Indigenous development of Novel Magnesium Precursor and High Performance Ziegler-Natta Catalysts for Polypropylene & Polyethylene

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INDIA

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Polyolefin Catalysts

- **PP catalyst market to reach $1.33 bn by 2020 (CAGR of 5-6%)**
- **ZN catalysts - ~80 percent PP Catalyst market share by value in 2014**

http://www.business-standard.com/

Indian Oil Corporation Ltd (IOCL)

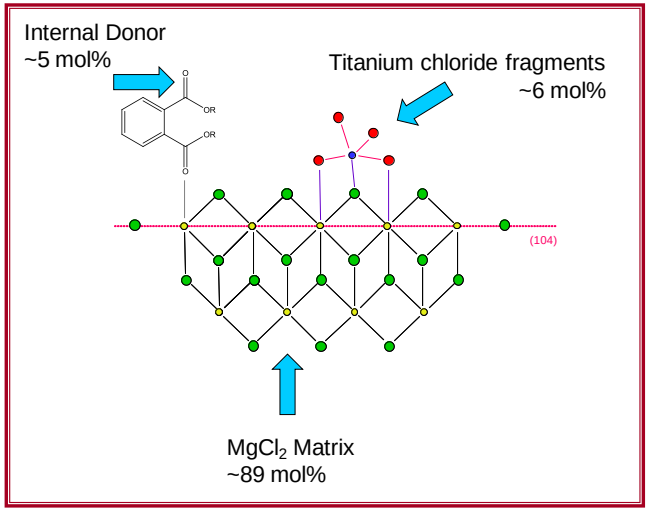
Second largest producer of PP & PE in India

300 KTA HDPE Production – Hostalen

600 KTA PP Production - Spheripol Technology

Another 700KTA Capacity –Under commissioning

Catalyst Producers	Catalyst Precursor
Lyondell-Basell	$MgCl_2.xROH$
Grace (DOW)	$Mg_3Ti(OEt)_8Cl_2$
Mitsui / BASF	$MgCl_2.xROH$
Ineos	$Mg(OR)_2.xCO_2$
Borealis	BOMAG

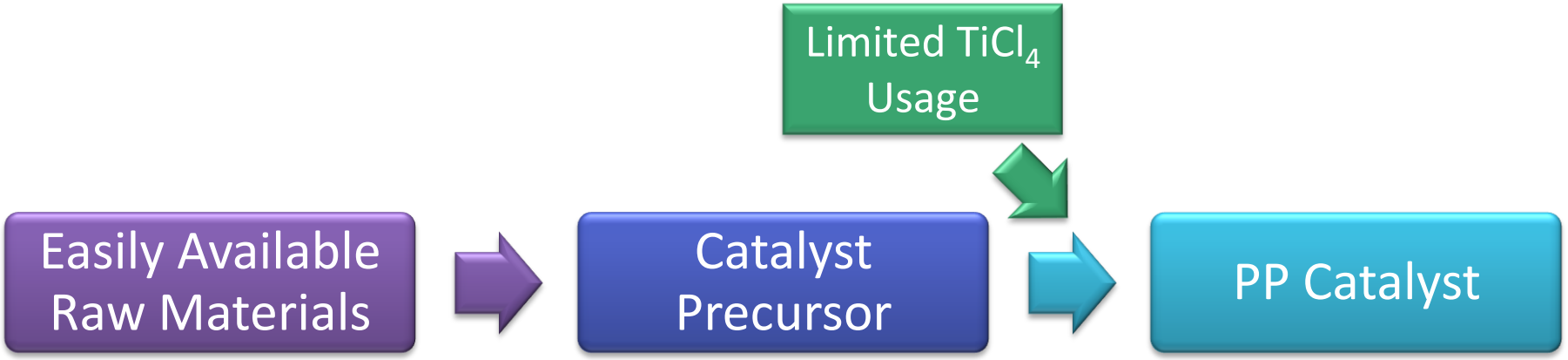


IOCL Targeting Novel Precursor

No Dependence on Exotic Raw Materials

IOCL Execution Strategy

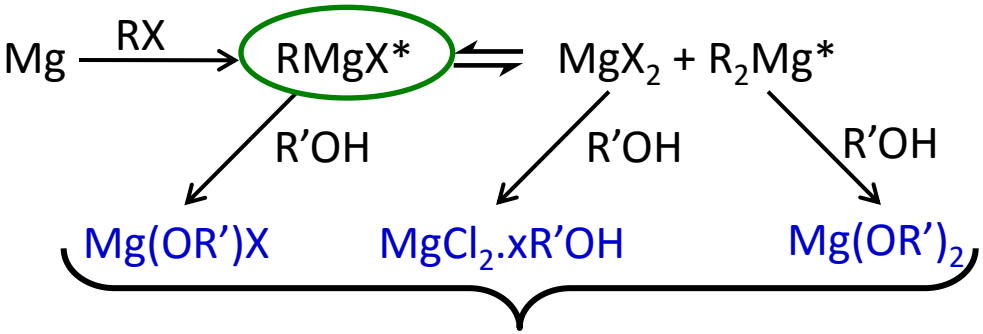
Turning Challenges into Opportunities



Constraints	Reasons	Effect	IOCL Strategy	Benefits
IP	•IOCL being late entrant	•Limited scope of operations	•White space analysis •Designing of unique process	•Patentable process •FTO
Limited availability of $MgCl_2$	•Limited vendors •Vendors are ZN catalyst manufacturers	•High cost •Availability constraints •Reduced competitiveness	•Designing of novel process •Synthesis of catalyst using basic and of the shelf available raw materials	•Cost competitive catalyst •Supply chain management
Handling of $TiCl_4$	Corrosive nature of $TiCl_4$	•Equipment life •Disposal issues •CAPEX & REVEX costs	•Reducing alcohol content in carrier •Synthesis of catalyst using basic and of the shelf available raw materials	•Energy efficient process •Environmentally sustainable •CAPEX & REVEX management

