

Chapter 2

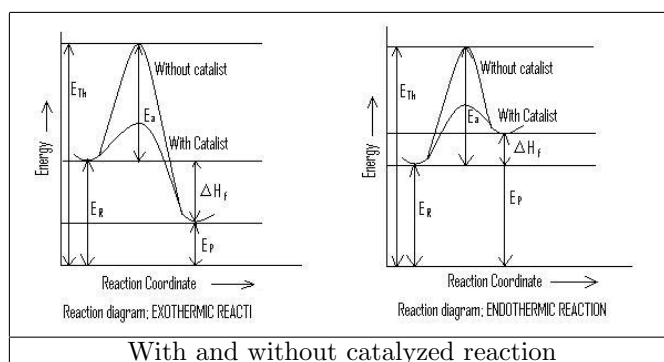
Chemical Kinetics Lecture/Lesson Plan -4

Chemical Kinetics

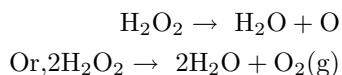
2.1 Catalysis

Some substrate can change the rate of a chemical reaction but they remain unchanged after the reaction is known as catalyst and the process is known as catalysis. Catalyst take part in chemical reaction but their chemical composition remain unchanged after the reaction, sometimes their physical state may be changed. If a catalyst enhance the rate of a reaction, is known as positive catalyst and if it retards the rate then it is known as negative catalyst.

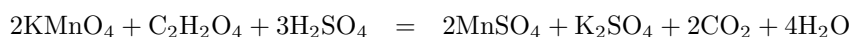
Positive catalyst: Potassium chlorate(KClO_3) liberates oxygen on thermal decomposition but the reaction rate is slow but in presence of manganese dioxide (MnO_2) the rate enhances and hence manganese dioxide acts as a positive catalyst in this particular reaction.



Negative catalyst: Decomposition of hydrogen peroxide (H_2O_2) is slowed down in presence of platinum (Pt) or concentrated sulphuric acid and hence platinum or concentrated sulphuric acid acts as negative catalyst here.



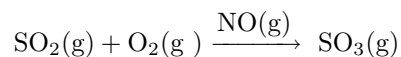
Auto catalyst: If the products of a chemical reaction act as catalyst and catalyze the reaction, the reaction is called an auto-catalyzed reaction and the produced compound is called an auto-catalyst.



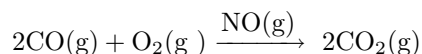
Homogeneous catalyst: If in a chemical reaction reactants and catalyst are present in the same phase, then it is a homogeneous catalyst.

Oxidation of sulphur dioxide to sulphur trioxide is catalyzed by nitric oxide. Both the reactant SO_2 and O_2 are gases and the catalyst nitric oxide (NO) is a gas and all are in the gaseous phase. This is homogeneous catalysis.

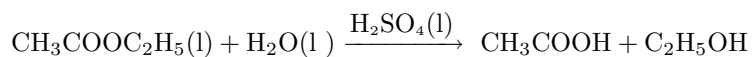
Gaseous phase; Catalyzed by $\text{NO}(\text{g})$



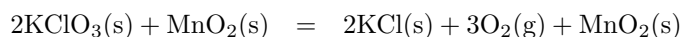
Gaseous phase; Catalyzed by $\text{NO}(\text{g})$



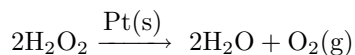
Liquid phase; Catalyzed by $\text{H}_2\text{SO}_4(\text{l})$



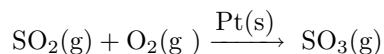
Heterogeneous catalyst: If in a chemical reaction reactants and catalyst are present in different phases or states, then it will be called heterogeneous catalysis.



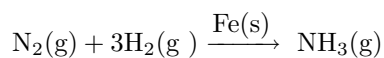
Liquid phase; Catalyzed by $\text{Pt}(\text{s})$



Gaseous phase; Catalyzed by $\text{Pt}(\text{s})$



Gaseous phase; Catalyzed by $\text{Fe}(\text{s})$



2.1.1 Theory of catalysis

Let us consider a uncatalyzed reaction, Reactant \rightarrow Product.

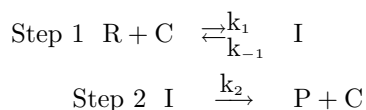
Let us consider it is a unimolecular reaction and this reaction will follow a reaction co-ordinate diagram with a transition state and corresponding activation energy. The rate of a reaction is slow because of high activation energy and reaction rate is fast because of low activation energy. Catalyst basically make a intermediate complex with the reactant and altered the energy of the transition state. It by complexation with catalyst, the activation energy comes down then the reaction rate will increase (the catalyst will be called positive catalyst) and if the energy of activation energy increases reaction rate will decrease (the catalyst will be called negative catalyst). The catalysis reaction is proceeds through two different way.

1) Intermediate complex formation theory

2) Adsorption theory

1) Intermediate complex formation theory: According to this theory the reactant and catalyst first react among themselves to form an unstable intermediate which then react with other reactant converted to product and catalyst in its original form. Kinetics of homogeneous catalyst:

A general reaction in presence of a catalyst can be written as



where R is reactant, C is catalyst, I is intermediate complex and P is product

The rate of formation of product = $k_2 \cdot [I]$ Now intermediate forms in forward reaction of step 1 and hence the rate of intermediate formation will be = $k_1 \cdot [R][C]$.

