CHAPTER 3

Homogeneously Catalyzed Industrial Processes

CHAPTER 3
OBJECTIVES

- Introduction to Homogeneous Catalysis.
- Industrial Processes:
  - Oxo Process.
  - Production of Acetic Acid by Carbonylation of Methanol.
  - Selective Ethylene Oxidation by the Wacker Process.
  - Oxidation of Cyclohexane.
  - Oligomerization of Ethylene (SHOP Process).

INTRODUCTION

- The share of homogeneous transition metal catalysis in catalytic processes is currently estimated at 10-15%.
- Homogeneous catalysts are often used internally in a company without this fact being made public. In many cases the catalysts are prepared in situ from metal compounds.
- Homogeneous transition metal catalyzed reactions are now used in nearly all areas of the chemical industry.
INTRODUCTION

Homolytic processes: the transition metals react with formation of radicals, and the oxidation or reduction steps are one-electron processes.

Heterolytic processes: normal two-electron steps of coordination chemistry.

Oligomerization reactions involve mono-olefins and dienes; polymerization reactions are mechanistically similar.

Polymerization or copolymerization with soluble or insoluble transition metal catalysts is used to produce:
1. Polyethylene and polypropylene (Ti- and Zr-based metallocene catalysts)
2. Ethylene-butadiene rubber
3. Poly(cis-1,4-butadiene)
4. Poly(cis-1,4-isoprene)
INTRODUCTION

- Polymers prepared with transition metal complexes have different physical properties to those prepared by radical polymerization.
- Reactions with CO (carbonylation) are one of the most important areas of application of homogeneous catalysis.
- The hydrocyanation of butadiene with two moles of HCN in the presence of nickel complexes to give adiponitrile with high regioselectivity has been developed to industrial scale by DuPont.

INTRODUCTION

<table>
<thead>
<tr>
<th>Production of Chemicals by Homogeneous Catalysis</th>
<th>$10^3$ t/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process</td>
<td>$10^3$ t/a</td>
</tr>
<tr>
<td>Oxidation</td>
<td>14.0</td>
</tr>
<tr>
<td>Reactions with CO</td>
<td>8.0</td>
</tr>
<tr>
<td>Hydrogenation</td>
<td>1.4</td>
</tr>
<tr>
<td>Oligomerization</td>
<td>0.8</td>
</tr>
<tr>
<td>Hydrocyanation</td>
<td>0.4</td>
</tr>
</tbody>
</table>

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Examples of Industrial Processes
Oxo Synthesis

- Oxo synthesis (hydroformylation): is an olefin/CO coupling reaction which in the presence of hydrogen leads to the next higher aldehyde.
- This reaction is the most important industrial homogeneous catalysis in terms of both scale and value.
- The most important olefin starting material is propylene, which is mainly converted to 1-butanol and 2-ethylhexanol via the initial product butyraldehyde:

\[
\begin{align*}
\text{CH}_3\text{CH}=\text{CH}_2 + \text{CO} + \text{H}_2 & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} \\
\text{CH}_3\text{CH} = \text{CH}_3 & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \\
\text{CH}_3\text{CH}=\text{CH}_2 & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \\
\text{H}_2 & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}
\end{align*}
\]

- The most important location for this reaction is Germany, with the plants of Hoechst (Ruhrchemie works in Oberhausen) and BASF in Ludwigshafen. Approximately 50% of world capacity is located in Europe and about 30% in the USA.
- Numerous industrial variants of Oxo synthesis are known. Cobalt and rhodium catalysts are used, the latter now being preferred.
Examples of Industrial Processes
Oxo Synthesis

- The original catalyst was [Co_2(CO)_8], which was modified with phosphines to increase the yield of the industrially more important linear aldehydes.
- A breakthrough was achieved in 1976 at Union Carbide with the introduction of rhodium catalysts such as [HRh(CO)(PPh_3)_3]. The process operates at ca. 100°C and 10-25 bars and gives a high ratio of linear to branched products.

- The low pressure allows the synthesis gas to be used directly under its normal production conditions, so that investments for compressors and high-pressure reactors can be saved.
- However, the economic advantages are strongly dependent on the lifetime of the expensive catalysts, and loss-free catalyst recovery is of crucial importance.
- The mechanisms of hydroformylation with rhodium and cobalt catalysts have been studied in detail and are very similar. In the case of the modified rhodium catalyst: the complex [HRh(CO)(PPh_3)_3] is the active catalyst.

