‘IndianOil’ Novel High Activity Ziegler-Natta Catalyst for Polyethylene and Polypropylene

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20th International Conference
INDIAN Petrochem – 2018

November 1, 2018
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Challenges - PP Catalyst

• Catalyst is the Heart- PP technology revolves around the catalyst
• Producers heavily dependent on technology licensors at their terms and pricing
• Entry of 3rd Party suppliers difficult due to Licensing Agreements
• Interruptions in catalyst supply leads to plant s/d - Huge financial loss
• IPR – Entry Barrier for Indian innovators
• Limited availability of raw materials - Market controlled by few MNCs

Strategic to Develop Indigenous PP Catalyst Technology
PO Catalyst @ IOCL

IndianOil - 2nd Largest producer of PE/PP in India

<table>
<thead>
<tr>
<th>Catalyst@IOCL</th>
<th>Capacity KTA</th>
<th>Annual Consump (MTA)</th>
<th>Approx Cost (INR, Crores)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene</td>
<td>600</td>
<td>17</td>
<td>60</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>650</td>
<td>15.5</td>
<td>38</td>
</tr>
</tbody>
</table>

Another 700KTA PP Capacity – Under commissioning
Two more capacities Planned (450 KTA and 200 KTA)

<table>
<thead>
<tr>
<th>Catalyst Producers</th>
<th>Catalyst Precursor</th>
</tr>
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<tbody>
<tr>
<td>Lyondell-Basell</td>
<td>MgCl₂.xROH</td>
</tr>
<tr>
<td>Grace (DOW/BASF)</td>
<td>Mg₃Ti(OEt)₃Cl₂, MgCl₂.xROH</td>
</tr>
<tr>
<td>Mitsui</td>
<td>MgCl₂.xROH</td>
</tr>
<tr>
<td>Ineos</td>
<td>Mg(OR)₂.xCO₂</td>
</tr>
<tr>
<td>Borealis</td>
<td>BOMAG</td>
</tr>
</tbody>
</table>

Magnesium Precursor is the Core Technology in ZN Catalyst Value Chain

IOCL Target
Novel Precursor
No Dependence on Exotic Raw Materials
ZN Catalyst Synthesis Philosophy

Off-the-Shelf Available Raw Materials

Catalyst Precursor-1

Catalyst Precursor-2

PP Catalyst

Designing of Multiple Catalyst Precursor – Providing Flexibility
Design of Precursor-1 (Solid)

**Attributes**

**Precursor Processing**
- Single-pot Synthesis
- Re-crystallize Precursor
- Precipitated Precursor
- Dissolved Precursor

**Precursor Yield**
- 100% Conversions

**Precursor Composition**
- Tunable Composition
- Reproducible Composition

Premature Patented Chemistry – Achieving Desired Targets
Design of Precursor-2 (Liquid)

Mg $\xrightarrow{RX}$ Mg(OR')$_2$ + RMgX* $\xrightarrow{R'OH}$ MgX$_2$.nR’OH $\xrightarrow{R'OH}$ MgX$_2$ + R$_2$Mg* $\xrightarrow{R'OH}$ Mg(OR')$_2$ $\xrightarrow{R'OH}$ Mg(OR')X

{Mg(OR')X}.a{MgX$_2$}.b{Mg(OR')$_2$}.c{R’OH}

Attributes

Stability of Precursor
• No precipitation for last 24 months

Precursor Processing
• Single-pot Synthesis
• Single-step synthesis

Precursor Yield
• 100% Conversions

Precursor Composition
• Tunable Composition
• Reproducible Composition

Novel Patented Chemistry – Achieving Desired Targets
Design of Precursor

Designed Precursor Through Reaction Profile Control

Perfection/tuning of catalyst through perfecting precursor synthesis
Catalyst Composition

• Mg – Complexometric Titration
• Ti – UV-Vis Analysis
• ID – DIBP Quantified using in-house method based on UV-Vis

1. Catalyst hydrolyzed
2. DIBP extracted in solvent
3. DIBP Quantified

Internal Donor – HPLC analysis revealed single species i.e. DIBP

Desired Catalyst Composition Achieved
Catalyst Characterization
XRD & BET Surface Area

PANalytical Empyrean

Crystallite width calculated from the diffraction peak at 50.28°; corresponding to (110) planes of α-MgCl₂ and β-MgCl₂, and to the (018) plane of α-MgCl₂.

