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 $>10^6$ 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

$L_nM + A\text{-}B \rightarrow L_nM(A)(B)$

Where: A-B = H_2, R-X, H-X, etc.
Oxidation State: Increases by 2
Coordination Number: Increases by 2

Examples:

1. **H_2 Addition:**
2. **Vaska's Complex**: trans-$[IrCl(CO)(PPh_3)_2] + H_2 \rightarrow [IrCl(H)_2(CO)(PPh_3)_2]$

C-X Bond Activation: $Pd(0) + R\text{-}X \rightarrow Pd(II)(R)(X)$

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

$L_nM(A)(B) \rightarrow L_nM + A\text{-}B$

Examples:

1. **Alkane formation:**

   $[Pt(CH_3)(H)(PPh_3)_2] \rightarrow Pt(0) + CH_4$
1. **C-C bond formation:** Important in coupling reactions

C. Migratory Insertion

$L_nM\text{-}X + Y\text{=}Z \rightarrow L_nM\text{-}Y\text{-}Z\text{-}X$

Common Types:

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

   $L_nM\text{-}R + CO \rightarrow L_nM\text{-}C(O)R$

Olefin Insertion:

$L_nM\text{-}H + CH_2\text{=}CH_2 \rightarrow L_nM\text{-}CH_2CH_3$

D. β-Hydride Elimination

$L_nM\text{-}CH_2CH_2R \rightarrow L_nM\text{-}H + CH_2{=}CHR$

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

$RhCl(PPh_3)_3 \rightleftharpoons RhCl(PPh_3)_2(S) + PPh_3$

(S = solvent molecule)

Step 2: Oxidative Addition of H_2

$RhCl(PPh_3)_2(S) + H_2 \rightarrow RhCl(H)_2(PPh_3)_2(S)$

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

Step 3: Olefin Coordination

$RhCl(H)_2(PPh_3)_2(S) + CH_2{=}CHR \rightarrow RhCl(H)_2(CH_2{=}CHR)(PPh_3)_2$

Step 4: Migratory Insertion

$RhCl(H)_2(CH_2{=}CHR)(PPh_3)_2 \rightarrow RhCl(H)(CH_2CH_2R)(PPh_3)_2$

Step 5: Reductive Elimination

$RhCl(H)(CH_2CH_2R)(PPh_3)_2 \rightarrow RhCl(PPh_3)_2(S) + CH_3CH_2R$

Complete Cycle:

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Catalyst → H₂ addition → Olefin coordination → Insertion → Elimination → Catalyst
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Selectivity Features

1. **Chemoselectivity:**
    - Reduces alkenes > alkynes > carbonyls
    - Terminal alkenes faster than internal
2. **Stereoselectivity:**
    - Syn addition of H_2
    - Less stereoselective than heterogeneous
3. **Functional Group Tolerance:**
    - Does not reduce: $-NO_2$, -CN, -COOR, -C=O
    - Sensitive to sulfur, phosphorus compounds

Modified Catalysts

1. **Crabtree's Catalyst:** $[Ir(COD)(PCy_3)(py)]PF_6$
    - 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