Heterogeneous Ziegler-Natta catalysts

MgCl$_2$
Heterogeneous Ziegler-Natta catalysts

$\text{MgCl}_2 + \text{TiCl}_4$
These chlorides are displaced by one alkyl and the metal is being reduced, which forms the active site.
Heterogeneous Ziegler-Natta catalysts

\[ \text{MgCl}_2 + \text{TiCl}_4 \]
Heterogeneous Phillips catalysts

Applied for mainly HDPE.

- Chromium based e.g. CrO$_3$/SiO$_2$
- High temperature activation required
- Co-catalyst: none, B(CH$_2$CH$_3$)$_3$, AlR$_3$
- Non-uniform active species, leading to
  - Broad molecular weight distribution (typical $>10$)
  - Heterogeneous melting behavior
  - Reactor blend
Over 30% of the HDPE is currently synthesized using the Phillips catalyst.

No hydrogen response, $M_w$ can only be altered by temperature.
Homogeneous single-site catalysts

Applied for \textit{i-PP, s-PP, HDPE, LLDPE, VLDPE, ...}

- Group 4 metal (Ti, Zr, Hf) based
- Co-catalysts: MAO, boranes, borates, ...
- Uniform active species yielding narrow molecular weight distribution
- In general improved product quality
- In principle easier product/catalyst tailoring
- Depending on the process the catalysts are supported on SiO$_2$ or MgCl$_2$
Homogeneous single-site catalysts

Advantages of well-defined single-site catalysts.

- Tunability of the catalyst performance through designed ligand modification
- Enhanced stereo control
- Uniform, random and tunable comonomer incorporation
Early metallocene catalysis

- Ferrocene (18 VE)
- Titanocene dichloride (16 VE)

Breslow, 1955

\[ \text{Cl-Ti-Cl} + \text{AlEt}_2\text{Cl} \rightarrow \text{HDPE} \text{ (very low yield)} \]

- Limited activity
- Propene; only dimerization
- Active species unclear
Inactive in ethylene polymerization unless a small amount of water is added.

Careful hydrolysis of AlMe₃ yields methylaluminoxane (MAO) with unprecedented cocatalyst abilities.

Catalyst precursor: 

\[
\text{Cl-Zr-Cl + AlMe}_3 \rightarrow \text{Zr-CH}_3
\]

Active species: 

Catalyst precursor: 

\[
\text{Cl-Zr-Cl + [MeAlO]_n} \rightarrow \text{polyethylene} + \text{atactic polypropylene}
\]

high activity
Metalloocene catalysts – $C\nu$ symmetric

$C\nu$ symmetric – no stereo control
Metalloocene catalysts – $C_v$ symmetric

No preference for the position of the polymer chain.
Metalloocene catalysts – $C_2$ symmetric

$C_2$-symmetric – stereo control

Ziegler-Natta catalyst
Metalloocene catalysts – $C_2$ symmetric

Growing chain preferentially points away from the steric bulk of the ligand system.

Growing chain is responsible for "indirect stereo control". Without growing chain, there is no stereo control.
Metalloocene catalysts – $C_2$ symmetric

(isospecific)
Metallocene catalysts – $C_s$ symmetric

$C_s$-symmetric – stereo control
Metalallocene catalysts – $C_s$ symmetric

Growing chain preferentially points away from the steric bulk of the ligand system.

Growing chain is responsible for "indirect stereo control". Without growing chain, there is no stereo control.
Metalloocene catalysts – $C_s$ symmetric

syndiospecific

syndiospecific

syndiospecific
By designing the catalyst's ligand system, various including some unprecedented types of polypropylene are available.

$D_h$ (atactic)

$C_2$ (isotactic)

$C_s$ (syndiotactic)

What if we remove the symmetry?

$C_1$ (???)
The effective steric hindrance of the methyl group is comparable to that of the fused aryl group.
Metallocone catalysts – \( C_1 \) symmetric

\[
\begin{align*}
\text{aspecific} & \quad \text{isospecific} & \quad \text{aspecific}
\end{align*}
\]
Metalloocene catalysts – $C_1$ symmetric

One side is sterically too crowded for the polymer chain. As a result, directly after insertion of a propylene molecule the polymer chain skips back to the less crowded side.
Metalloocene catalysts – $C_1$ symmetric

Insertion

Back skipping

Isospecific
Development of metalloocene catalysts

Different ligand structures lead to different types of polypropylene.