Mechanism of the hydroformylation of propylene with (HRh(CO)(PPh_3)_3)
Examples of Industrial Processes
Oxo Synthesis

The dissociation of a phosphine ligand leads to a coordinatively unsaturated complex $2$, to which the olefin coordinates. This is followed by the familiar steps of olefin insertion, CO insertion to give the Rh acyl complex $6$, and hydrogenolysis of the acyl complex with liberation of the aldehyde, which completes the cycle.

Examples of Industrial Processes
Oxo Synthesis

The Shell process: the cobalt-catalyzed process in which phosphine-modified catalysts of the type $[\text{HCo(CO)}_3(\text{PR}_3)]$ are used. Such catalysts, which are stable at low pressures, favor the hydrogenation of the initially formed aldehyde so that the main products are Oxo alcohols.

Examples of Industrial Processes
Oxo Synthesis

The disadvantage of the cobalt-catalyzed process is the lower catalyst activity and increased extent of side reactions, especially the hydrogenation of the olefin starting material. The superiority of the low-pressure rhodium process can be seen from the process data.
Examples of Industrial Processes
Oxo Synthesis

The advantages of the rhodium catalysis can be summarized as follows:

- Rhodium is about 1000 times more active than cobalt as a hydroformylation catalyst.
- The large excess of PPh₃ allows high aldehyde selectivity and a high fraction of linear product to be achieved and at the same time inhibits hydrogenation reactions.
- The presence of PPh₃ dramatically increases the stability of the catalyst and prolongs its life. The low volatility of the catalyst allows the product to be distilled from the reactor with minimal rhodium losses (< 1 ppm).
- Efficient purification of the reactants avoids catalyst poisons and prolongs catalyst life.

Examples of Industrial Processes
Oxo Synthesis

The costs of the rhodium process are higher owing to the required work up, catalyst recycling, and corrosion problems.

- Intensive research is being carried out to develop heterogeneous rhodium catalysts.
- A recent breakthrough: two-phase technology, commercialized in the Ruhrchemie/Rhone Poulenc process, which uses a new water-soluble rhodium complex with polar SO₃Na groups on the phenyl rings of the phosphine (TPPTS).

Examples of Industrial Processes
Oxo Synthesis

The Ruhrchemie works of Hoechst AG in Oberhausen produces over 300000 t/a of butyraldehyde using a two-phase water/organic phase system.

- The process gives improved product selectivity (n/i ratio > 95/5), and the separation of the catalyst and its recycling are straightforward.
### Examples of Industrial Processes

**Oxo Synthesis**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co</th>
<th>Co / phosphine</th>
<th>Rh / phosphine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction pressure (bar)</td>
<td>200-300</td>
<td>50-100</td>
<td>7-25</td>
</tr>
<tr>
<td>Reaction temperature (°C)</td>
<td>140-180</td>
<td>180-200</td>
<td>90-125</td>
</tr>
<tr>
<td>Selectivity C₄ (%)</td>
<td>82-85</td>
<td>&gt;85</td>
<td>&gt;90</td>
</tr>
<tr>
<td>n/iso-Aldehyde</td>
<td>80/20</td>
<td>up to 90/10</td>
<td>up to 95/15</td>
</tr>
<tr>
<td>Catalyst</td>
<td>[HCo(CO)₄]</td>
<td>[HCo(CO)₃(PBu₃)]</td>
<td>[HRh(CO)(PPh₃)₃]/PPh₃, up to 1:500</td>
</tr>
<tr>
<td>Main products</td>
<td>aldehydes</td>
<td>alcohols</td>
<td>aldehydes</td>
</tr>
<tr>
<td>Hydrogenation to alkane (%)</td>
<td>1</td>
<td>15</td>
<td>0.9</td>
</tr>
</tbody>
</table>

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**Examples of Industrial Processes**

**Oxo Synthesis**

Ruhrchemie/Rhône Poulenc process for the hydroformylation of propylene

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  - Oligomerization of Ethylene (SHOP Process).
Another industrially important process with soluble rhodium catalysts is the direct carbonylation of methanol to acetic acid.

