Catalysis - continue

Catalysts provide an alternative reaction pathway with a lower activation energy

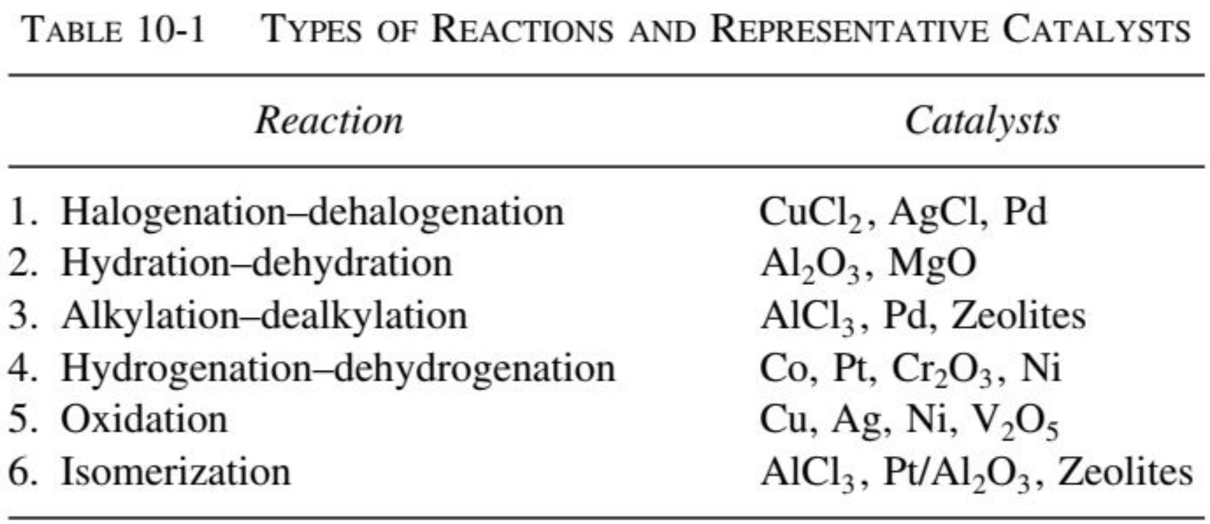
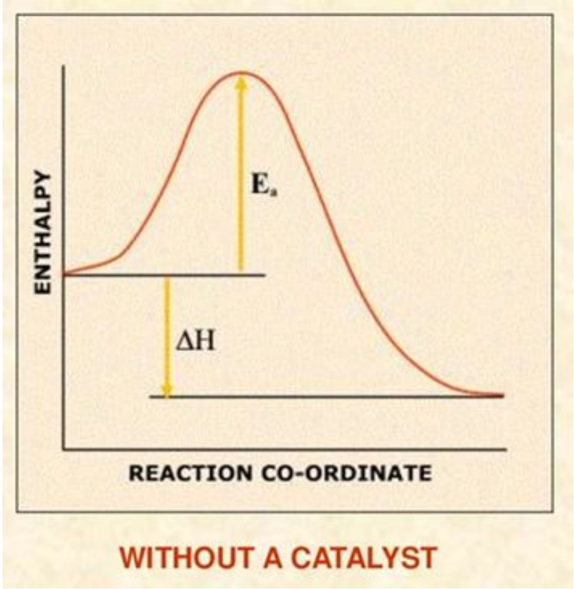
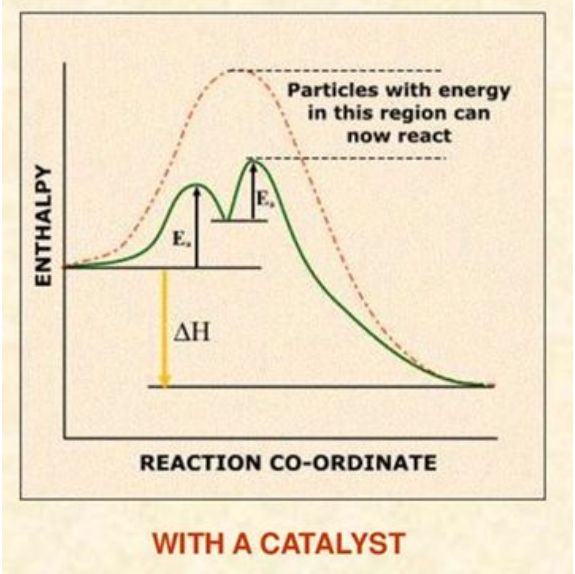


