

# Surface reaction

Heterogeneous catalytic reaction mechanisms

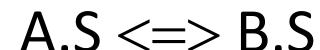
✓ Adsorption of reactant is necessary for a reaction to happen on a solid catalyst.  
Once a reactant is adsorbed on a solid catalytic surface, it can react in a number of ways to form product(s).

Consider a chemical reaction  $A \rightleftharpoons B$ ,

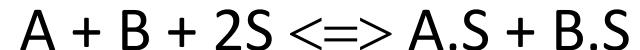
The adsorption of species A onto a solid catalyst surface is shown as,



Then reaction step on the solid catalyst surface can be written as,

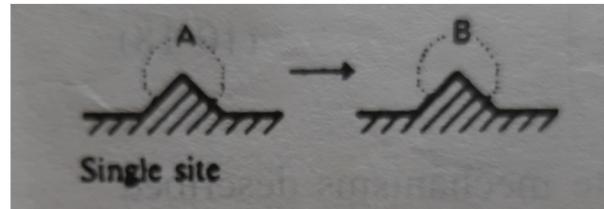


If the reaction is  $A + B \rightleftharpoons C + D$ , then adsorption step is



## ➤Single site mechanism

The surface reaction may be a single site mechanism where the single site on which the reactant is adsorbed is involved in the reaction.



Considering the reaction step is elementary, the rate law can be written as,

$$r_s = k_s C_{A.S} - k_{-s} C_{B.S}$$

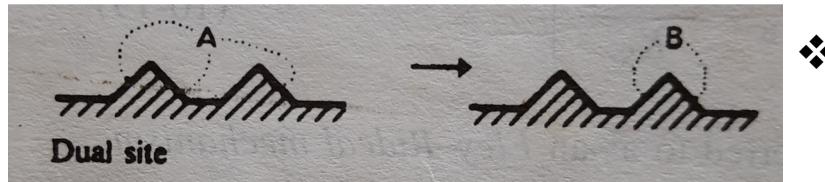
$$r_s = k_s \left( C_{A.S} - \frac{C_{B.S}}{K_s} \right)$$

Where,  $K_s$ = equilibrium constant for the reaction=  $\frac{k_s}{k_{-s}}$

$k_s$  and  $k_{-s}$  are the forward and reverse reaction rate constants respectively.

## ➤ Dual site mechanism

In this mechanism, the adsorbed molecule in one site may interact with an adjacent vacant or occupied site to form product.

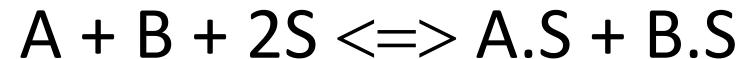


❖ In this type, the reaction step is  
 $A.S + S \rightleftharpoons B.S + S$

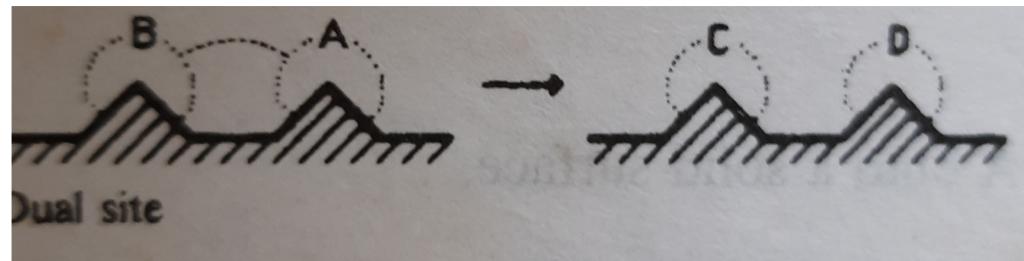
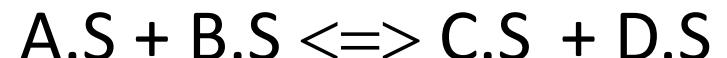
## Rate of reaction

$$\begin{aligned} r_s &= k_s C_{A.S} C_v - k_{-s} C_{B.S} C_v \\ &= k_s (C_{A.S} C_v - \frac{C_{B.S} C_v}{K_s}) \end{aligned}$$