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

The process was commercialized by Monsanto and has replaced the original high-pressure cobalt-catalyzed BASF process.

The rate-determining step is oxidative addition of methyl iodide to the four-coordinate 16-electron complex \([\text{RhI}_2(\text{CO})_2^-]\) (A) to give the six-coordinate 18-electron complex (B).

This is followed by CO insertion to give the 18-electron acyl complex (C).

Further coordination of CO to the metal center leads to the 18-electron complex (D), which undergoes reductive elimination of acetyl iodide, re-forming the active catalyst (A).

The acetyl iodide is then hydrolyzed by water to acetic acid and HI. The strong acid HI converts the methanol starting material to methyl iodide.
Production of Acetic Acid by Carbonylation of Methanol

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

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

Particularly advantageous are the mild reaction conditions (30-40 bar, 150-200°C) and the high selectivity with respect to methanol (99%) and CO (>90%) compared to the older cobalt process. Methanol carbonylation is one of the few industrially important catalytic reactions whose kinetics are known in full.

The economics of the process depend on loss-free rhodium recycling, which is now readily achievable. A disadvantage is the corrosivity of the iodide, which requires the use of expensive stainless steels for all plant components.

Today, methanol carbonylation is carried out exclusively in plants using the Monsanto process, which has been licensed worldwide.

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Selective Ethylene Oxidation by the Wacker Process

- The Wacker process is mainly used for the production of acetaldehyde from ethylene and oxygen.

\[
\text{CH}_2=\text{CH}_2 + \frac{1}{2} \text{O}_2 \xrightarrow{\text{Pd Cat.}} \text{CH}_3\text{CHO}
\]

- The process proceeds by homogeneous catalysis on PdCl₂.
- A closed-cycle process was developed in which an excess of the oxidizing agent Cu²⁺ re-oxidizes the palladium formed in the process without its depositing on the reactor walls.
- The Cu⁺ formed in the redox process is re-oxidized to Cu²⁺ by oxygen.

A mechanistic study of the Wacker process involving detailed stereochemical investigations showed that CO bond formation occurs with trans stereochemistry; that is, the ethylene molecule is not attacked intramolecularly by a coordinated water molecule. Instead, an additional, uncomplexed water molecule attacks the double bond.

The formation of B by addition of water is followed by two further steps in which the coordinated alcohol is isomerized. First, a β-hydride elimination gives C, and then an insertion reaction forms D. The elimination of the product acetaldehyde and H⁺ gives Pd⁰, which is oxidized back to Pd²⁺ by Cu²⁺/O₂. With the exception of this last step, the oxidation state of palladium in all steps of the cycle is +2.
In industry, bubble column reactors are used to react the gaseous starting materials ethylene and air (or oxygen) with the aqueous hydrochloric acid solution of the catalyst. Two process variants compete with one another.

- In the one-step process, reaction and regeneration with oxygen are carried out simultaneously.
- In the two-step process they are carried out separately. In the latter case, air can be used for regeneration, and complete ethylene conversion is achieved.

Acetaldehyde production in the two-stage Wacker-Hoechst process

A disadvantage is the higher energy requirement for catalyst circulation compared to the gas circulation used in the one-stage process. In addition, the double reactor design for higher pressures and the use of corrosion-resistant materials lead to higher investment costs.

The two-step process operates at 100-110°C and 10 bar; catalyst regeneration carried out at 100°C/10 bars. Selectivities of 94% are attained.
Selective Ethylene Oxidation by the Wacker Process

- Side products, such as acetic acid and crotonaldehyde, and chlorinated compounds are removed by two-stage distillation, and the crude aldehyde is concentrated. This process accounts for about 85% of total acetaldehyde production.
- The oxidation of ethylene in the presence of acetic acid produces vinyl acetate, and in the presence of alcohols, vinyl ethers. In this case heterogeneous catalysts are mainly used.

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Oxidation of Cyclohexane

- Normally, catalytic oxidations proceed by chain reactions initiated by radical intermediates. Well-known products of such reactions are hydroperoxides, which themselves often undergo further reaction to give other products.
- Radical reactions are characterized by complex product distributions since oxygen exhibits high reactivity towards organic reactants, metal centers, and many ligands.
- Metals play an important role as initiators for radical chain reactions. Radicals are often generated by metal-catalyzed decomposition of organic hydroperoxides.
An industrially important example of such a process is the oxidation of cyclohexane to cyclohexanone and cyclohexanol. Cobalt salts are used as multifunctional catalysts.

