T.Y.B.Sc. Chemistry

Paper –II Inorganic Chemistry

Sem- IV

Chapter -4. Homogeneous Catalysis

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CHAPTER 4. HOMOGENEOUS CATALYSIS

Definition of catalysis:

The phenomenon of changing the rate of chemical reaction by the action of substances that do not alter their own chemical composition during this reaction is called catalysis.

Definition of Homogeneous catalysis:

- Homogeneous catalysis are catalytic reactions in which the catalyst is in the same phase as the reactants. It is generally a catalysis in a solution by a soluble catalyst.
- Proton is the main universal homogeneous catalyst. This is because water is the most common solvent.

Types of homogeneous catalysis:

Type- I

In this type of catalysis, Reactants as well as catalyst are in gaseous state.

- e.g. Oxides of Nitrogen – NO, NO_2 acts as a catalyst for the oxidation of SO_2 to SO_3
- In this process SO_2, O_2 and the catalyst NO, NO_2 all are in the gaseous state.

Type- II

In this type of catalysis, Reactants as well as catalyst are in liquid state.

e.g. Sulphuric acid is used as a catalyst for the formation of diethyl ether from ethyl alcohol.

Type- III

In this type of catalysis, Reactants as well as catalyst are in solution state.

e.g. Redox reaction, Iodide ions are oxidized by persulphate ions and Fe(II) or Fe(III) ions in solution acts as catalyst.

Type- IV

In this type of catalysis, acids or bases act as catalyst. According to Bronsted, an acid is a molecule that can give up a proton and base is a molecule that takes up a proton.

Properties of Homogeneous catalysis:

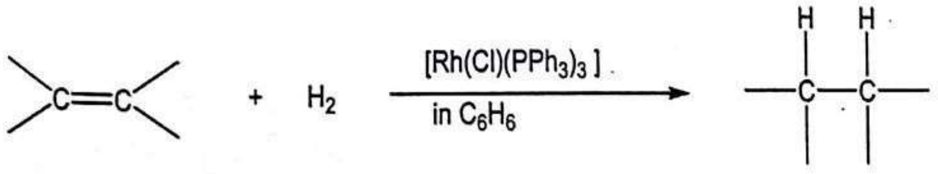
1) They are consumed during a chemical reaction
2) They increase the energy of the reactants.
3) They offer high degree of interaction between catalyst and reactant molecule.
4) They lower the energy of activation for the reaction.
5) They increase the rate of reaction without increase of temperature.
6) They shift the equilibrium to favour the formation of products.

Catalytic Reactions-

Wilkinson's Catalyst

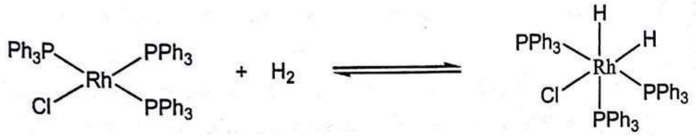
- Wilkinson's catalyst is the familiar name for Chlorotris(tri-phenylphosphine) rhodium (I) -RhCl(PPh3)3
- This reaction has given name after the chemist and Nobel Laureate Sir Geoffrey Wilkinson who popularised its use.
- The compound RhCl(PPh3)3 is a square planar, 16 -electron complex. It is obtained byreaction of rhodium (III) chloride with excess of tri-phenylphosphine.

Hydrogenation of alkene is a reaction of major industrial importance being used in petrochemical and in the pharmaceutical industries where the preparation of drugs often involves the hydrogenation of specific double bonds. The effective homogenous catalysts for this process is [Rh(Cl)(PPh3)3] chlorotris (triphenylphosphine)rhodium(I). This catalyst is known as Wilkinson's catalyst. The effective catalyst for hydrogenation of alkene is [Rh(Cl)(PPh3)3]. The net reaction is

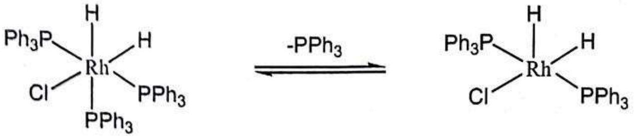


Mechanism of hydrogenation of alkene using Wilkinson's catalyst:

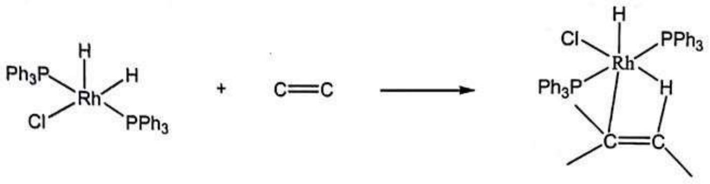
1) The first step involves the oxidative addition of H2 to the 16 electron complex[Rh(Cl)(PPh3)3] to form the 18 electron dihydrido complex.



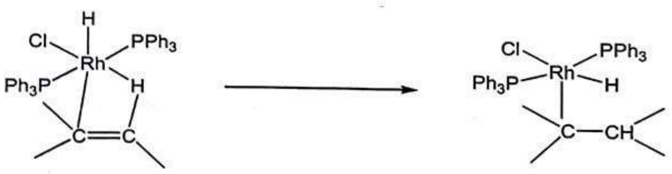
2) In the second step, dissociation of phosphine ligand results in the formation of thecoordinately unsaturated complex.

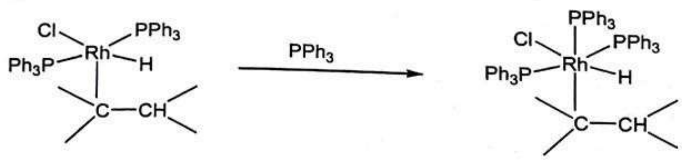


3) In this step, the coordination of alkene to the potential vacant site, on the 5 coordinate dihydrido complex to six coordinate species.

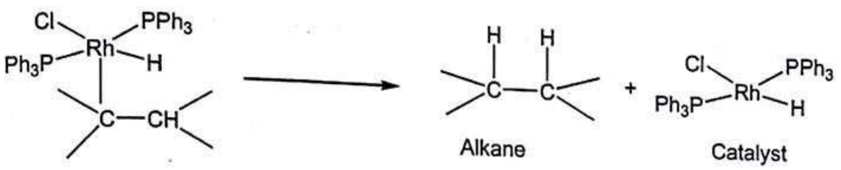


4) Step 4 involves the insertion of olefins into metal hydrogen bond to give metal alkylderivatives.