Team Work ↔ Brainstorming ↔ Efficient Project Execution ↔ Knowledge Creation

Design of Precursor-1



Precursor-1

Mg:Alcohol as low as 1:1

Attributes

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

Precursor Yield
- 100% Conversions

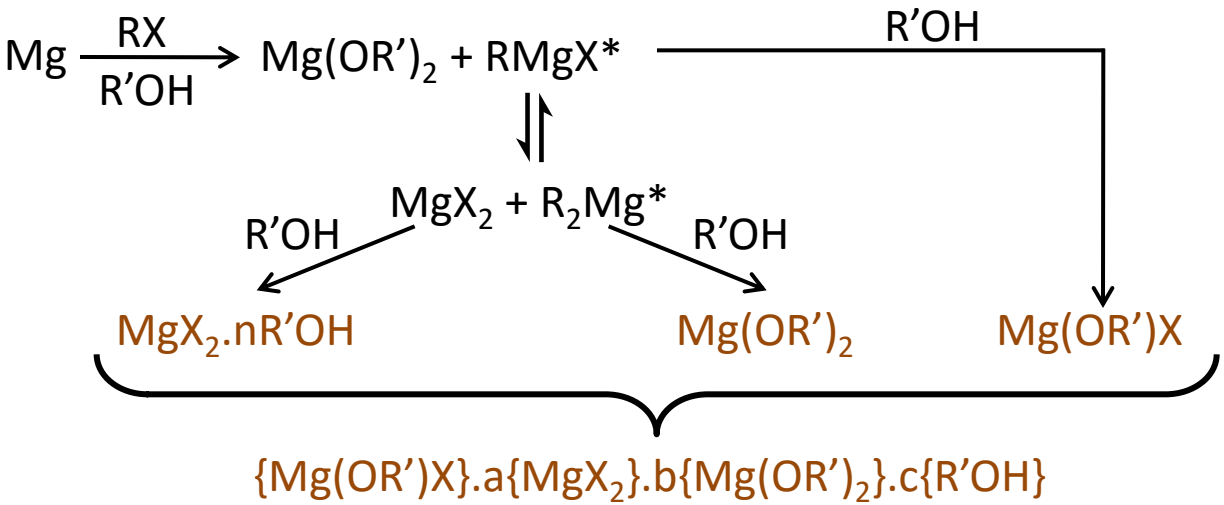
Precursor Composition
- Tunable Composition
- Reproducible Composition

Temperature: Schlenk Equilibrium Control

Halide: To control $MgCl_2$ Formation (Butyl chloride, Benzyl chloride)

Alcohol: EHA, Isobutanol, Benzyl alcohol, Catechol, 3-Methoxy 1-butanol

Design of Precursor-2



{Mg(OR')X}.a{MgX_2}.b{$Mg(OR')_2$}.c{R'OH}

Precursor-2

Mg:Alcohol :: 1:1 to 1:1.5

Temperature: Schlenk Equilibrium Control

Halide: $MgCl_2$ Formation (Butyl chloride, Benzyl chloride)