TABLE 10-1 TYPES OF REACTIONS AND REPRESENTATIVE CATALYSTS

Reaction	*Catalysts*
1. Halogenation–dehalogenation	$CuCl_2$, AgCl, Pd
2. Hydration–dehydration	Al_2O_3, MgO
3. Alkylation–dealkylation	$AlCl_3$, Pd, Zeolites
4. Hydrogenation–dehydrogenation	Co, Pt, Cr_2O_3, Ni
5. Oxidation	Cu, Ag, Ni, V_2O_5
6. Isomerization	$AlCl_3$, Pt/Al_2O_3, Zeolites



WITHOUT A CATALYST



WITH A CATALYST

Steps in a Catalytic Reaction

1. Mass transfer (diffusion) of the reactant(s) (e.g., species A) from the bulk fluid to the external surface of the catalyst pellet
2. Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface
3. Adsorption of reactant A onto the catalyst surface
4. Reaction on the surface of the catalyst (e.g., A B)
5. Desorption of the products (e.g., B) from the surface
6. Diffusion of the products from the interior of the pellet to the pore mouth at the external surface
7. Mass transfer of the products from the external pellet surface to the bulk fluid

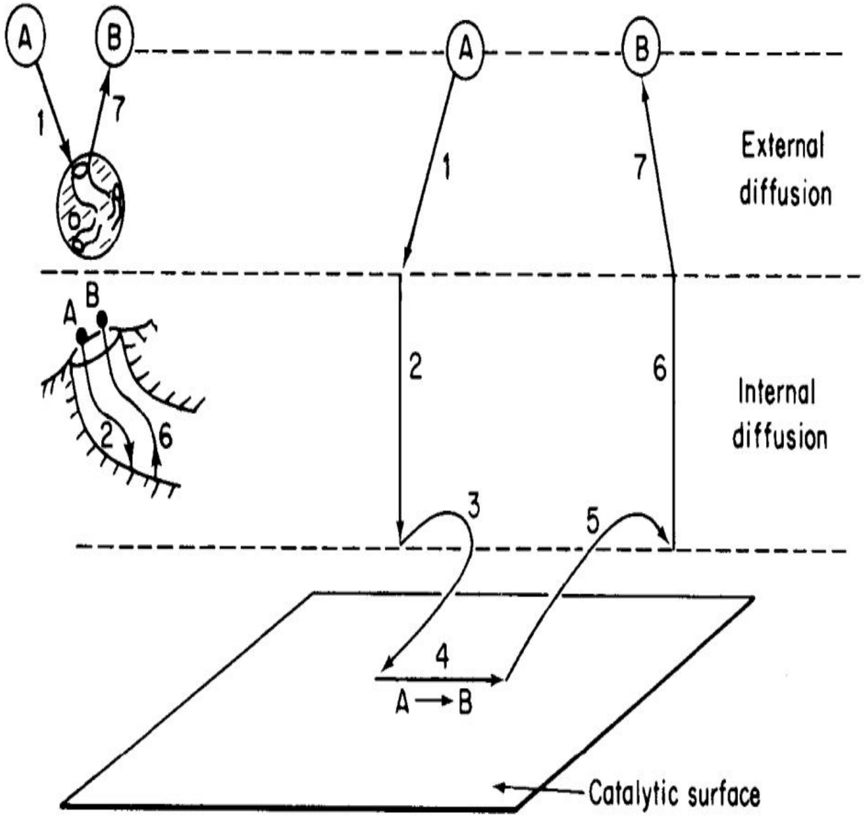
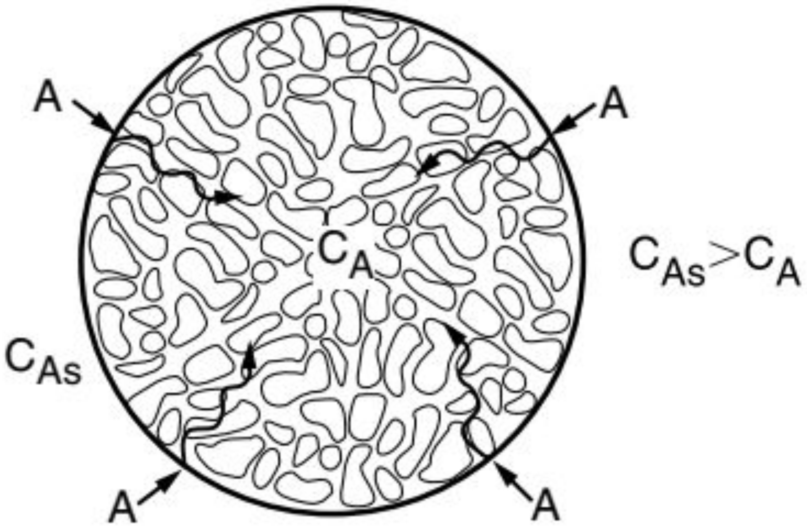