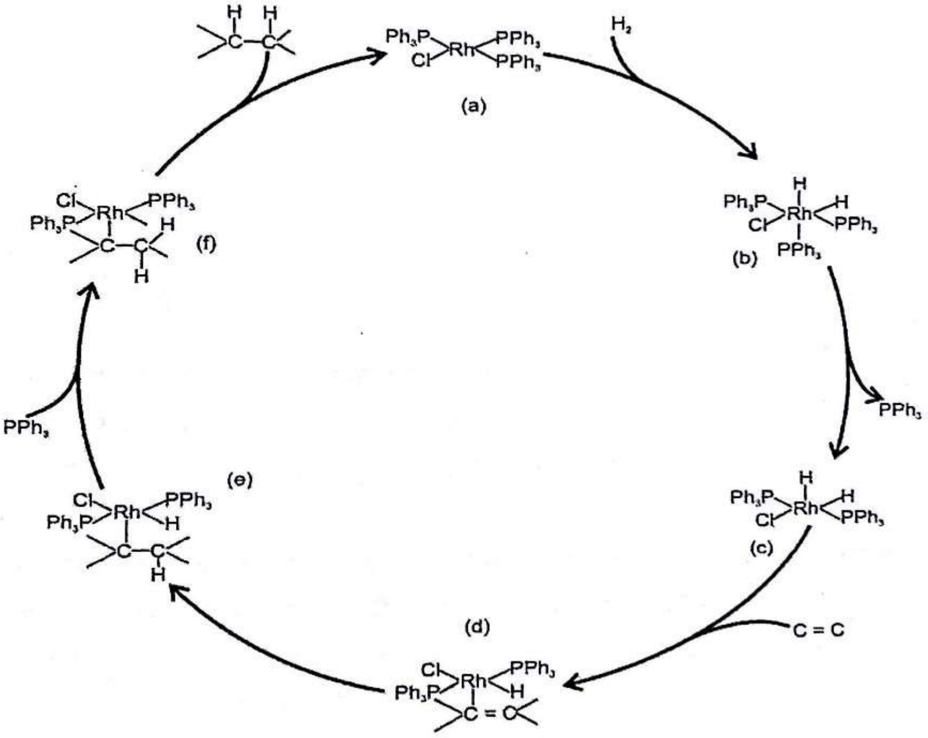


5) Step 5 is the reductive elimination step, the metal is reduced from +III to +I state and coordination number of the metal is decreased from +6 to +4. In this step the product alkane is formed. The role of the catalyst, namely the transfer of hydrogen fragments to the alkene with the formation of alkane.



The catalyst used in this process is being soluble, it can’t be removed easily at the end of the reaction by simple filtration. Due to this imperfect separation of alkane and rhodium complex at the end of the hydrogenation, rhodium is lost.

Catalytic cycle for hydrogenation of Alkenes by Wilkinson’s catalyst

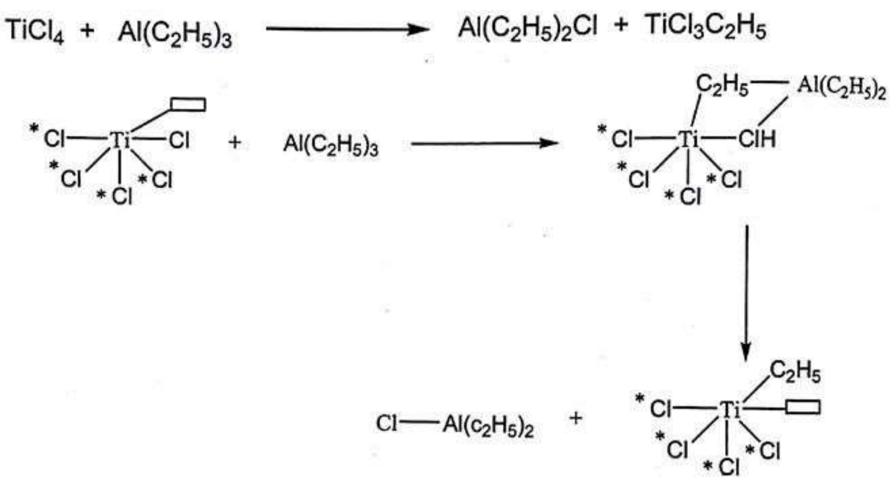


Ziegler Natta catalysis:

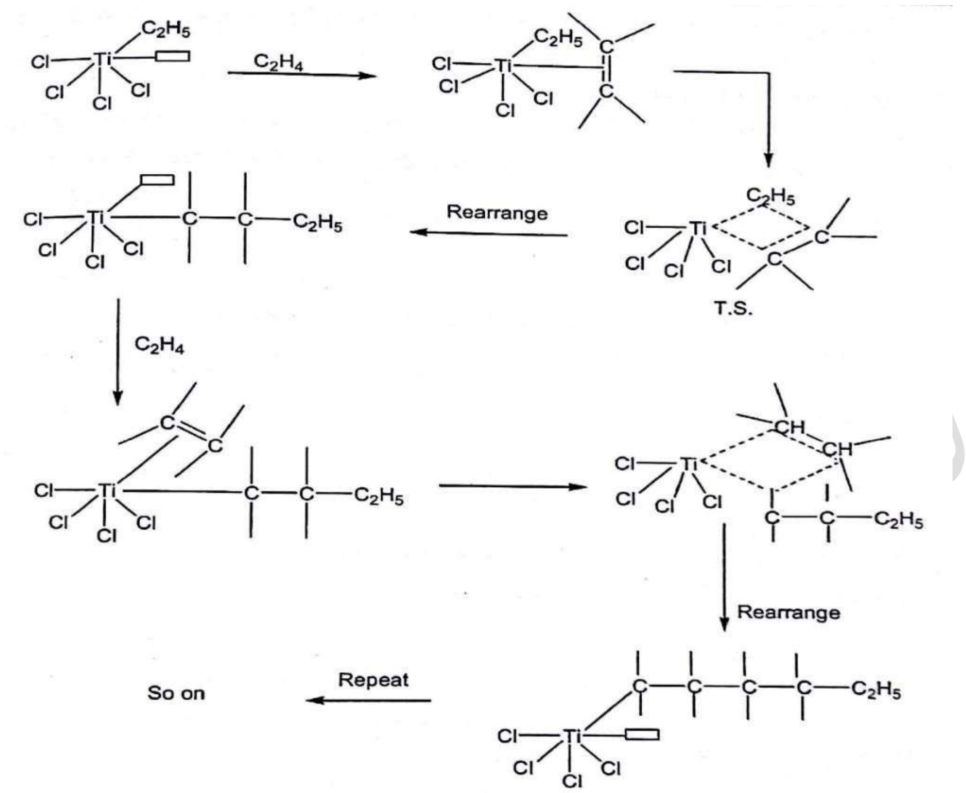
An efficient and stereospecific catalytic polymerization method was developed by K. Ziegler and G. Natta. In this method, a catalyst based on titanium tetrachloride and diethyl aluminium chloride as co-catalyst can polymerize ethylene to high density ethylene (HDPE) at moderate to low temperature and standard pressure.

Aluminium alkyls act as the electron acceptor and the titanium halides acts as electron donor. Their combination forms coordination complexes. The complex is insoluble in the solvent and is hence heterogeneous in nature. Both Ziegler and Natta were jointly awarded Nobel Prize for chemistry in 1963.

In this product, the vacancy in the coordination shell of the titanium atom is still occur but in another position. This vacant site is potentially capable of coordinating to an alkene. The alkene coordination to the titanium atom as a π donor in its vacant coordination sites. When an alkene and alkyl group are bound to adjacent sites on a metal atom, they react to give product.

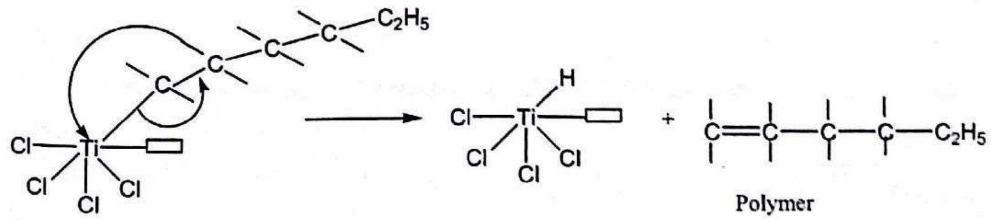


The alkyl group shifts to one carbon of the alkene double bond, while the other carbon develops σ bond to the titanium atom.



When the rearrangement of the alkyl on to the alkene carbon is over, a new coordinationsite is opened on the titanium atom cis to the new longer alkyl group. This regeneration of thevacant site enables the process to be repeats to yield the polymer.

Hydride ion shifts to the metal ion by termination, which would occur by a reverse insertion reaction.



Currently Ziegler Natta catalysts most often applied are heterogeneous. They are of titanium tetrachloride supported on magnesium chloride with diethyl aluminium as co catalyst.