- **s-PP (80% rrrr)**
- **s-PP (90% rrrr)**
- **s-PP (90% rrrr)**
- **Hemi-i-PP**
- **i-PP (83% mmmm)**
- **i-PP (89% mmmm)**
- **i-PP (92% mmmm)**
- **i-PP (93% mmmm)**
- **i-PP (99% mmmm)**
- **UHMW α-PP**
- **i-PP (95% mmmm)**

> 0°C α-PP
-45°C i-PP (83% m)
Synthesis of metalloocene catalysts

- **Ligand synthesis**
  - the carbon skeleton is the most difficult part

- **Metal halide complexes**
  - there is no standard synthetic route for metalloccenes
  - problem with formation of meso species.

- **Metal alkyl complexes**
  - relatively unstable
  - several improved routes are available

- **Well-defined metal alkyl cations**
  - unstable
  - boranes or borates are the standard cation generators
Synthesis of metallocene catalysts

Ligand synthesis is often a multi-step process giving low overall yields.

A problem with $C_2$ symmetric catalysts is that is $C_s$ product is also formed. Whereas the $C_2$ symmetric catalysts yields $i$-PP, the $C_s$ symmetric one affords $a$-PP.
Characteristics of metallocene catalysts

- Single-site catalyst afford low PDI
- Homogeneous comonomer incorporation
- Polymerization rates can be extremely high ($> 10^7 \text{ g} \cdot \text{g}(\text{Zr})^{-1} \cdot \text{h}^{-1}$)
- Difficult to get high molecular weight polypropylene
- Metallocenes are somewhat less sensitive to $\text{H}_2$ for $M_w$ control
Early transition metal post-metalloccenes

Activated with MAO gave an excellent copolymerization catalyst. Copolymerizes α-olefins (short chain branching) and re-inserts macromonomers (long chain branching).

Living 1-hexene polymerization.
Development of metallocene catalysts
Characteristics of post-metallocene catalysts

- Easy to synthesize – allows parallel synthesis and high throughput screening
- No isomer separation needed
- Robust – can be used at high temperature
- Open ligand system comonomer incorporation

Generally less suitable for the synthesis of highly isotactic PP, exception forms the new generation of octahedral complexes
Middle and late transition metal catalysts

Keim, Starzewski, Ittel oligomers, HDPE

Brookhart catalyst, HDPE

Brookhart catalyst, HDPE

Brookhart Gibson catalyst, α-olefins → HDPE

Grubbs catalyst, moderately branched PE

Brookhart catalyst, highly branched PE
Very active catalysts (easily $10^7 – 10^8 \text{g}_{\text{pol}} \cdot \text{mol}_{\text{cat}}^{-1} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$)

Very reactive catalyst - difficult to investigate

$[\text{M}]$-P (with agostic interaction) is the resting state

Coordination is rate limiting?

Very active catalysts (easily $10^2 – 10^3 \text{g}_{\text{pol}} \cdot \text{mol}_{\text{cat}}^{-1} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$)

Easy to study by NMR

$[\text{M}]$($\text{C}_2\text{H}_4$)-P is the resting state

Insertion is rate limiting
Early versus late transition metal catalysts

Polymerization rate is dependent on $[\text{C}_2\text{H}_4]$
- Linear polyethylene
- Also excellent for $\alpha$-olefins
- Poorly tolerant to polar groups

Polymerization rate is zero-order with respect to $[\text{C}_2\text{H}_4]$
- Branched polyethylene
- Poor activity for $\alpha$-olefins
- Tolerant to polar groups
Advantages of immobilization:
- Can be applied in existing processes
- Polymer particle morphology control by replication
- High bulk density
- No reactor fouling
- Less cocatalyst required

Immobilization of homogeneous catalysts

Homogeneous solution process  \[ \text{Zr} \]  \rightarrow \text{Heterogeneous slurry process}

Images of catalyst particles in homogeneous and heterogeneous processes.
Advantages of immobilization:
- Can be applied in existing processes
- Polymer particle morphology control by replication
- High bulk density
- No reactor fouling
- Less cocatalyst required
Amorphous silica is most commonly used support.
- High (and tunable) degree of surface functionalities (silanols) to anchor catalyst
- High surface area and pore volume
- Fragments evenly

**Grafting**

**Advantage:**
- easy to prepare
- well-defined
- single sites

**Disadvantage:**

**Electrostatic interaction with grafted cocatalyst**

**Advantage:**
- no leaching
- single sites

**Tethering**

**Advantage:**
- easy to prepare
- well-defined

Disadvantage:
Importance of catalyst immobilization

**When do we need catalyst immobilization?**

When we want to use a homogeneous catalyst in a gas-phase or slurry/suspension process.

**When can we use homogeneous catalysts?**

- When the polymer is soluble in the polymerization medium: amorphous (non-crystalline) elastomers (EPDM) or plastomers containing high comonomer content (VLDPE)

- When the polymer is crystalline but the polymerization temperature is higher than the melting point of the polymer produced (solution process for LLDPE: 150 – 250 °C)