Crystallite Size in the Range of 40-60Å

Surface Area = 350-400 m²/g

Achieving Desired Microstructure
Catalyst Characterization
Particle Size Studies

Mean Diameter can be tuned from 10µm to 40µm

Narrow & Tunable Particle Size Distribution According to End Use Technology
PP Catalyst Performance

Donor Response

<table>
<thead>
<tr>
<th>Donor</th>
<th>Productivity (Kg PP/g Cat)</th>
<th>XS (wt%)</th>
<th>MFI (g/10min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-Donor</td>
<td>13.3</td>
<td>5.3</td>
<td>6.2</td>
</tr>
<tr>
<td>NPTMS</td>
<td>11.1</td>
<td>4.5</td>
<td>6.5</td>
</tr>
<tr>
<td>NPTES</td>
<td>9.2</td>
<td>4.3</td>
<td>4.3</td>
</tr>
<tr>
<td>DPDMS</td>
<td>12.2</td>
<td>4.8</td>
<td>2.5</td>
</tr>
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</table>

C-Donor: Cyclohexylmethyl dimethoxysilane
NPTMS: n-Propyl trimethoxy silane
NPTES: n-Propyl triethoxy silane
DPDMS: Diphenyl dimethoxy silane

Compatibility of Catalyst Systems Across Different External Donors
Morphology, PSD & Isotacticity

Regular Morphology

Narrow Particle Size Distribution

Nil resin in the Pan

NMR Isotacticity

**mmmmm** Content in the range of 85-87%

Desired PP Morphology and Microstructure Achieved
Third Party (Norway) @ 17L Scale
2 IOCL Catalysts evaluated against reference commercial catalyst

Granular PP Morphology

Desired Performance Achieved with IOCL Catalysts
Better Donor Response Obtained with IOCL Catalysts
**REACH-Compliant Internal Donor**

**Registration, Evaluation, Authorisation and Restriction of Chemical substances (REACH) – EU Regulation**

- **Conventional High Yield-High Stereospecific ZN catalyst - Di-isobutyl Phthalate as Internal donor**
- **DIBP is listed in authorization list as per REACH**
REACH Compliant Non-Pthalate Donors for PP

IOCL ID coupled with IOCL patented precursor provides niche grade of PP
Phthalate Free Niche PP

- Ex-reactor Fractional MFI PP
- No penalty on throughput of reactor
- Catalyst gets activated even at low hydrogen concentration

Enabling Production of Niche PP Grades
Molecular Modeling
Design of Internal Donor

Computer-aided Donor design uses Computational Chemistry

From In Vitro to In Silico Development

Effective Donors
PE catalyst Elemental Composition

Elemental Composition wt%

Stable Elemental Composition Achieved
PE Catalyst
Product Evaluation

MFI @ 21.6 Kg; H2 @ 1 bar
In-house > Cat-1 > Cat-2 > Cat-3

MFI @ 2.16 Kg/5Kg; H2 @ 1 bar
In-house > Cat-1 > Cat-2 > Cat-3

Exceeding Benchmark Hydrogen Response
Flow Rate Ratio:
In-house ≈ Cat-1 ≈ Cat-3 > Cat-2

Density of PE samples

Achieving Targeted Composition and Performance at Minimum TiCl₄
In-house catalysts are superior with respect to productivity and hydrogen response.

PE catalyst independently evaluated and validated by Third Party (abroad).
Establishing Versatile Precursor and Catalyst Platform
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<th>Attributes</th>
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<tr>
<td>PP Catalyst</td>
<td>• Commercial catalyst equivalent activity</td>
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<tr>
<td></td>
<td>• Superior hydrogen response</td>
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<tr>
<td></td>
<td>• Desired donor response</td>
</tr>
<tr>
<td>PE Catalyst</td>
<td>• ~30% Higher catalyst activity over commercial benchmark catalyst</td>
</tr>
<tr>
<td></td>
<td>• Superior hydrogen response</td>
</tr>
<tr>
<td></td>
<td>• Lower fines levels</td>
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<td></td>
<td>• Better resin morphology</td>
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9 Patent Families / 65 Patents Covering Synthesis of Novel Magnesium Precursors & Subsequent Ziegler-Natta Class of Catalysts and Internal Donors filed to Protect IOCL Innovation
Conclusions

- Robust catalyst precursors developed using extensive parallel and automated process
- Both the Precursors established for synthesis of high productivity Ziegler-Natta catalysts
- Both PP and PE catalysts provided excellent performance and desired product characteristics
- Third party evaluation of catalysts established performance of both PP & PE catalyst systems
- REACH compliant catalyst chemistry – Niche PP products (Fractional MFR and Broad MWD)
- Formidable (>65) Patent portfolio by IOCL

The Catalyst Recipe is under Scale up / Commercialization
Polyolefin R&D at IOCL

Set up in 2010
Focus on Development of Indigenous Products, Processes & Technologies
Thank You All