Figure 10-5 Steps in a heterogeneous catalytic reaction.

Catalyst & Active Sites

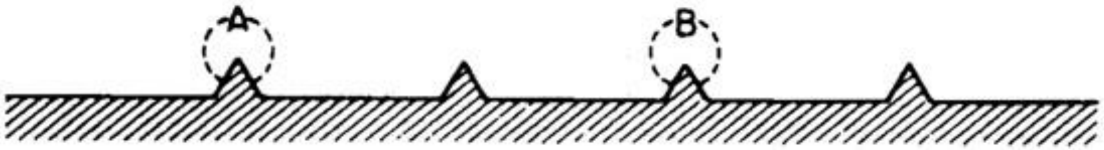
Reactions are not catalyzed over the entire surface but only at certain active sites or centers that result from unsaturated atoms in the surface.

An ***active site*** is a point on the surface that can form strong chemical bonds with an adsorbed atom or molecule.



The Adsorption Step

$$A + S \rightleftarrows A \cdot S$$



Vacant and occupied sites

For the system shown, the total concentration of sites is

$$\mathbf{C_t = C_v + C_{A.S} + C_{B.S}}$$

C_t = Total sites on the surface of catalyst, including adsorbed and vacant ones

C_v = Total vacant sites

$C_{A.S}$ = Total sites that accommodate the adsorbed A species

$C_{B.S}$ = Total sites that accommodate the adsorbed B species

Adsorption of species A

$$\mathrm{A} + \mathrm{S} \leftrightarrow \mathrm{A} \bullet \mathrm{S}$$

$$\begin{aligned} r_{AD} &= k_f C_A C_v - k_b C_{A\bullet S} \\ &= k_A [C_A C_V - C_{A\bullet S}/K_A] \end{aligned}$$

$K_A = \mathrm{k_f}/k_b$ [atm^{-1}]

@ equilibrium: $r_{AD} = 0$

$r_{AD}/k_A \approx 0$

$C_{AS} = k_A\, C_A\, C_V$

$C_{AS} = k_A\, C_A\, C_V$

$$\begin{aligned} C_t &= C_V + C_{A\bullet S} \\ &= C_V + K_A C_A C_V \\ &= C_V(1 + K_A C_A) \end{aligned}$$