Alcohol: EHA, Isobutanol, Benzyl alcohol, Catechol, 3-Methoxy 1-butanol

Attributes

Stability of Precursor
- No precipitation for last 18 months

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

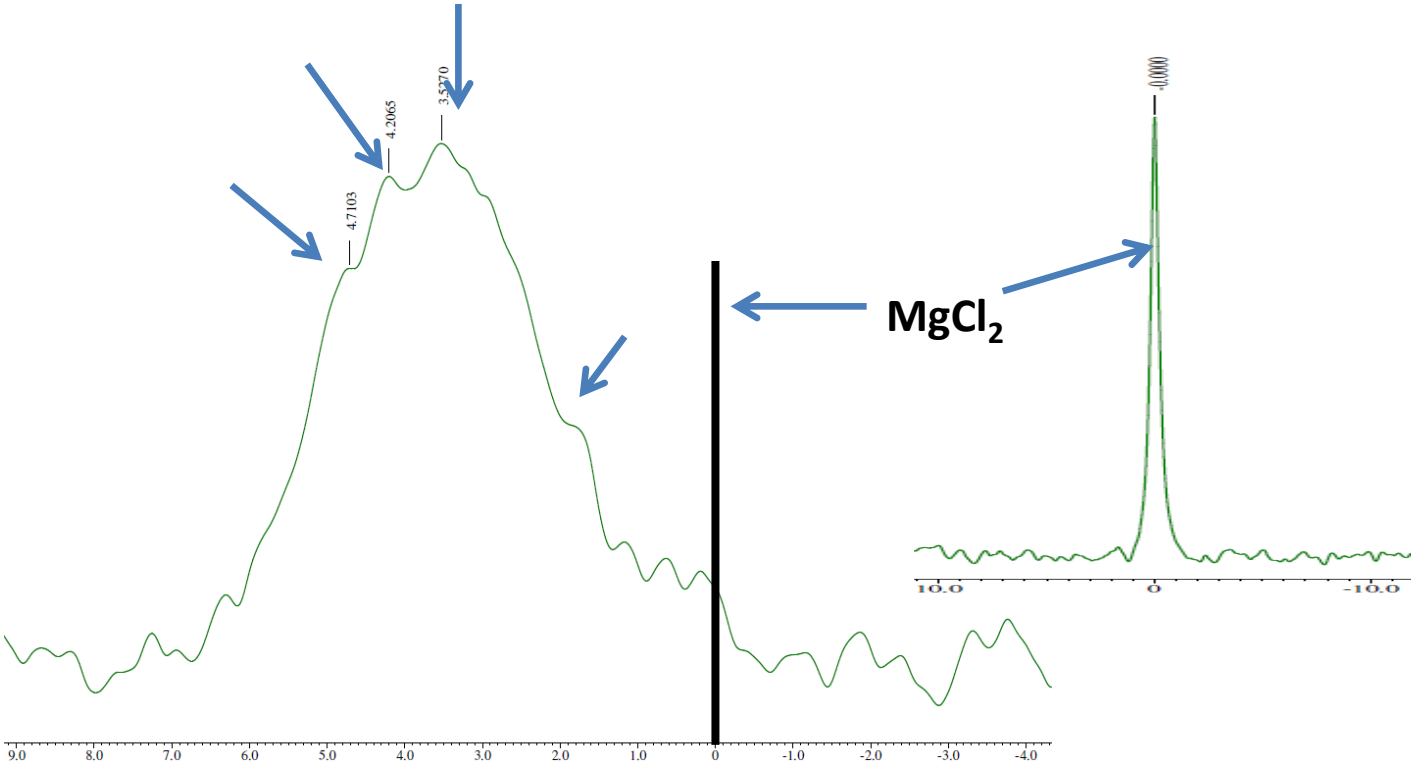
Precursor Yield
- 100% Conversions

Precursor Composition
- Tunable Composition
- Reproducible Composition

Precursor-1: ^{25}Mg NMR

Different Mg Environments

IOCL
1; CPMG with 200us tau delay
CDCl3



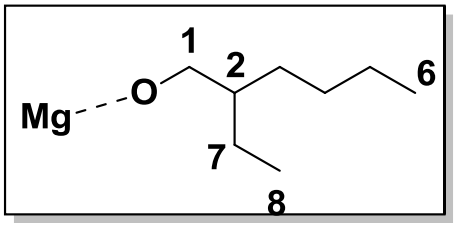
BRUKER

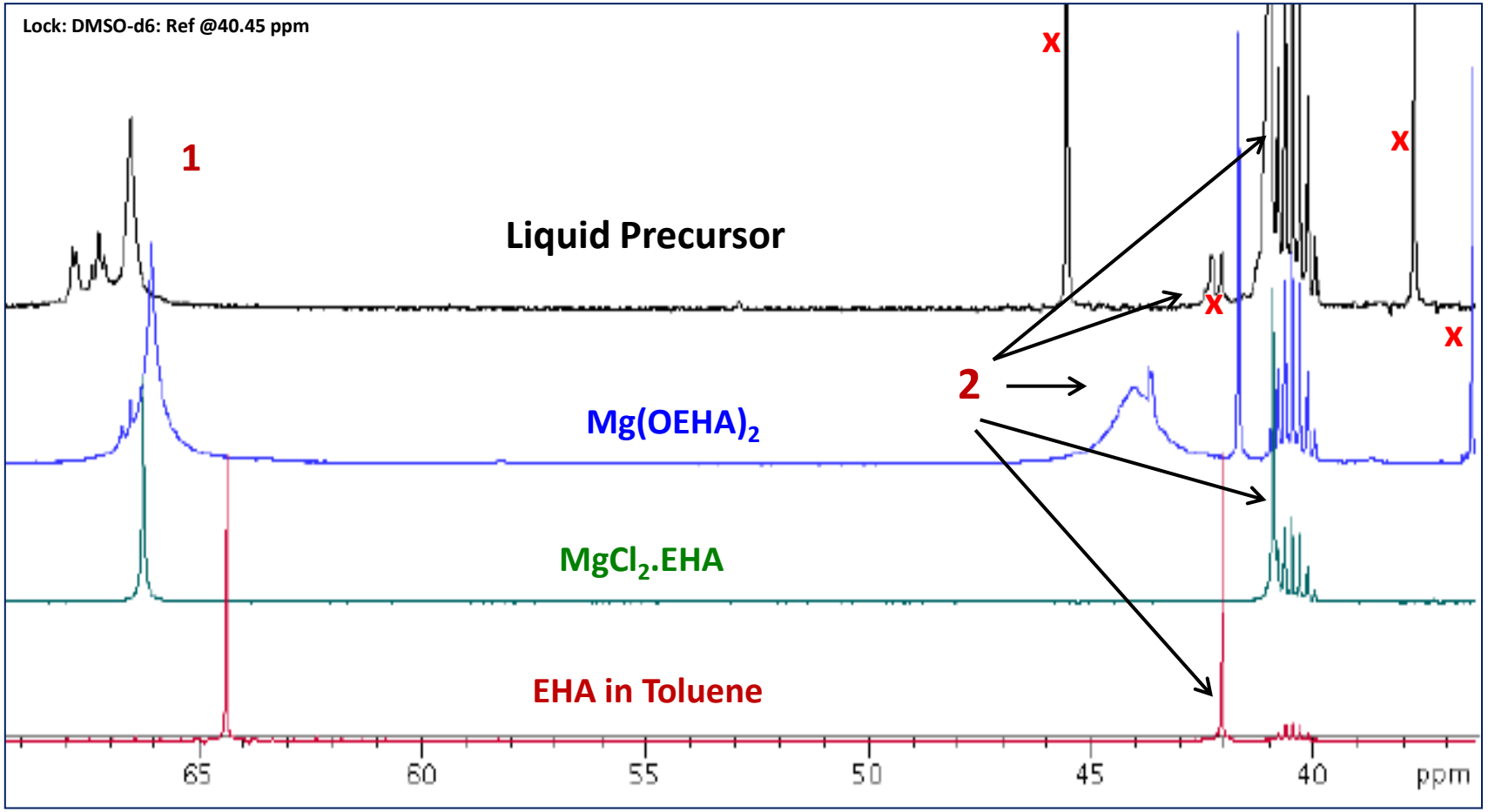
```
NAME            IOCL Mg Sample
EXPNO                       10
PROCNO                       1
Date_                 20150720
Time                     18.21
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 cpmg1d
TD                       32768
SOLVENT                  CDCl3
NS                        1000
DS                           8
SWH                  50000.000 Hz
FIDRES               1.525879 Hz
AQ                   0.3277300 sec
RG                         128
DW                      10.000 usec
DE                       6.00 usec
TE                      299.0 K
D1                 1.00000000 sec
D11                0.03000000 sec
D20                0.00020000 sec
L4                           1
TD0                          1

======== CHANNEL f1 ========
NUC1                      25Mg
P1                      18.00 usec
p2                      36.00 usec
PL1                      1.00 dB
SFO1               30.6161481 MHz
SI                       16384
SF                 30.6161483 MHz
WDW                         EM
SSB                          0
LB                      25.00 Hz
GB                           0
PC                       1.40
```