Intermediate decomposition happens in backward reaction of step 1 and in step 2 and hence the rate of decomposition = $k_{-1}[I] + k_2[I]$

At steady state

$$\begin{aligned} k_1 \cdot [R] \cdot [C] &= k_{-1}[I] + k_2[I] \\ k_1 \cdot [R] \cdot [C] &= (k_{-1} + k_2)[I] \\ [I] &= \frac{k_1 \cdot [R] \cdot [C]}{(k_{-1} + k_2)} \end{aligned}$$

Putting this value in rate of product formation we can get, rate

$$\begin{aligned} &= k_2 \cdot \frac{k_1 \cdot [R][C]}{(k_{-1} + k_2)} \\ \text{rate} &= k' [R][C] \\ \text{where } k' &= \frac{k_1 k_2}{(k_{-1} + k_2)} \end{aligned}$$

Here k' is the observed rate constant and which is very high. This high observed rate constant indicates that catalyst must be involved in the reaction.

2) Adsorption theory: Adsorption is sticking of solid, liquid or gas on the surface of solid. As the surface of any solid is not a plane surface actually there are some cracks, corners, and bottle pores present, any material is adsorbed on the surface either by Van-der-Waals' force of attraction or by chemical reaction.

Adsorbate: Substance which adsorbed on the surface of adsorbent is called adsorbate.

Adsorbent: The substance on the surface of which adsorbate is adsorbed is called adsorbent.

Adsorption is mainly two types-

- 1) Physical adsorption(Physisorption)
- 2) Chemical adsorption(Chemisorption)

(1) Physical adsorption(Physisorption): A reversible, multilayered adsorption where adsorbate is adsorbed on the surface of adsorbent by weak Van-der-Waals force of attraction and the heat of adsorption(20 kJ/mole) is very low is called Physical adsorption.

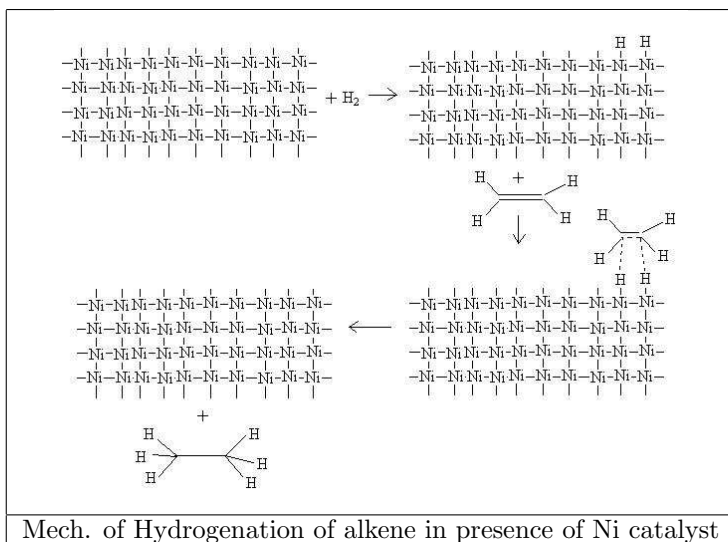
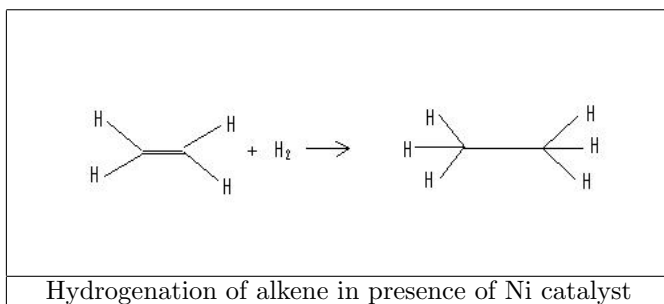
Example - Chalk(adsorbent) adsorbed ink(adsorbate)

(2) Chemical adsorption(Chemisorption): An irreversible, monolayer adsorption where adsorbate is adsorbed on the surface of adsorbent by means of chemical bond and the heat of adsorption is very high(200 kJ/mole or more) is called Physical adsorption.

Example - Hydrogenation of alkene in presence of Ni catalyst

Here, hydrogenation of alkene in presence of Ni catalyst takes place in two steps-

In the first step gaseous alkene and hydrogen gas is adsorbed in the surface of Ni at hot condition as there is some unsatisfied valencies like cracks, corner and pores present on the surface of Ni. Their high concentration in the pores lead to increase the frequency of collision as well as the rate of reaction. After chemical reaction the saturated hydrocarbon leaves the surface of the catalyst.



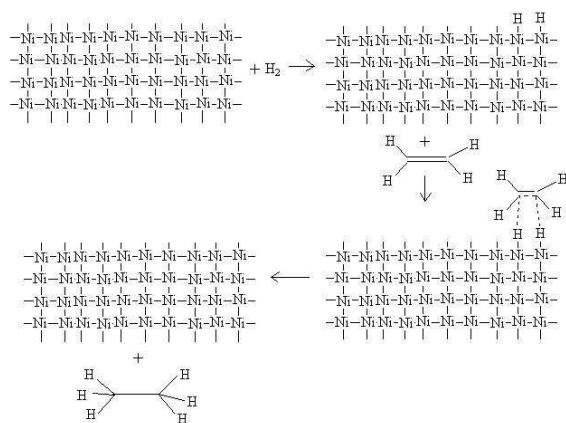


Figure 2.1: Mech. of Hydrogenation of alkene in presence of Ni Catalyst