

Unit-III EC-1a Inorganic Chemistry Special

Homogeneous catalysis

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

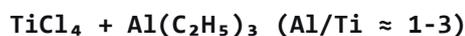
- **1953:** Karl Ziegler (Germany) - Polymerization of ethylene at low pressure
- **1954:** Giulio Natta (Italy) - Stereospecific polymerization of propylene
- **1963:** Nobel Prize in Chemistry

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Catalyst Systems

First Generation (Ziegler-Natta)



- **Active Species:** Ti(III) with vacant sites
- **Product:** Isotactic polypropylene (50-60%)

Modern Supported Catalysts

- TiCl_4 on MgCl_2 support
- Lewis base modifiers (esters)
- Higher activity and stereospecificity

- **Mechanism of Polymerization**

- **Cossee-Arman Mechanism**

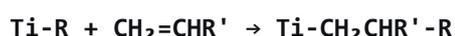
- **Step 1: Catalyst Activation**

- $\text{TiCl}_4 + \text{AlR}_3 \rightarrow \text{TiCl}_3\text{R} + \text{AlR}_2\text{Cl}$
- Reduction: $\text{Ti(IV)} \rightarrow \text{Ti(III)}$

Step 2: Olefin Coordination

- π -complex formation at vacant site

Step 3: Migratory Insertion



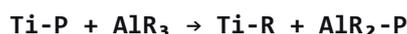
- Chain propagation

Step 4: Chain Transfer

1. β -H elimination:



With AlR_3 :



Stereochemical Control

- **Isotactic:** All chiral centers same configuration
- **Syndiotactic:** Alternating configuration
- **Atactic:** Random configuration

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Factors Affecting Stereoselectivity:

1. **Catalyst Structure:** Chiral environment
2. **Monomer Structure:** Steric bulk
3. **Temperature:** Lower temperatures favor isotactic

4. Types of Ziegler-Natta Catalysts

Type	Components	Applications
Heterogeneous	$\text{TiCl}_4/\text{MgCl}_2 + \text{AlR}_3$	Polyethylene, polypropylene
Homogeneous	$\text{Cp}_2\text{ZrCl}_2 + \text{MAO}$	Polyethylene, elastomers
Metallocene	Bridged metallocenes + MAO	Stereoregular polymers

Industrial Applications

1. **High-Density Polyethylene (HDPE):**
 - Linear chains, high crystallinity
 - Ziegler-Natta catalyst
2. **Polypropylene:**
 - Isotactic (molding), syndiotactic (films)
 - Worldwide production: ~70 million tons/year
3. **Ethylene-Propylene Rubber (EPR):**
 - Copolymerization with dienes

5. Catalytic reactions involving CO

A. HYDROFORMYLATION (OXO REACTION)

Introduction

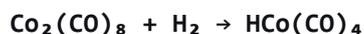
- **Discovery:** Otto Roelen (1938, Ruhrchemie)
- **Reaction:**
 - $\text{R-CH=CH}_2 + \text{CO} + \text{H}_2 \rightarrow \text{R-CH}_2\text{-CH}_2\text{-CHO}$ (linear) + $\text{R-CH(CH}_3\text{)-CHO}$ (branched)
- **Products:** Aldehydes \rightarrow Alcohols (by hydrogenation)

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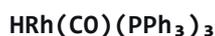
Catalyst Systems

1. Cobalt Carbonyl Catalysts:



- **Conditions:** 100-200°C, 200-300 atm
- **n/iso ratio:** 3:1 to 4:1

2. Rhodium Catalysts:



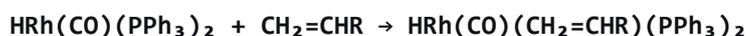
- **Conditions:** 80-120°C, 10-30 atm
- **Higher n/iso ratio:** 10:1 to 20:1
- **Higher activity:** 10^3 times Co catalyst

Mechanism (Rh-catalyzed)

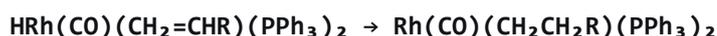
Step 1: Catalyst Activation



Step 2: Olefin Coordination

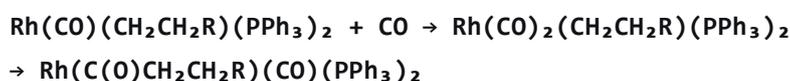


Step 3: Migratory Insertion

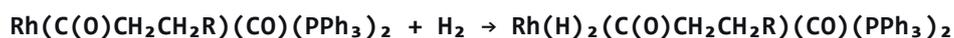


Regioselectivity determined here: Markovnikov vs anti-Markovnikov

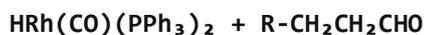
Step 4: CO Coordination and Insertion



Step 5: Oxidative Addition of H₂



Step 6: Reductive Elimination



Factors Affecting Selectivity

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1. Ligand Effects:

- **Bulky phosphines:** Higher n/iso ratio
- **Electronic effects:** Electron-donating ligands favor linear product

2. Pressure Effects:

- Higher CO pressure favors branched product

3. Temperature Effects:

- Lower temperatures favor linear product

Industrial Applications

1. **Butyraldehyde:** From propylene → n-butanol, 2-ethylhexanol
 2. **Plasticizers:** Phthalates from C₇-C₁₀ alcohols
 3. **Detergents:** C₁₂-C₁₅ alcohols
- **Global capacity:** ~10 million tons/year

• B. HYDROCARBONYLATION OF OLEFINS

- **Related to hydroformylation but with different nucleophiles**
- **Monsanto Acetic Acid Process:**



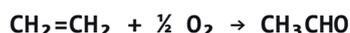
- **Catalyst:** Rh/Ir with iodide promoter
- **Mechanism:** Similar to hydroformylation but with methanol

6. OXOPALLADATION REACTIONS

Wacker Process (Ethylene → Acetaldehyde)

Discovery: 1957 by J. Smidt (Wacker-Chemie)

Reaction



Catalyst: PdCl₂/CuCl₂ in aqueous HCl

Mechanism

Step 1: Ethylene Coordination