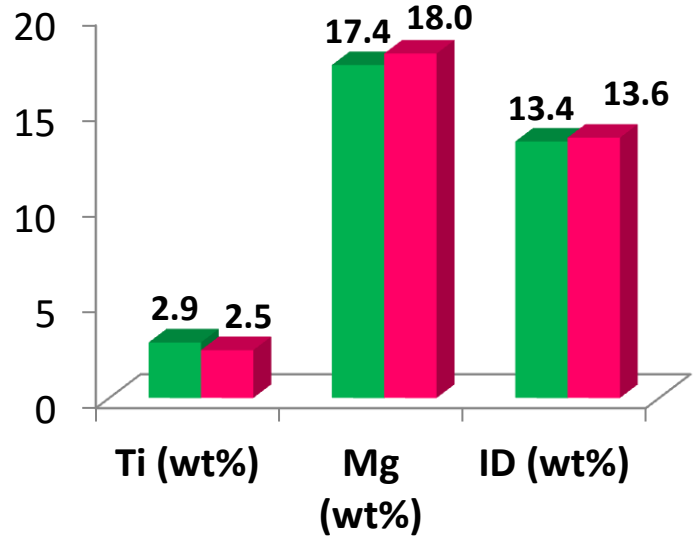
Precursor-2: $^{13}C\{^1H\}$ NMR

{Mg(OR')X}.a{MgX_2}.b{$Mg(OR')_2$}.c{R'OH}





ZN Catalyst Synthesis



Composition

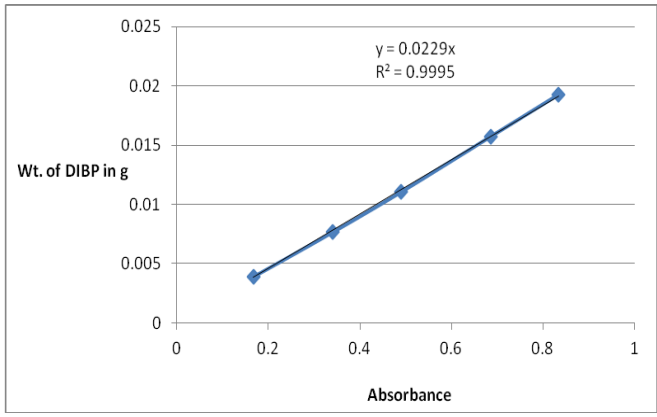
Precursor

Internal Donor

3X Titanations

Hx Washings

PP Catalyst

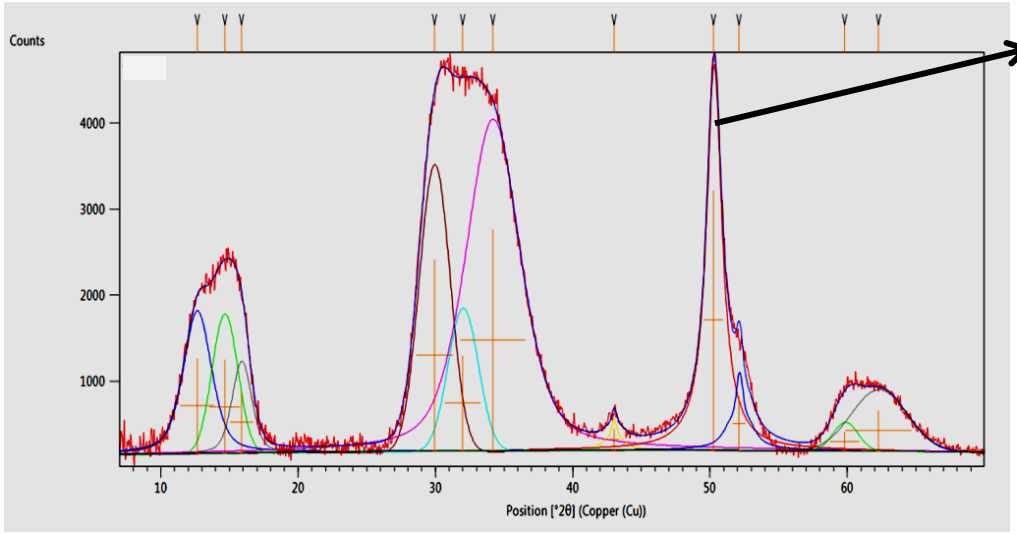


Method Development

Catalyst Characterization

XRD & BET Surface Area

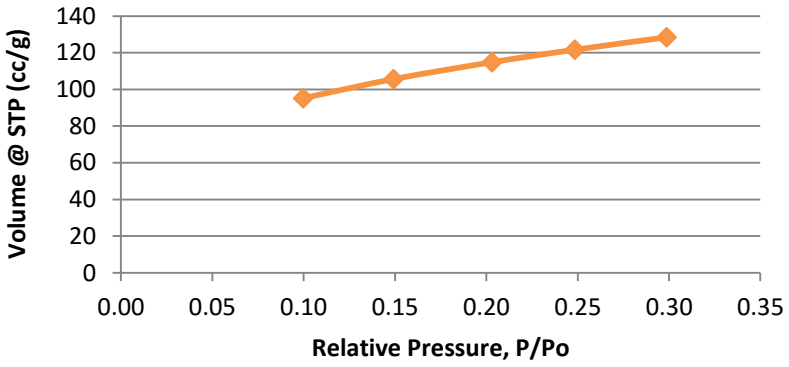
PANalytical Empyrean

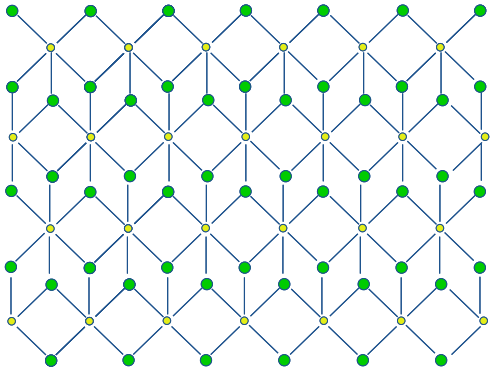


Crystallite width calculated from the diffraction peak at 50.3 2θ → (110) planes of α-$MgCl_2$ and β-$MgCl_2$ and (018) plane of α -$MgCl_2$