For the reaction  $A + B \rightleftharpoons C + D$ , the adsorption step is

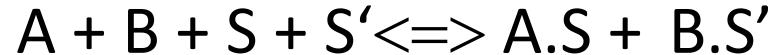


Here the reaction following the dual site mechanism is



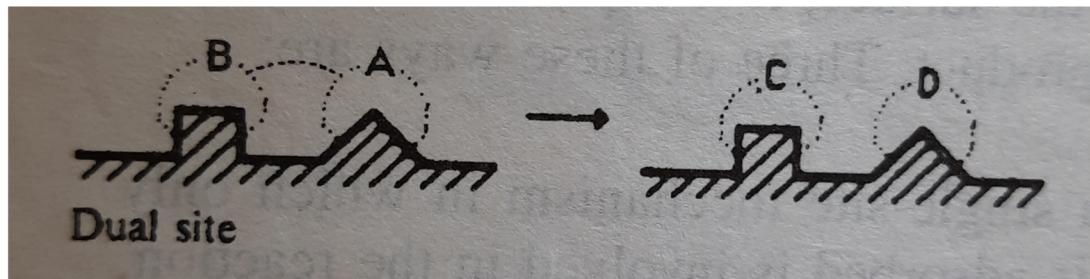
$$\begin{aligned} \text{The rate equation is, } r_s &= k_s C_{A.S} C_{B.S} - k_{-s} C_{C.S} C_{D.S} \\ &= k_s (C_{A.S} C_{B.S} - \frac{C_{C.S} C_{D.S}}{K_s}) \end{aligned}$$

For the same reaction, another dual site mechanism can be proposed, where two reactants are adsorbed on two different types of active sites,



And the reaction step is  $A.S + B.S' \rightleftharpoons C.S + D.S'$

The mechanism is

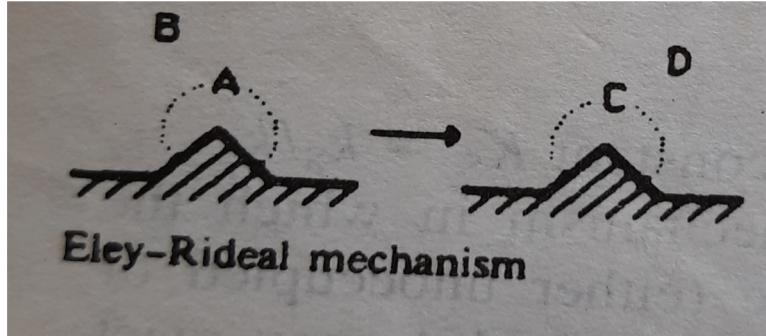


Rate of the reaction is

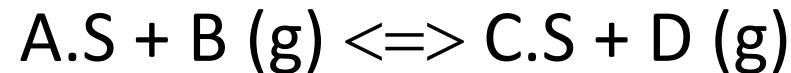
$$\begin{aligned} r_s &= k_s C_{A.S} C_{B.S'} - k_{-s} C_{C.S} C_{D.S'} \\ &= k_s (C_{A.S} C_{B.S'} - \frac{C_{C.S} C_{D.S'}}{K_s}) \end{aligned}$$

The kinetics of reaction where all the reactants and products are adsorbed on the active sites either by single or dual site mechanism is named as Langmuir-Hinshelwood kinetics.

Another single/dual site mechanism is that where one of the reactants is in gas phase and reacts with the adsorbed reactant on the catalyst surface.



The reaction is



The rate of the reaction is

$$r_s = k_s (C_{A.S} \cdot P_B - \frac{c_{C.S} P_D}{K_S})$$

The rate kinetics is called Eley-Rideal kinetics.

# Desorption

After the reaction, the product(s) formed on the adsorbed site is desorbed from the catalyst surface.

The desorption equation is,  $C.S \rightleftharpoons C + S$ ,  $C$  is a product

Desorption rate equation is,  $r_D = k_D(C_{C.S} - \frac{C_v P_C}{K_{D_C}})$

Where,  $K_{D_C}$  is the desorption equilibrium constant of  $C$ .

Note that, desorption step of  $C$  is just reverse of the adsorption step of  $C$ , therefore,  
rate of desorption  $r_D = -r_{AD}$  rate of adsorption

And, desorption equilibrium constant ( $K_{D_C}$ ) is the reciprocal of adsorption equilibrium constant ( $K_C$ ),