Monsanto Acetic acid synthesis

The Monsanto Company of USA used this method to produce acetic acid by carbonylation of methanol in the presence of catalyst rhodium.

$$CH_3OH + CO \xrightarrow[\text{HI}]{\text{Rhodium catalyst}} CH_3COOH$$

Mechanism:

1) RhX3 Rhodium trihalides is converted to a complex [RhI2 (CO)2] in presence of CO and I

$$RhX_3 \xrightarrow[\text{CO}]{I^-} [RhI_2(CO)_2]^-$$

2) Methanol reacts with HI to produce iodomethane

$$CH_3OH + HI \longrightarrow CH_3I + H_2O$$

3) In this step, addition of iodomethane takes place to the $[Rh\ I_2\ (CO)_2]^-$ Complex forming$[CH_3\ Rh\ I_3\ (CO)_2]^-$

$$[Rh\ I_2\ (CO)_2]^- + CH_3I \longrightarrow [CH_3\ Rh\ I_3\ (CO)_2]^-$$

18 e- complex

4) Rearrangement giving acyl complex

$$[CH_3\ Rh\ I_3\ (CO)_2]^- \leftrightarrow [CH_3CO\ Rh\ I_3(CO)]^-$$

16 e- complex

5) In the next step, the addition of CO takes place in acyl complex

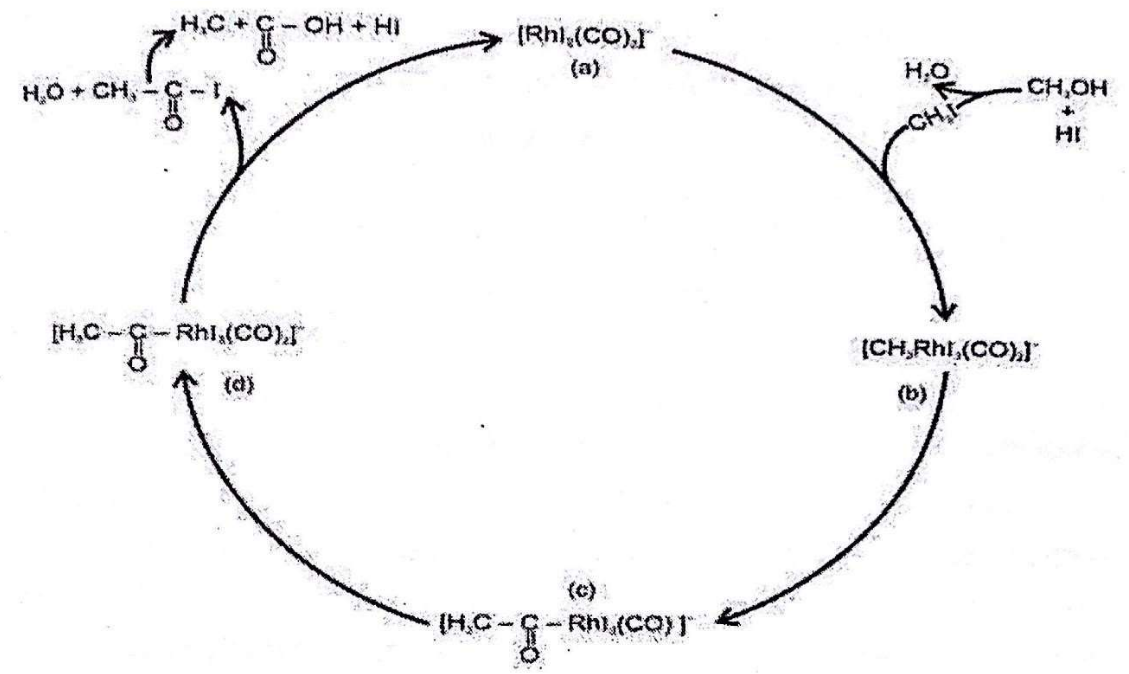
$$[CH_3CO\ Rh\ I_3(CO)]^- + CO \longrightarrow [CH_3CO\ Rh\ I_3(CO)_2]^-$$

6) This complex undergoes reductive elimination of acyl iodide to regenerate $[Rh\ I_2\ (CO)_2]^-$$[CH_3CO\ Rh\ I_3(CO)_2]^- \longrightarrow CH_3COI + [Rh\ I_2\ (CO)_2]^-$

7) The acetyl iodide undergoes hydrolysis to form acetic acid

$$CH_3COI + H_2O \longrightarrow CH_3OH$$

Cycle for Monsanto Acetic acid synthesis



Reference :

1. **Text book of Inorganic Chemistry by Manali Publication**