Crystallite Size in the Range of 40-60Å

Quantachrome Autosorb

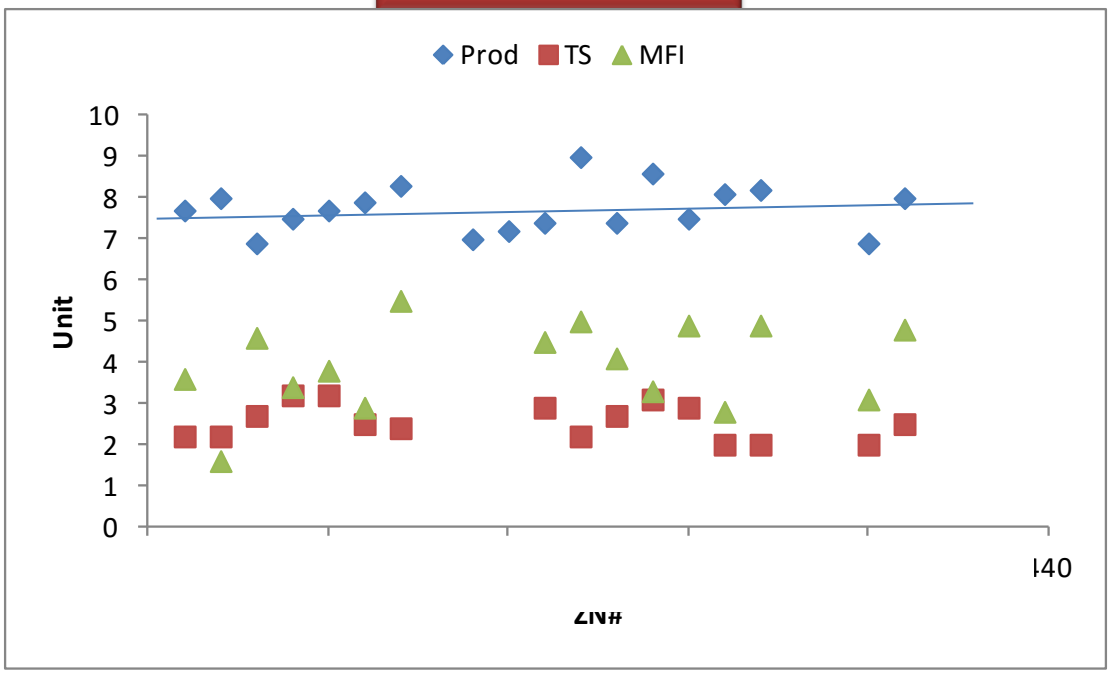




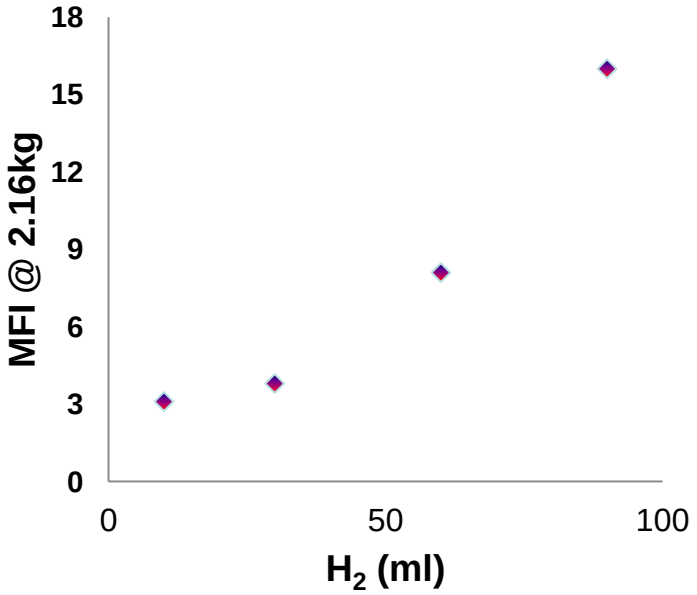
Surface Area = 350-400 m^2/g

PP Catalyst Performance

Productivity



Hydrogen Response

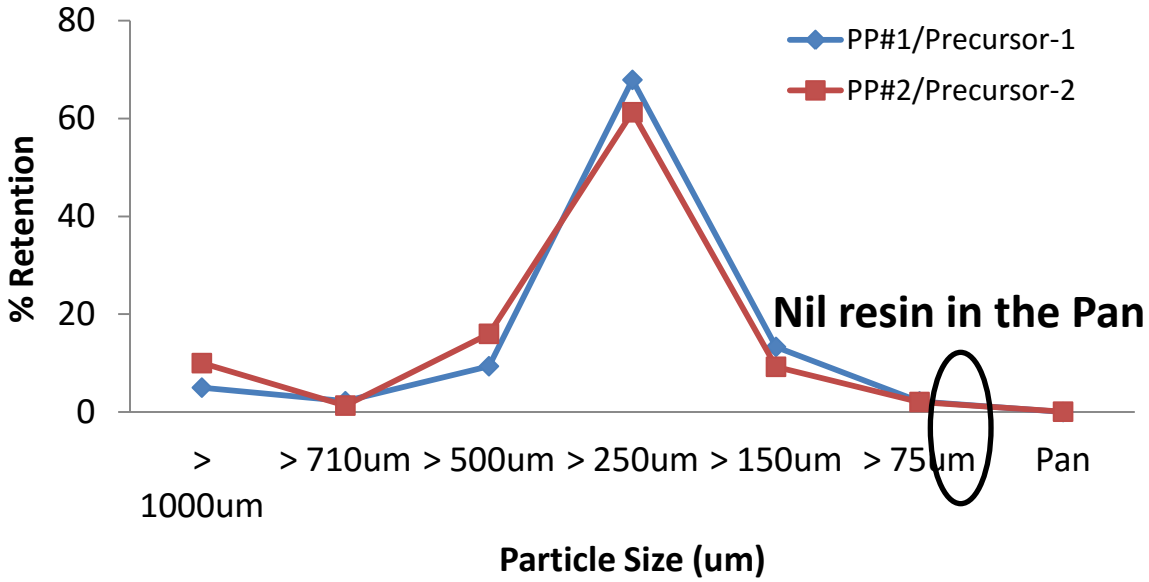


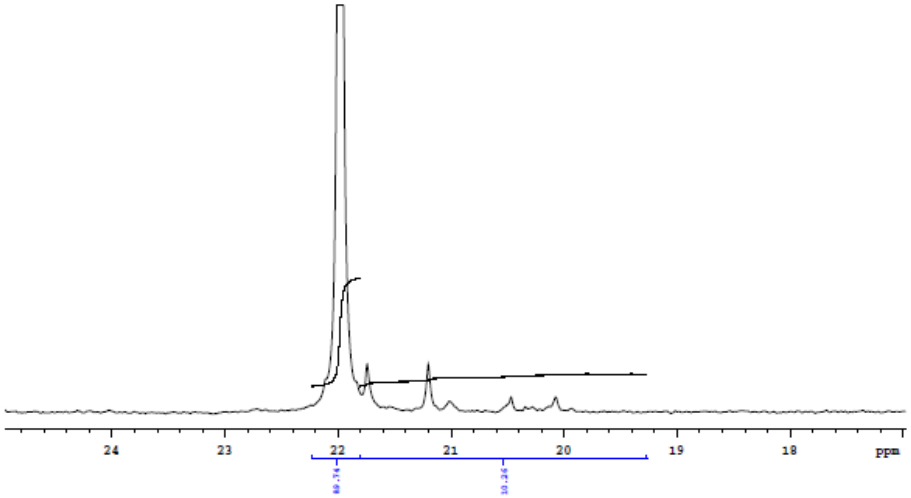
Prod – Productivity (Kg PP/g Cat)
TS – Total Soluble (wt%)
MFI (g/10min)

