Homogeneous Catalytic Processes

Hydroformylation
\[ RCH_2CH_2 + CO + H_2 \xrightarrow{\text{Co(I), Rh(I) or Pt(II)}} RCH_2CH_2CHO \]

Oxidation
\[ H_2C=CH_2 + O_2 \xrightarrow{\text{Pd(II) or Cu(II)}} H_3CCHO \]

Carbonylation
\[ CH_3OH + CO \xrightarrow{[\text{RhI}_2(\text{CO})_2]^+} H_3CCHOH \]

Hydrocyanation
\[ H_2C=C\equiv C\equiv CH_2 + 2\text{HCN} \xrightarrow{[\text{Ni}\{\text{P(OR)}_3\}_4]} \text{NCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CN} \]

Cyclotrimerization
\[ 3\text{HC≡CH} \xrightarrow{\text{Ni(acac)}_2} \text{C}_6\text{H}_6 \]
Hydrogenation of Alkenes

The most commonly used catalyst is the Wilkinson’s Catalyst

\[
\text{Alkene} + \text{H}_2 \xrightarrow{\text{Catalyst}} \text{Alkane}
\]

Wilkinson’s catalyst is highly sensitive to the nature of the phosphine ligand and the alkene substrate.

Many alkenes are hydrogenated with hydrogen at 1 atm pressure or less.

Analogous catalysts with alkyl phosphine ligands are inactive.

Highly hindered alkenes and ethylene are not hydrogenated by the catalyst.
Wilkinson’s Catalyst

Reductive Elimination

Oxidative Addition

Ligand Association

Ligand Dissociation

Migratory Insertion

Alkene Coordination
Hydroformylation

\[
\text{R} + \text{CO} + \text{H}_2 \xrightarrow{\text{Catalyst}} \text{RCH}_2\text{CH}_2\text{CHO}
\]

A less common, but more appropriate name is hydrocarbonylation

Both cobalt and rhodium complexes are used as catalysts.

Alkene isomerization, alkene hydrogenation and formation of branched aldehydes are the possible side reactions.

Cobalt catalysts operate at 150 °C and 250 atm, whereas Rhodium catalysts operate at moderate temperatures and 1 atm.

Rhodium catalysts promotes the formation of linear aldehydes. Cobalt catalysts do so if modified with alkylphosphine ligands.
Hydroformylation

\[ \text{Co}_2(\text{CO})_8 + \text{H}_2 \rightleftharpoons \text{H} \]

- **Reductive Elimination**
- **Oxidative Addition**
- **Ligand Association**
- **Migratory Insertion**
- **Alkene Coordination**
- **Ligand Dissociation**
**Monsanto Acetic Acid Synthesis**

\[
\text{CH}_3\text{OH} + \text{CO} \xrightarrow{[\text{RhI}_2(\text{CO})_2]^+} \text{CH}_3\text{COOH}
\]

All three members of the group 9 (Co, Rh and Ir) can catalyze this reaction. A cobalt complex was initially used, which was replaced with the rhodium complex later on.

Methanol initially reacts with hydroiodic acid to give methyl iodide and H\textsubscript{2}O. Methyl iodide reacts with the 16\textsuperscript{e}\textsuperscript{-} catalyst, which forms the rate-determining step.

\[
\text{CH}_3\text{OH} + \text{HI} \rightarrow \text{CH}_3\text{I} + \text{H}_2\text{O}
\]

The final product formed after the catalytic cycle is acetyl iodide, which is hydrolyzed by water to acetic acid and HI.

\[
\text{CH}_3\text{COI} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{HI}
\]
Monsanto Acetic Acid Synthesis

Oxidative Addition

CH₃COI

Reductive Elimination

CH₃I

Migratory Insertion
Alkene Polymerization

If only a few monomers couple together, the short chains formed are called oligomers.

Initiation

\[ L_nM-Cl + AlR_3 \rightarrow L_nM-R + AlR_2Cl \]

Propagation

\[ L_nM-R \rightarrow L_nM-R \rightarrow L_nM-R \]

Termination

\[ L_nM-\text{alkyl} \rightarrow M-H + \text{alkene} \]

\[ H_2 \rightarrow M-H + \text{alkane} \]
Alkene Polymerization

The commonly used catalyst has a tetrahydrofuran molecule occupying the fourth coordination site of zirconium.
**Ziegler-Natta Catalyst**

Karl Ziegler in 1953, discovered a catalyst based on TiCl₃ and AlCl₃ for the polymerization of ethylene.

Giulio Natta extended the method for the polymerization of other olefins like propylene and made a number of different variations.

The Ziegler-Natta catalyst family includes halides of titanium, chromium, vanadium and zirconium, typically activated by aluminum halide compounds.

Ziegler and Natta received the Nobel Prize in Chemistry in the year 1963.
Alkene Metathesis

Metathesis catalysis refers to the reaction of two unsaturated substrates (typically alkenes or alkynes) that leads to a switching of the atom groups on each end of the bond with the unsaturation. This is shown below for the reaction of two C₈ dienes.
Alkene Metathesis

\[
2 \text{H}_2\text{C} = \text{CH} - \text{CH}_3 \rightleftharpoons \text{H}_2\text{C} = \text{CH}_2 + \text{H}_3\text{C} - \text{CH} = \text{CH} - \text{CH}_3
\]
Alkene Metathesis
Nobel Prize in Chemistry 2005.

Metathesis – a molecular dance

The atoms let go of each other for a moment – the bonds are broken. All of a sudden a new molecule approaches. A new bond, or...? Everything happens at breakneck speed and the dancers are so exceedingly small... This makes the challenge of working out what really happens all the greater. That’s what chemistry is all about – keeping up with the dancing molecules.

Grubbs Catalyst
Ring Closing Metathesis
Ring Opening Metathesis Polymerization

\[
\text{cat.} = \text{[Mo}(=\text{CHBu}^t)(\text{NAr})(\text{OR})_2]\]

norbornene \quad \rightarrow \quad \text{polynorbornene}

endo-dicyclopentadiene \quad \rightarrow \quad \text{poly(endo-dicyclopentadiene)}

crosslinked polymer