$$C_V = \frac{C_t}{1 + K_A C_A}$$

$C_{AS} = k_A \, C_A \, C_V$ **and** $C_V = \dfrac{C_t}{1 + K_A C_A}$

$$C_{A\cdot S} = \frac{K_A C_A}{1+K_A C_A} C_t$$

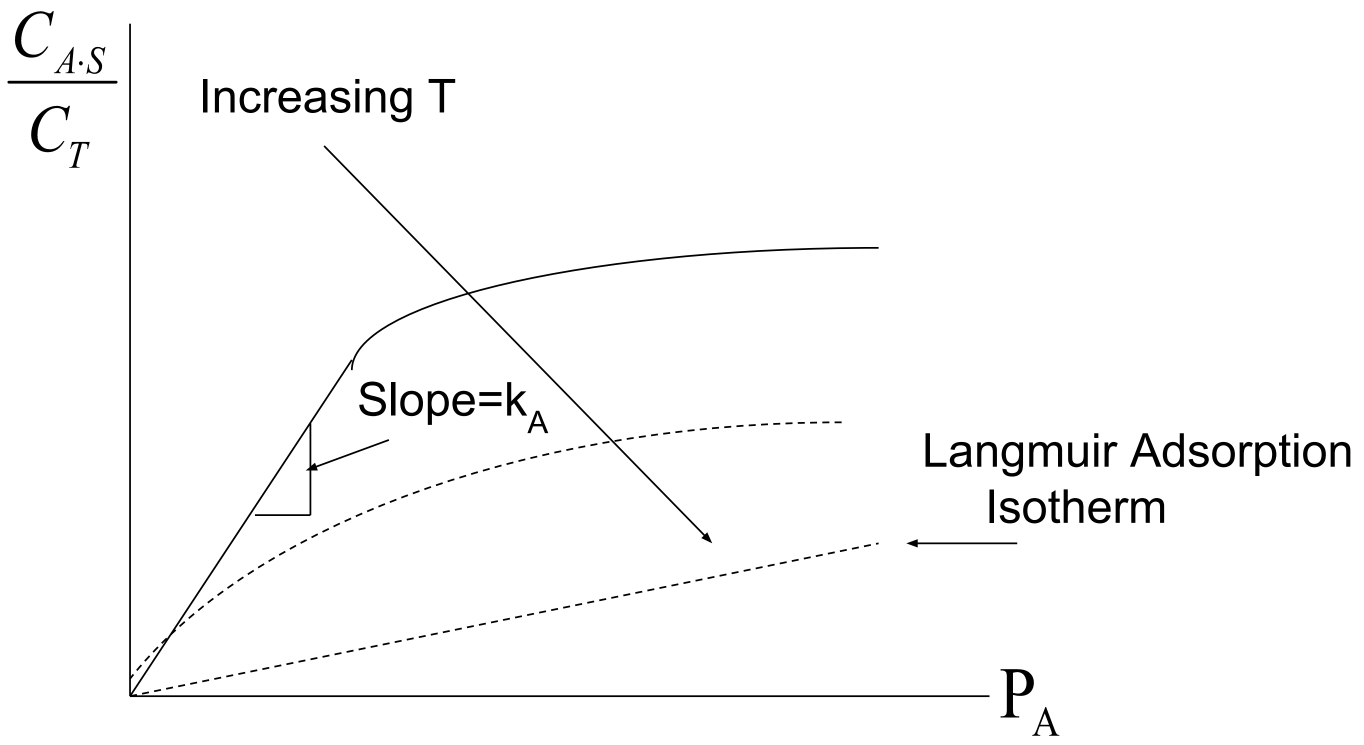
$$\frac{C_{A\cdot S}}{C_t} = \frac{K_A C_A}{1 + K_A C_A}$$

This is Langmuir Adsorption Isotherm

Langmuir Adsorption Isotherm

Langmuir Adsorption Isotherm also can be written in term of partial or total pressure as

$$\frac{C_{A \bullet S}}{C_t} = \frac{K_A P_A}{1 + K_A P_A}$$



Types of adsorption

1. Non-dissociative

The adsorbed molecules will be adsorbed as is with out being break down to fragments.

The adsorption of carbon monoxide molecules will be considered. Because the carbon monoxide does not react further after being adsorbed, we need only to consider the adsorption process as:

Molecular Adsorption $$CO + S \rightleftarrows CO \cdot S$$

Rate of attachment $= k_A P_{CO} C_v$ Rate of detachment $= k_{-A} C_{CO \cdot S}$