Desired Performance

Morphology, PSD & Isotacticity

Regular Morphology





Narrow Particle Size Distribution

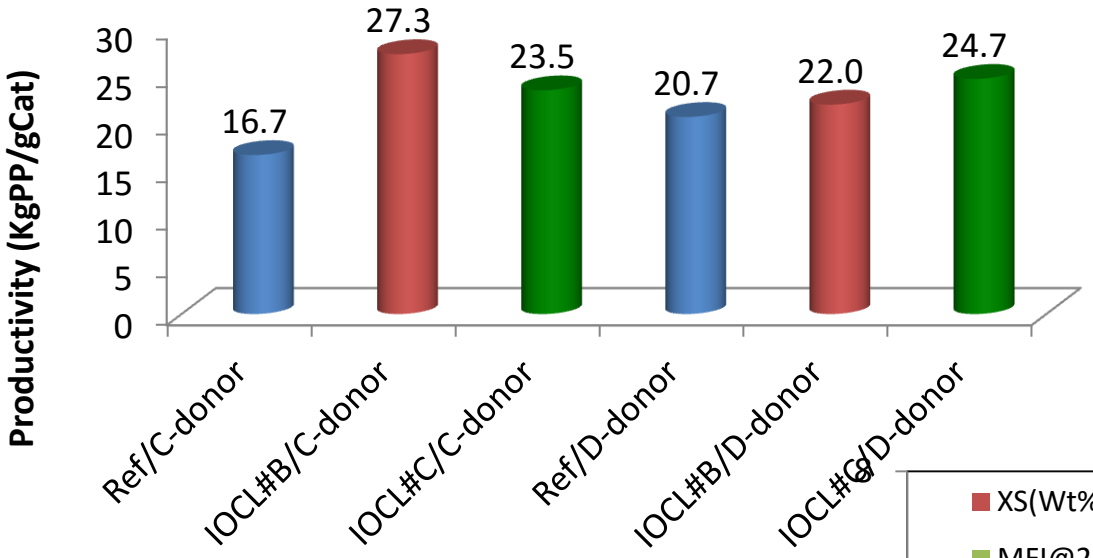
NMR Isotacticity

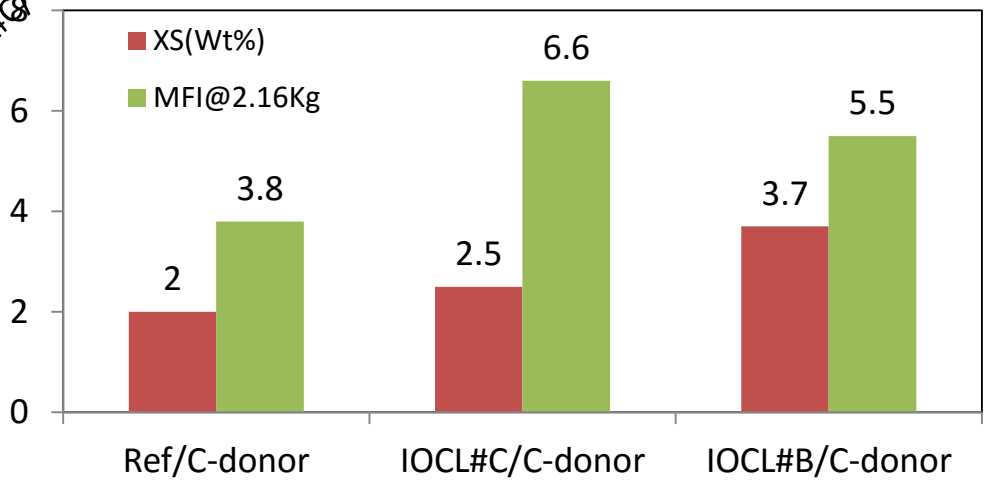
mmmm Content in the range of 85-87%

Evaluation @ 17L Reactor –Bulk

3rd Party Evaluation

2 IOCL Catalysts evaluated against reference commercial catalyst

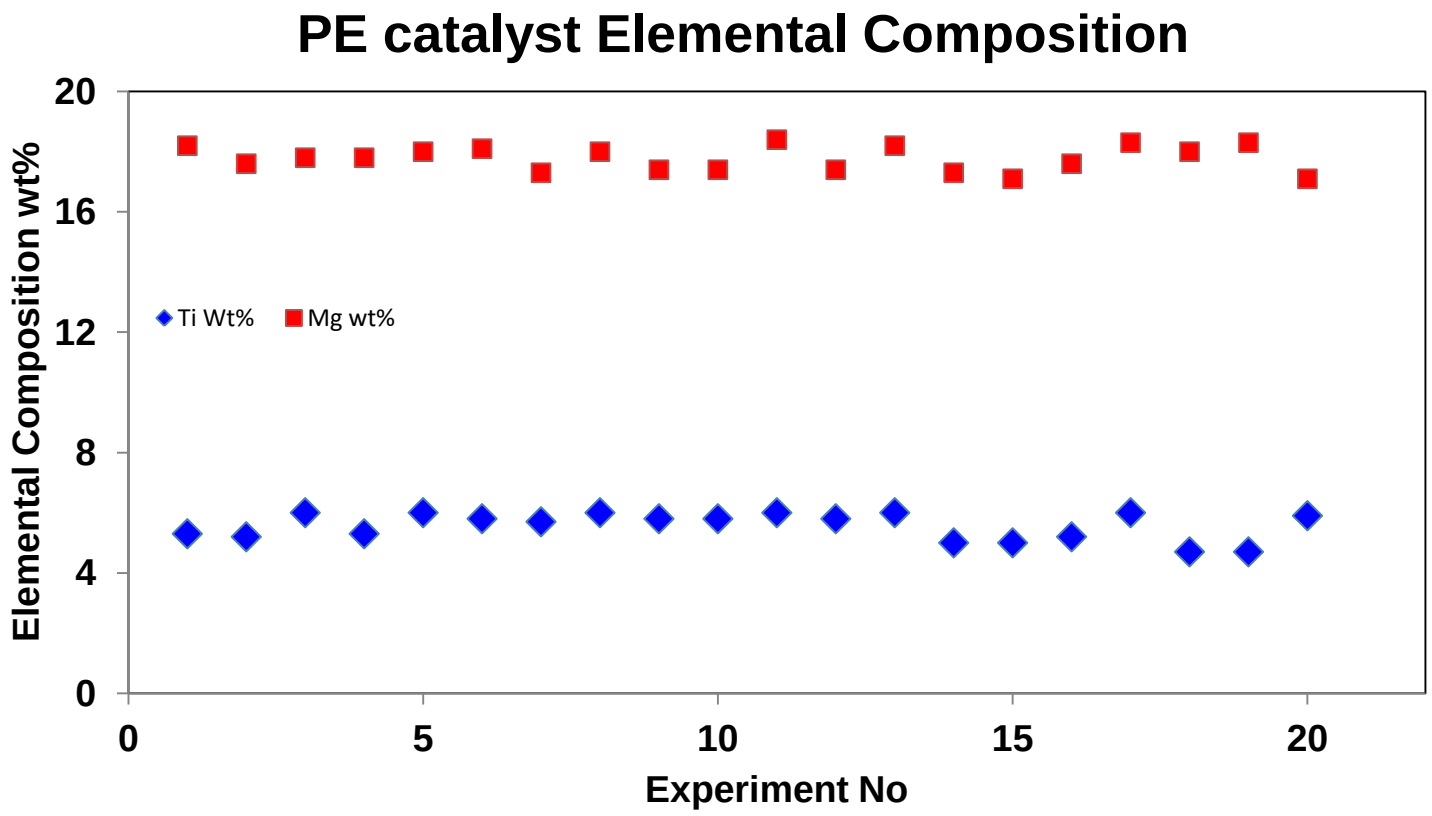




Desired Performance Achieved with IOCL Catalysts

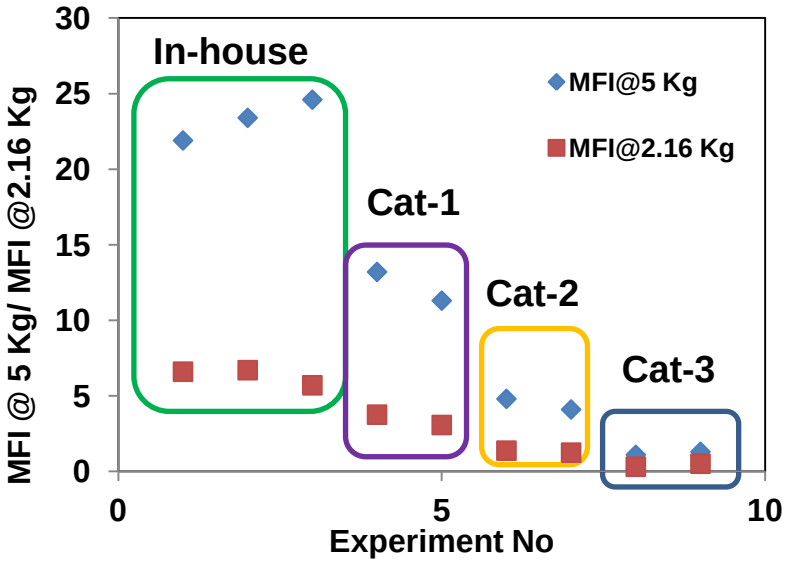
PE Catalyst

Catalyst Evaluation



Stable Elemental Composition Achieved

PE Catalyst
Product Evaluation

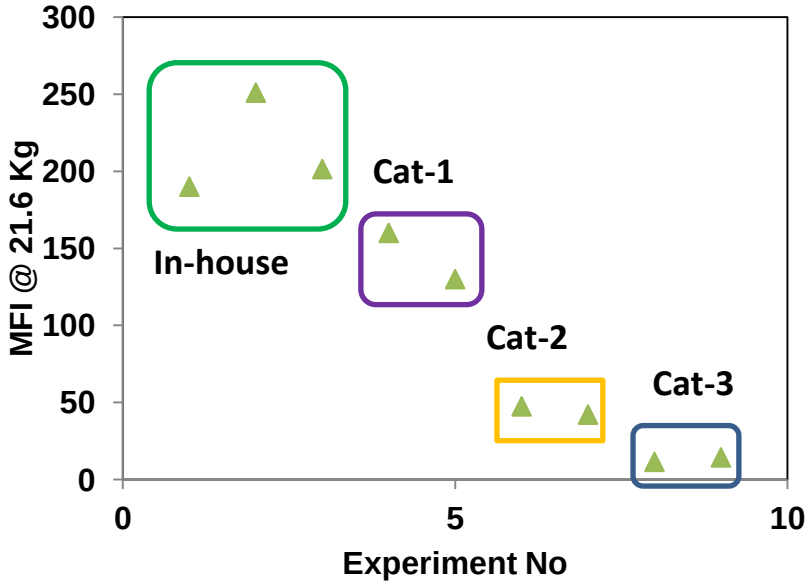