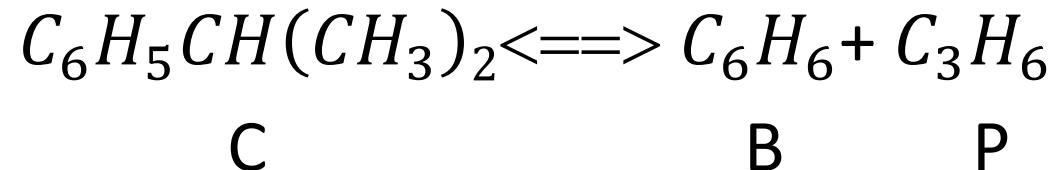
$$K_{D_C} = \frac{1}{K_C}$$

# Synthesising a Rate law, Mechanism and Rate limiting Step:

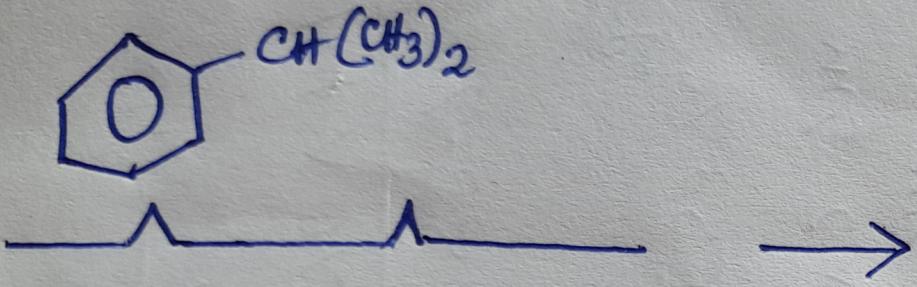
In this section, we will not consider any mass transfer step involved in the solid catalytic reaction.

Only three steps, adsorption, surface reaction and desorption are considered.

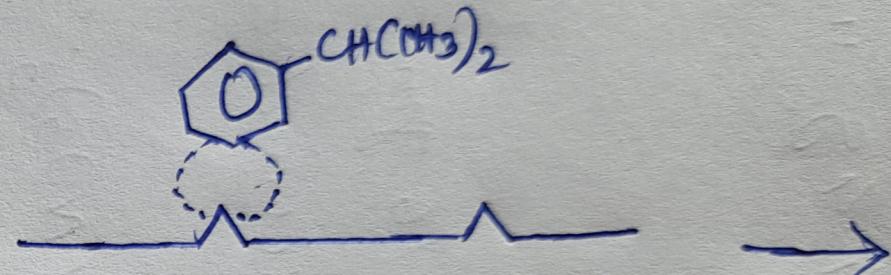
Taking an example of the reaction, Cumene disproportionation reaction to form Benzene and propylene.



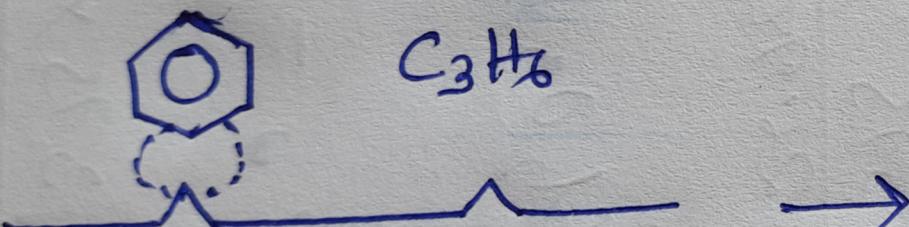
# Sequence of steps:



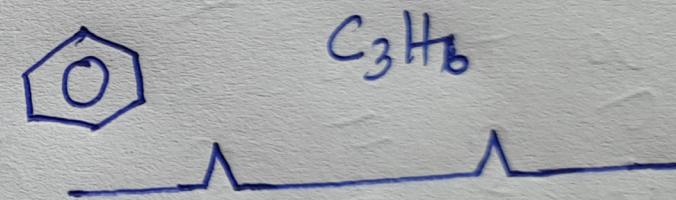
Cumene in gas phase



Adsorption of Cumene  
on active site



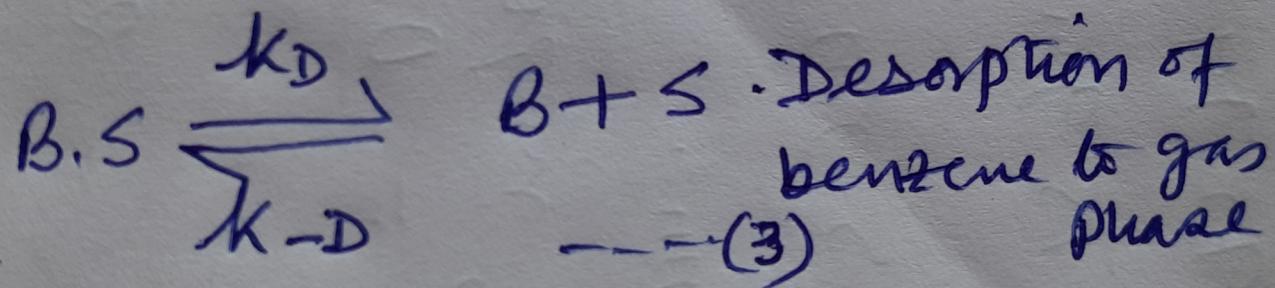
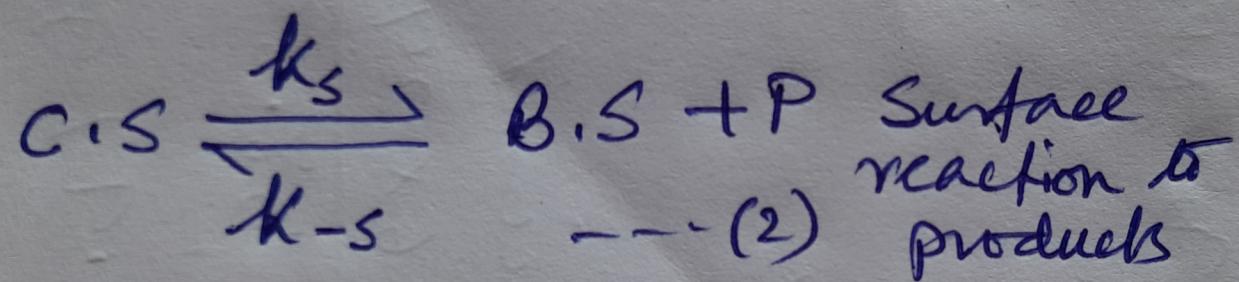
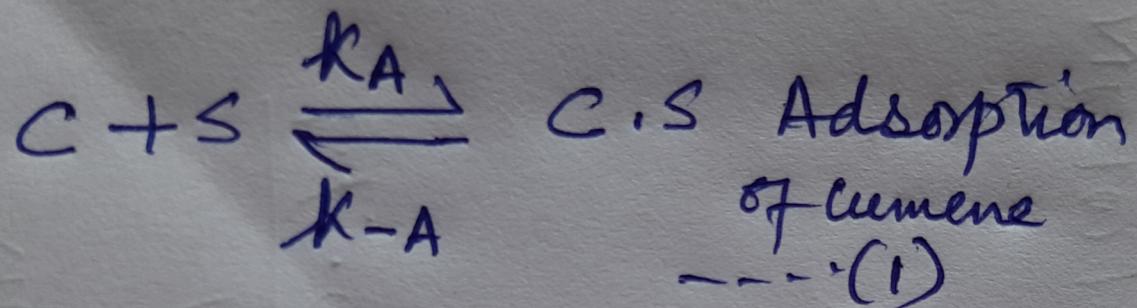
Surface reaction to  
products



Desorption of Benzene

## Contd...

The reaction can be written as,



All the steps are treated as elementary steps.

For gas reactants the concentrations will be expressed in partial pressures

So, the rate expression for step (1), i.e adsorption is,

$$\begin{aligned}r_{AD} &= k_A P_C C_v - k_{-A} C_{C.S} \\&= k_A \left( P_C C_v - \frac{C_{C.S}}{K_{AD}} \right),\end{aligned}$$

where  $K_{AD}$  = equilibrium constant for adsorption of Cumene

Units:  $r_{AD}$  = mol.(g of catalyst) $^{-1}$ .s $^{-1}$

$C_{C.S}$  = (mol of cumene adsorbed) .(g of catalyst) $^{-1}$

$k_A$  = (Kpa.s) $^{-1}$  or (atm.h) $^{-1}$

$k_{-A}$  = h $^{-1}$  or s $^{-1}$

$$K_{AD} = \frac{k_A}{k_{-A}} = \frac{(atm.h)^{-1}}{h^{-1}} = atm^{-1}$$

The rate expression for the surface reaction (2),

$$r_s = k_s C_{C.S} - k_{-s} C_{B.S} P_p = k_s \left( C_{C.S} - \frac{C_{B.S} P_p}{K_s} \right)$$

Where,  $K_s = \frac{k_s}{k_{-s}}$  = Equilibrium constant for surface reaction

The rate expression for desorption (3),

$$r_D = k_D C_{B.S} - k_{-D} P_B C_v = k_D \left( C_{B.S} - \frac{P_B C_v}{K_{D_B}} \right)$$

$K_{D_B}$  is the desorption equilibrium constant of B.

Propylene is not adsorbed on the surface, so,  $C_{P.S}=0$

As, the desorption  $B.S \rightleftharpoons B + S$  is just opposite to the adsorption equation of B, it can be written, for benzene,

$$K_B = \frac{1}{K_{D_B}}$$

the adsorption equilibrium constant of B is the reciprocal of desorption equilibrium constant of B.

Hence, the rate equation for desorption can be written as,

$$r_D = k_D (C_{B,S} - K_B P_B C_v)$$

At steady state, rates of all steps are equal, as there is no accumulation of reacting species on the surface.

Therefore, rate of the reaction  $-r_C = r_{AD} = r_D = r_s$