$$r_{AD} = k_A P_{CO} C_v - k_{-A} C_{CO \cdot S}$$

The ratio $K_A = k_A / k_{-A}$ is the *adsorption equilibrium constant*

$$r_{AD} = k_A \left(P_{CO} C_v - \frac{C_{CO \cdot S}}{K_A} \right)$$

$$C_t = C_v + C_{CO \cdot S}$$

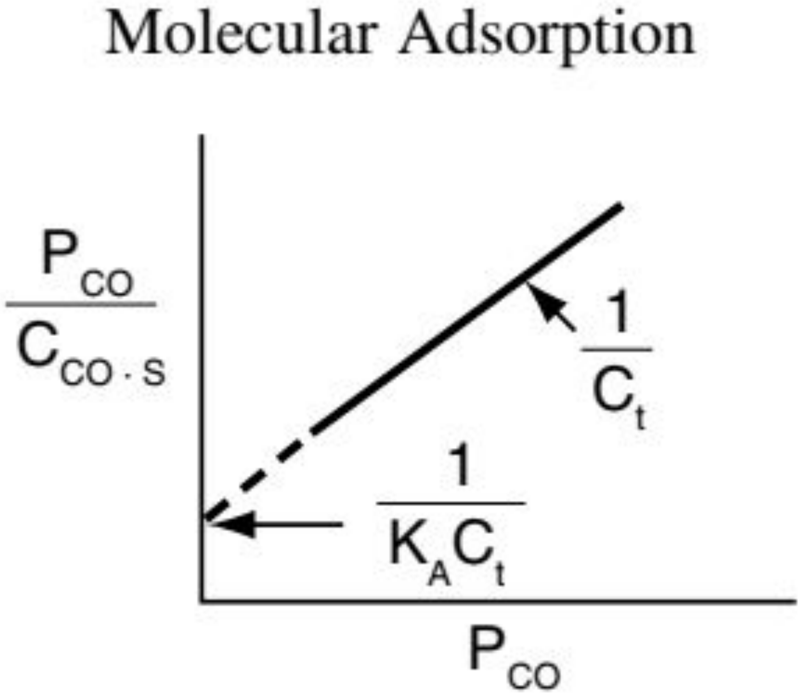
$$C_{CO\cdot S} = K_A C_v P_{CO} = K_A P_{CO}(C_t - C_{CO\cdot S})$$

$$C_{CO\cdot S} = \frac{K_A P_{CO} C_t}{1 + K_A P_{CO}}$$

The molecular adsorption isotherm, equation above may be arranged in the form

$$\frac{P_{CO}}{C_{CO\cdot S}} = \frac{1}{K_A C_t} + \frac{P_{CO}}{C_t}$$

A plot of $P_{CO}/C_{CO\,S}$ as a function of P_{CO} will determine if the data conform to molecular adsorption, i.e., a Langmuir single-site isotherm.



Types of adsorption

1. Dissociative

The adsorbed molecules will be break down to fragments. For example CO instead of being adsorbed as on CO per one active site, it is break down to C and O and adsorbed in two vacant sites as

$$CO + 2S \rightleftarrows C\cdot S + O\cdot S$$

$$r_{AD} = k_A P_{CO} C_v^2 - k_{-A} C_{O\cdot S} C_{C\cdot S}$$

$$r_{AD} = k_A \left(P_{CO} C_v^2 - \frac{C_{C\cdot S} C_{O\cdot S}}{K_A} \right)$$

$$K_A = \frac{k_A}{k_{-A}}$$

At equilibrium, $r_{AD} \equiv 0$

$$k_A P_{CO} C_v^2 = k_{-A} C_{C\cdot S} C_{O\cdot S}$$

For $C_{C \cdot S} = C_{O \cdot S}$ $\qquad$ $(K_A P_{CO})^{1/2} C_v = C_{O \cdot S}$

$$C_t = C_v + C_{O \cdot S} + C_{C \cdot S}$$

$$= C_v + (K_{CO} P_{CO})^{1/2} C_v + (K_{CO} P_{CO})^{1/2} C_v = C_v (1 + 2(K_{CO} P_{CO})^{1/2})$$

$$C_v = C_t / (1 + 2(K_{CO} P_{CO})^{1/2})$$

Dissociative Adsorption

$$C_{O \cdot S} = \frac{(K_A P_{CO})^{1/2} C_t}{1 + 2(K_A P_{CO})^{1/2}}$$

$$\frac{(P_{CO})^{1/2}}{C_{O \cdot S}} = \frac{1}{C_t (K_A)^{1/2}} + \frac{2(P_{CO})^{1/2}}{C_t}$$