MFI @ 2.16 Kg/5Kg; H2 @ 1 bar

In-house > Cat-1 > Cat-2> Cat-3

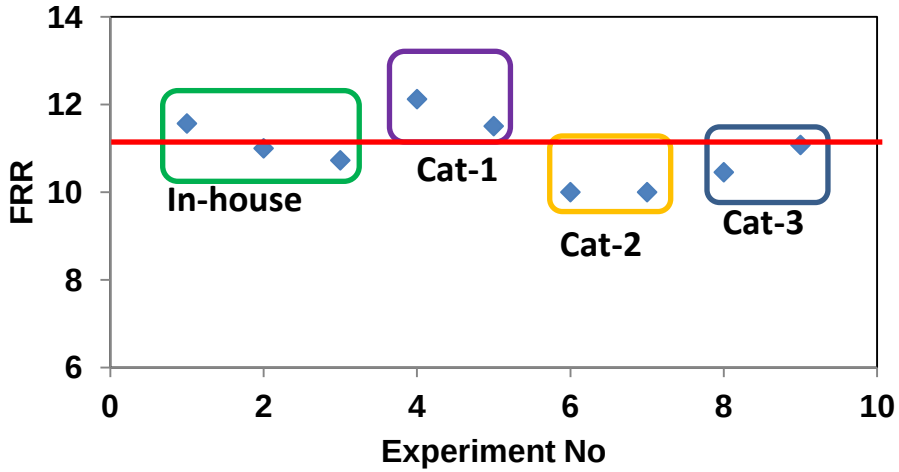
MFI @ 21.6 Kg;H2 @ 1 bar

In-house > Cat-1 > Cat-2> Cat-3



PE Catalyst
Product Evaluation

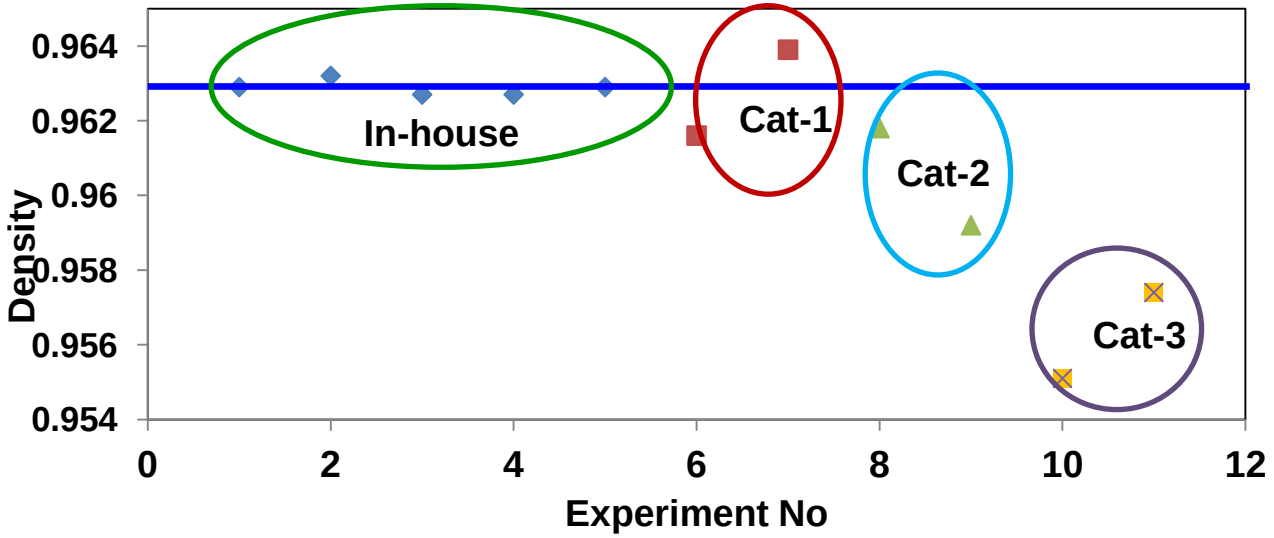
Flow Rate Ratio



Flow Rate Ratio:

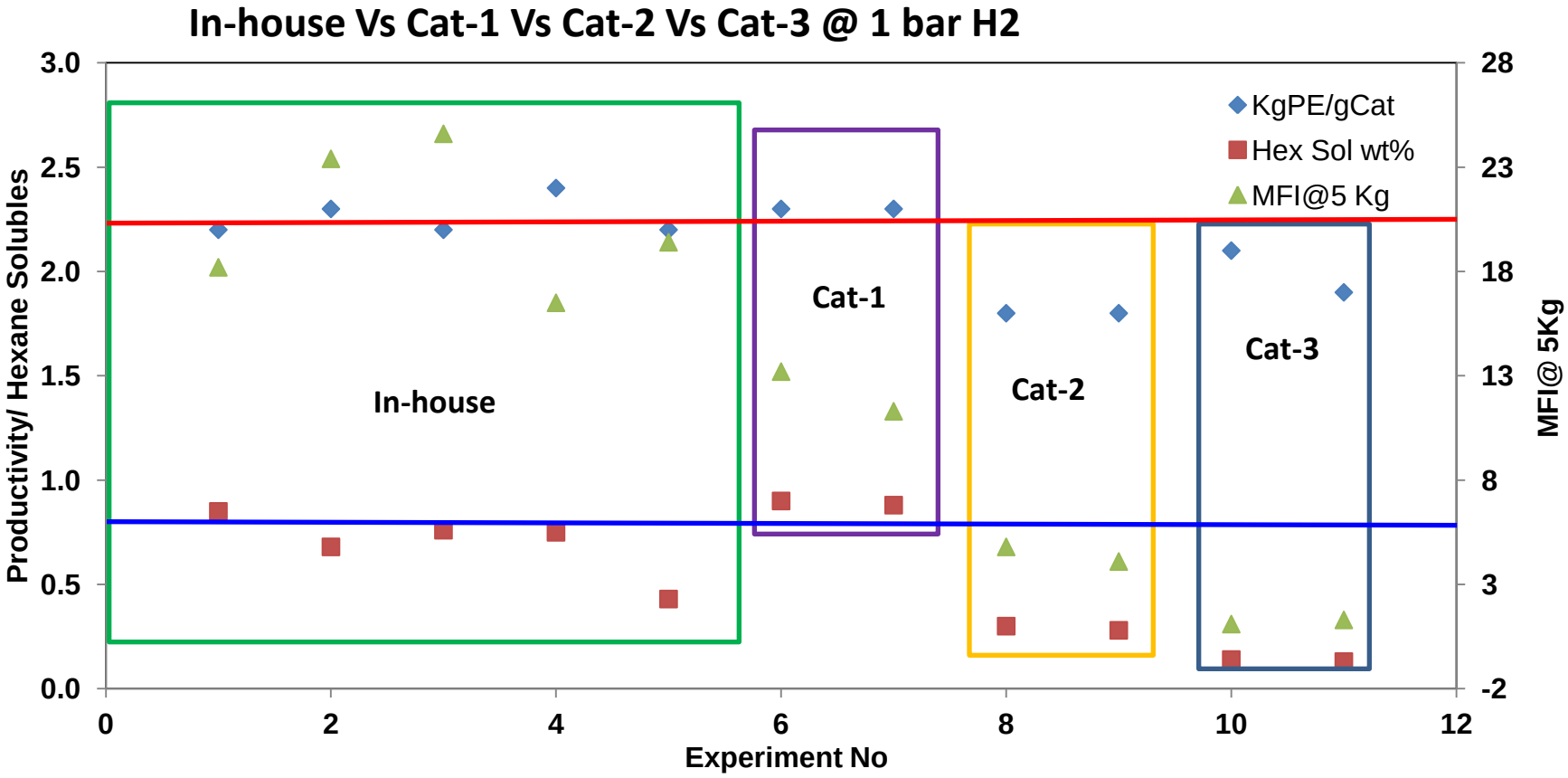
In-house ≈ Cat-1 ≈ Cat-3 > Cat-2

Density of PE samples



PE Catalyst

Performance Evaluation



In-house catalysts are superior with respect to productivity and hydrogen response

Patents

US9593172

US9587041

JP5909817

JP5984173

JP6026662

JP6026661

SA4895

SA5014

EU2897985

2649/MUM/2012

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China

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2213/MUM/2014

268/MUM/2015

3512/MUM/2014

591/MUM/2015

2457/MUM/2015

9 Patent Families Covering Synthesis of Novel Magnesium Precursors & Subsequent Ziegler-Natta Class of Catalysts filed to Protect IOCL Innovation

Conclusions

- Robust precursors developed using extensive parallel and automated process
- Precursors established for synthesis of high productivity Ziegler-Natta catalysts for producing PP & PE
- The catalysts showed excellent performance and desired PP & PE product characteristics
- Extensive IPR protection – 10 Foreign Patents Granted, 51 Patents filed

Thank You All