

Unit-III EC-1a Inorganic Chemistry Special

Homogeneous catalysis

Introduction to homogeneous catalysis

Definition and Characteristics

- **Homogeneous Catalysis:** Catalyst and reactants exist in the same phase (usually liquid)
- **Contrast with Heterogeneous Catalysis:** Catalyst in different phase (solid catalyst, liquid/gas reactants)

Advantages of Homogeneous Catalysis:

1. **High Selectivity:** Molecular-level interaction
2. **Mild Conditions:** Lower temperatures and pressures
3. **Better Understanding:** Mechanisms easier to elucidate
4. **High Turnover Frequency (TOF):** Often $>10^6 \text{ h}^{-1}$
5. **No Diffusion Limitations:** All molecules equally accessible

Disadvantages:

1. **Separation Difficulties:** Catalyst recovery challenging
2. **Thermal Stability:** Limited compared to solid catalysts
3. **Sensitivity:** Poisoning by impurities
4. **Cost:** Expensive metal complexes

Components of Homogeneous Catalyst

- **Transition Metal Complexes:** Rh, Pd, Pt, Ru, Co, Fe
- **Ligands:** Phosphines, CO, hydrides, halides
- **Solvents:** Polar/aprotic, coordinating/non-coordinating

2. Stoichiometric reactions for catalysis

Concept

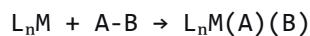
- **Stoichiometric Reaction:** Consumes one equivalent of reagent per equivalent of substrate
- **Catalytic Cycle:** Regenerates catalyst after each turnover
- **Stoichiometric Studies:** Used to understand catalytic mechanisms

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Important Stoichiometric Reactions

A. Oxidative Addition



Where: A-B = H₂, R-X, H-X, etc.

Oxidation State: Increases by 2

Coordination Number: Increases by 2

Examples:

1. **H₂ Addition:**



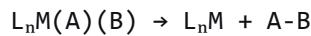
C-X Bond Activation: Pd(0) + R-X → Pd(II)(R)(X)

Mechanisms:

1. **Concerted (σ-bond metathesis):** For non-polar bonds (H-H, Si-H)
2. **SN2-type:** For polar bonds (C-X, H-X)
3. **Radical:** For certain aryl halides

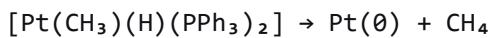
B. Reductive Elimination

Reverse of oxidative addition



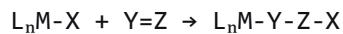
Examples:

1. **Alkane formation:**



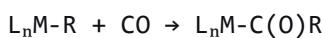
1. **C-C bond formation:** Important in coupling reactions

C. Migratory Insertion

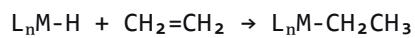


Common Types:

1. **CO Insertion (Alkyl migration):**



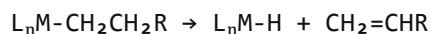
Olefin Insertion:



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D. β -Hydride Elimination



Requirements:

1. β -Hydrogen must be present
2. Empty coordination site cis to alkyl group
3. Proper orbital alignment

Reverse Reaction: Hydrometallation

3. Homogeneous catalytic hydrogenation

Wilkinson's Catalyst: $RhCl(PPh_3)_3$

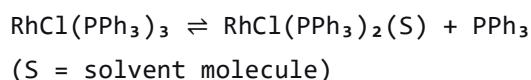
Discovery: 1965 by Geoffrey Wilkinson (Nobel 1973)

Catalyst Structure and Properties

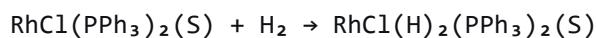
- **Formula:** $RhCl(PPh_3)_3$
- **Geometry:** Square planar (16-electron complex)
- **Color:** Red-violet crystals
- **Solubility:** Organic solvents (benzene, toluene)

Mechanism of Hydrogenation

Step 1: Catalyst Activation



Step 2: Oxidative Addition of H_2

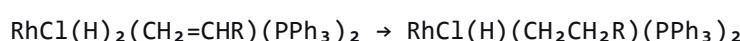


- $16e^- \rightarrow 18e^-$ complex
- **Stereochemistry:** cis-dihydride

Step 3: Olefin Coordination



Step 4: Migratory Insertion



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Step 5: Reductive Elimination



Complete Cycle:

Catalyst \rightarrow H₂ addition \rightarrow Olefin coordination \rightarrow Insertion \rightarrow Elimination \rightarrow Catalyst

Selectivity Features

1. Chemoselectivity:

- Reduces alkenes > alkynes > carbonyls
- Terminal alkenes faster than internal

2. Stereoselectivity:

- Syn addition of H₂
- Less stereoselective than heterogeneous

3. Functional Group Tolerance:

- Does not reduce: -NO₂, -CN, -COOR, -C=O
- Sensitive to sulfur, phosphorus compounds

Modified Catalysts

1. Crabtree's Catalyst: [Ir(COD)(PCy₃)(py)]PF₆

- More active for hindered alkenes

2. Noyori's Catalyst: Ru-BINAP complexes

- Asymmetric hydrogenation (Nobel 2001)

4. Ziegler-natta polymerization of olefins

Historical Background

- **1953:** Karl Ziegler (Germany) - Polymerization of ethylene at low pressure
- **1954:** Giulio Natta (Italy) - Stereospecific polymerization of propylene
- **1963:** Nobel Prize in Chemistry