10-25 Schematic of decay by coking; loss of reactive surface area.

The amount of coke on the surface after a time t has been found to obey the following empirical relationship

$$C_{\mathrm{C}} = At^{n}$$

where C_{C} is the concentration of carbon on the surface (g/m^2) and n and A are fouling parameters, which can be functions of the feed rate.

Different functionalities between the activity and amount of coke on the surface have been observed. One commonly used form is

$$a = \frac{1}{k_{\mathrm{C}k} C_{\mathrm{C}}^{p} + 1}$$

or, in terms of time, we combine Equations above

$$a = \frac{1}{k_{\mathrm{C}k} A^{p} t^{np} + 1} = \frac{1}{1 + k' t^{m}}$$

3. Poisoning

Irreversible chemisorption of the reactant(s) on the surface of the active site. Example of sulfur containing compounds that leads to H2S.

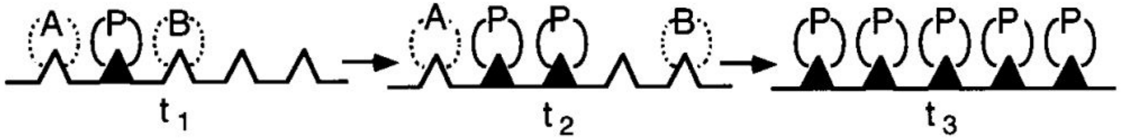
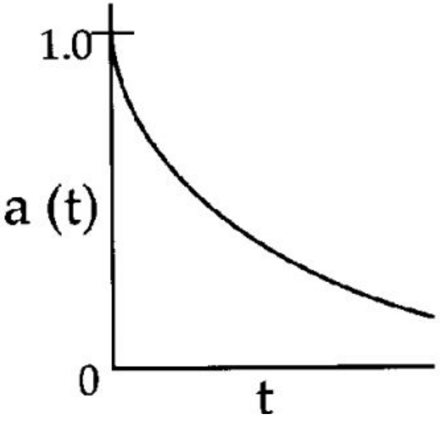


Figure 10-27 Decay by poisoning.

Let the activity of the catalyst denoted by a and is varied with time, i.e. $a = f(t)$

$$a = \frac{rate\ of\ deactivated\ catalyst}{rate\ of\ fresh\ catalyst} = \frac{r_d}{r_o}$$



From the concept of adsorption you learned, this activity is a function of vacant sites to that of total sites. Note that for freshly new catalyst, the vacant site is the same as total site;

$$a = \frac{C_v}{C_T}$$

For the case of an impurity, P, in the feed stream, such as sulfur, for example, in the reaction sequence

$$\text{Main reaction:} \quad \left.\begin{cases} \mathrm{A+S} \rightleftarrows (\mathrm{A\cdot S}) \\ \mathrm{A\cdot S} \rightleftarrows (\mathrm{B\cdot S+C}(g)) \\ \mathrm{B\cdot S} \rightleftarrows (\mathrm{B+S}) \end{cases}\right\} -r'_{\mathrm{A}} = a(t)\,\frac{kC_{\mathrm{A}}}{1+K_{\mathrm{A}}C_{\mathrm{A}}+K_{\mathrm{B}}C_{\mathrm{B}}}$$

$$\text{Poisoning reaction:} \quad \mathrm{P+S} \longrightarrow \mathrm{P\cdot S} \qquad r_d = -\frac{da}{dt} = k'_d C_p^m a^q$$

The rate of removal of the poison, $r_{P\cdot S}$, from the reactant gas stream onto the catalyst sites is proportional to the number of sites that are un-poisoned (C_{t0}-$C_{P.S}$) and the concentration of poison in the gas phase is C_P then

$$r_{\mathrm{P\cdot S}} = k_d(C_{\mathrm{t}0} - C_{\mathrm{P\cdot S}})C_{\mathrm{P}}$$

where $C_{P.S}$ is the concentration of poisoned sites and C_{t0} is the total number of sites initially available.

$$-\frac{dC_t}{dt} = \frac{dC_{\mathrm{P\cdot S}}}{dt} = r_{\mathrm{P\cdot S}} = k_d(C_{t0} - C_{\mathrm{P\cdot S}})C_{\mathrm{P}}$$

Dividing through by C_{t0} and letting *f* be the fraction of the total number of sites that have been poisoned yields

$$\frac{df}{dt} = k_d(1 - f)C_P$$

The fraction of sites available for adsorption (*1 - f*) is essentially the activity *a(t)*. Consequently, the equation above becomes

$$-\frac{da}{dt} = a(t)k_dC_P$$