Cyclohexane is generally oxidized in the presence of about 20 ppm of a soluble cobalt salt such as cobalt naphthenate in the liquid phase at 125-165 °C and 8-15 bars up to a conversion of 10-12 %.

Higher conversions are undesirable as the selectivity decreases because the products are more reactive than cyclohexane.

Sometimes boric acid is added to stabilize the oxidation mixture.

The selectivities with respect to cyclohexanone and cyclohexanol are 80-85 %.

Unreacted cyclohexane is removed by distillation and recycled. The high-boiling components, mainly cyclohexanone and cyclohexanol, are purified by distillation.

The most important intermediate in cyclohexane oxidation is cyclohexyl hydroperoxide.

The radical-transfer agents $R^\bullet$ and $ROO^\bullet$ ($R = C_6H_{11})$ are formed.

Cobalt acts as an electron-transfer catalyst and redox initiator in the process. In a one-electron step, the oxidation state of the metal varies between +2 and +3, and radicals are released from the cyclohexane hydroperoxide.

The function of cobalt is purely catalytic, and thus only small amounts of catalyst are required. Other metals such as ~ Cr, Mo, Mn can also be used.
Oxidation of Cyclohexane
Mechanism

Industrial variants of the process have been developed by companies such as BASF, Bayer, DuPont, ICI, Inventa, Scientific Design, and Vickers-Zimmer.

The mixture of cyclohexanone and cyclohexanol can be converted to adipic acid \([\text{HOOC(CH}_2\text{)}\text{}_4\text{COOH}]\) in a second step by oxidation with nitric acid \((\text{HNO}_3)\) in the presence of metal compounds such as Cu(II) or V(V) salts as homogeneous catalysts.

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Oligomerization of Ethylene (SHOP Process)

- Long-chain α-olefins are of major industrial importance in the production of detergents, plasticizers, and lubricants.
- Today α-olefins are mainly produced by oligomerization of ethylene.
- Homogeneous transition metal catalysts on the basis of Co, Ti, and Ni have been described for this reaction.

\[ n \text{CH}_2\text{CH}_2 \rightarrow \text{CH}_2\text{CH}_2\left( \text{CH}_2\text{CH}_2 \right)_{n-2}\text{CH} = \text{CH}_2 \]

- The nickel-catalyzed Shell higher olefin process (SHOP) is of major industrial importance.
- Ethylene is converted to α-olefins with a statistical distribution in which the lower oligomers are favored (so-called Schulz-Flory distribution).

The process is carried out at 80-120 °C and 70-140 bars in the presence of a nickel catalyst with phosphine ligands such as Ph₂PCH₂COOK.

- The product mixture is separate separated into C₄-10, C₁₂-18, and C₂₀+ fractions by distillation.
- The C₁₂-18 fraction contains α-olefins with the desired chain length for the detergent industry.
- The top and bottom olefins are subjected to a combination of double-bond isomerization and metathesis.

Isomerization gives a mixture of inner (or internal) olefins with a statistical distribution of the double bond, metathesis of which gives a new mixture of inner olefins from which the C₁₀-₁₄ olefins can be separated by distillation.

If the inner olefins are cleaved with ethylene over heterogeneous catalysts (e.g., Re₂O₇/Sn(CH₃)₄/Al₂O₃), a mixture of unbranched terminal olefins is obtained.
Mechanistic investigations with special nickel complex catalysts have shown that nickel hydrides with chelating P-O groups are the catalytically active species. The metal hydride reacts with ethylene to give alkynickel intermediates, which can grow further by ethylene insertion or eliminate the corresponding α-olefins.

The products 1-hexene and 1-octene are copolymerized with ethylene to give high tensile strength polyethylenes for use in packaging materials. 1-Decene is used for producing high-temperature motor oils, and the higher olefins are converted to tensides. Prior to introduction of the SHOP process α-olefins were produced by pyrolysis of waxes above 500°C (e.g., Chevron process) or by olefin oligomerization with triethylaluminium (Gulf process).