Catalysis & Catalytic Reactions

catalyst is a substance that affects the rate of Rxn by promoting different molecular paths (mechanisms) for Rxn, where this material does not change during Rxn.

Example : Methyl tert-butyl ether (MTBE) is produced by Rxn of i-butylene with methanol according

$$m\ i\text{-}C_4H_8 + n\,CH_3OH \longrightarrow MTBE$$

if this Rxn takes place on dodeca tungsto-salicic acid ($H_4SiW_{12}O_{40}$), HSiW then the rate of Rxn is

$$-r = \frac{0.109\,K_3 K_1}{K_2^{n-1} K_4} P_{C_4H_8} P_{CH_3OH}^{1-n} P_{CH_3OH}^{1.76}$$

$$= \beta P_{C_4H_8} P_{CH_3OH}^{2.76-n}$$

However, if this Rxn takes place on the surface of MFI type zeolite, then the rate is

$$-r = \frac{K_S K_A^a K_B^b}{K_{eq}} \frac{C_{C_4H_8}^a C_{CH_3OH}^b - C_{MTBE}^c}{(1+K_A C_{C_4H_8} + K_B C_{CH_3OH} + K_c C_{MTBE})^{a+b}}$$

Therefore, different catalyst yield different Rxn rates and different yield & selectivity of the product.

Types of catalysis

1. solid catalysts (hetrogeneous)
2. Liquid (homogeneous)

it is supported such as transition metals on the the surface of support, non supported, porous or molecular sieve.

characteristics of the catalysts

1. unchange during the Rxn
2. has a large surface area w/ a specific active site
3. Rxn rate ↑ by decreasing the activation Energy
4. catalyst could change the selectivity of the Rxn

summary of catalytic Rxn steps

1. Transport of Rxnts from bulk to external surface
2. Diffusion of Rxnts from external surface into internal surface
3. Adsorption of Rxnts onto the internal surface
4. chemical Rxn on internal surface
5. Desorption of products from internal surface
6. Diffusion of product from internal to external surface
7. Transport of products into bulk.

special cases

A. Non porous catalyst (neglect 2 & 6)
B. Non porous + very quick adsorption & desorption (neglect 2, 6, 3 & 5)
C. Non porous + very rapid transport from / into bulk (neglect 2, 6, 1, 7)

So what is Adsorption ?

it is a binding of molecules to specific size on a surface by either physical or chemical mean.

Based on the binding type onto the surface of catalyst, adsorption can be classified as

1. undissociated (can not dissociate into fragments, where the adsorbent remain intact)

Example

$$A_2 + X \underset{k_d}{\overset{k_a}{\rightleftarrows}} X - A_2$$

here O_2 will not break to 2 O or

$$X \quad O_2 + X \not\rightleftarrows X-O + X-O \quad X$$

$$r = k_a C_A C_v - k_d C_A^*$$

C_A : conc of A in gaseous phase or Liquid phase
C_v : " " the vacant adsorption site
C_A^* : conc. of the adsorbed A

@ equilibrium $r_{eq} = 0$, $k_a C_A C_v = k_d C_A^*$

or $K_{eq} = \frac{k_a}{k_d}$

∴ $C_A^* = K_{eq} C_A C_v$

But $C_v = C_T - C_A^*$; C_T : total surface area

∴ $C_A^* = K_{eq} C_A (C_T - C_A^*)$

$C_A^* (1 + K_{eq} C_A) = K_{eq} C_A C_T$

$$\frac{C_A^*}{C_T} = \frac{K_{eq} C_A}{1 + K_{eq} C_A} = \frac{k_a C_A}{k_d + k_a C_A}$$

IN General $\boxed{C_A^* = q = \frac{K_{eq} C_T C_A}{1 + K_{eq} C_A}}$, $C_T = C_e$ monolaye

Langmuir model

what was the assumption

1. C_T is monolayer surface (no multi layer)
2. All surfaces have homogeneous energy (constant)
3. physical adsorption

How about if the surface has hetrogeneous energy?
use emirical formula (Fruendlich model)

$q = K C_A^{1/n}$ where $K \propto RTnb\, e^{\Delta H / RT}$

Shawabkeh & Tuhunji proposed a model for chemical adsorption @ the surface of catalyst

$$q = q_s (1 - \alpha C_A^{\beta})$$

$$\alpha = \frac{K \Delta t}{m_s q_s}$$