Molecular & Particle Level Approaches for the Development of New Olefin Polymerization Catalysts

Minoru Terano, Keisuke Goto, Toshiaki Taniike

School of Materials Science
Japan Advanced Institute of Sci. & Tech.

Molecular & Particle Level Approaches for the Development of New Olefin Polymerization Catalysts

- Ziegler-Natta catalyst
- Phillips catalyst

Minoru Terano, Keisuke Goto, Toshiaki Taniike

School of Materials Science
Japan Advanced Institute of Sci. & Tech.

Molecular & Particle Level Approaches for the Development of New Olefin Polymerization Catalysts

- Ziegler-Natta catalyst
- Phillips catalyst

Minoru Terano, Keisuke Goto, Toshiaki Taniike

School of Materials Science

Japan Advanced Institute of Sci. & Tech.

DEVELOPMENTS OF ZIEGLER-NATTA CATALYSTS FOR PP

① $TiCl_3 + AlEt_2Cl$

② ($TiCl_3$ + InD) + $AlEt_2Cl$

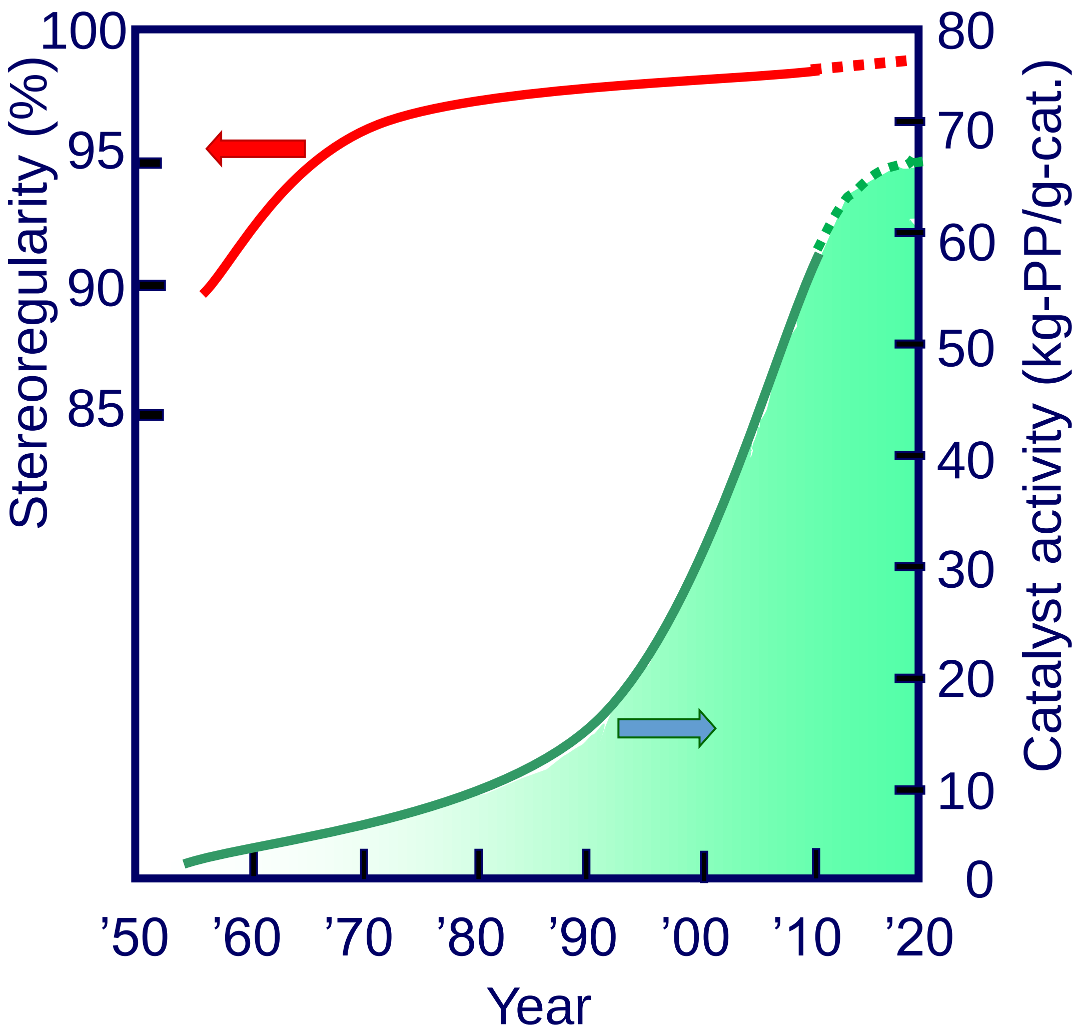
③ Modified $TiCl_3 + AlEt_2Cl$

④ ($TiCl_4$ + Benzoate) / $MgCl_2$
+ ($AlEt_3$+ExD)

⑤ ($TiCl_4$ + Phthalate) / $MgCl_2$
+ ($AlEt_3$+ExD)

⑥ ($TiCl_4$+Diether) / $MgCl_2$
+$AlEt_3$

⑦ ($TiCl_4$ + Succinate) / $MgCl_2$
+ ($AlEt_3$+ExD)



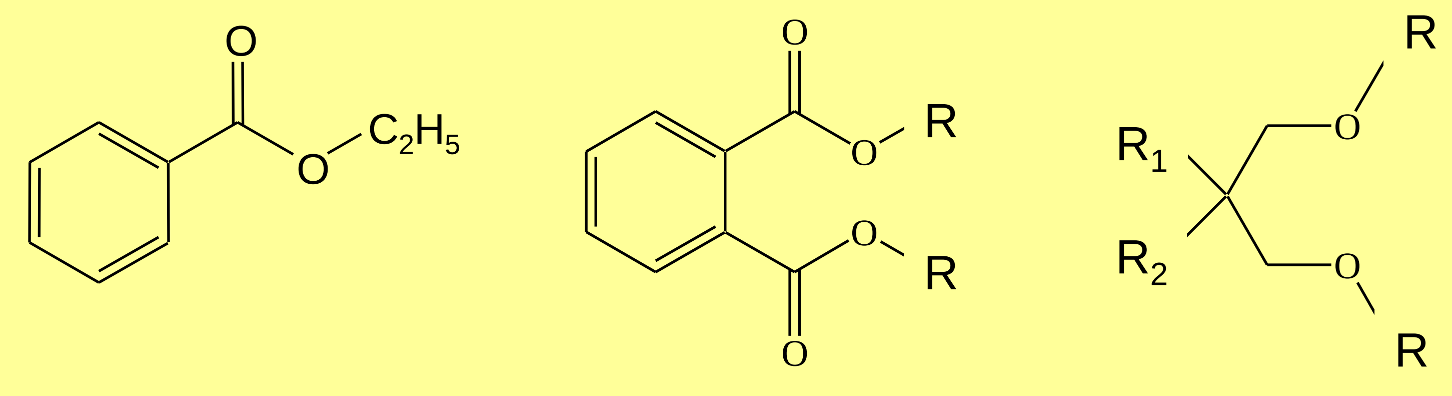
GENERAL PERFORMANCE OF DIFFERENT ELECTRON-DONORS

Cat.	InD	ExD	Yield (kg-PP/g-Cat)	mmmm (%)	Mw/Mn	H_2 response
⑤	Phthalate	Silane	70-40	94-99	6.5-8	medium/low
⑥	Diether	—	130-100	95-97	5-5.5	excellent
⑥	Diether	Silane	100-70	97-99	4.5-5	excellent/high
⑦	Succinate	Silane	70-40	95-99	10-15	medium/low

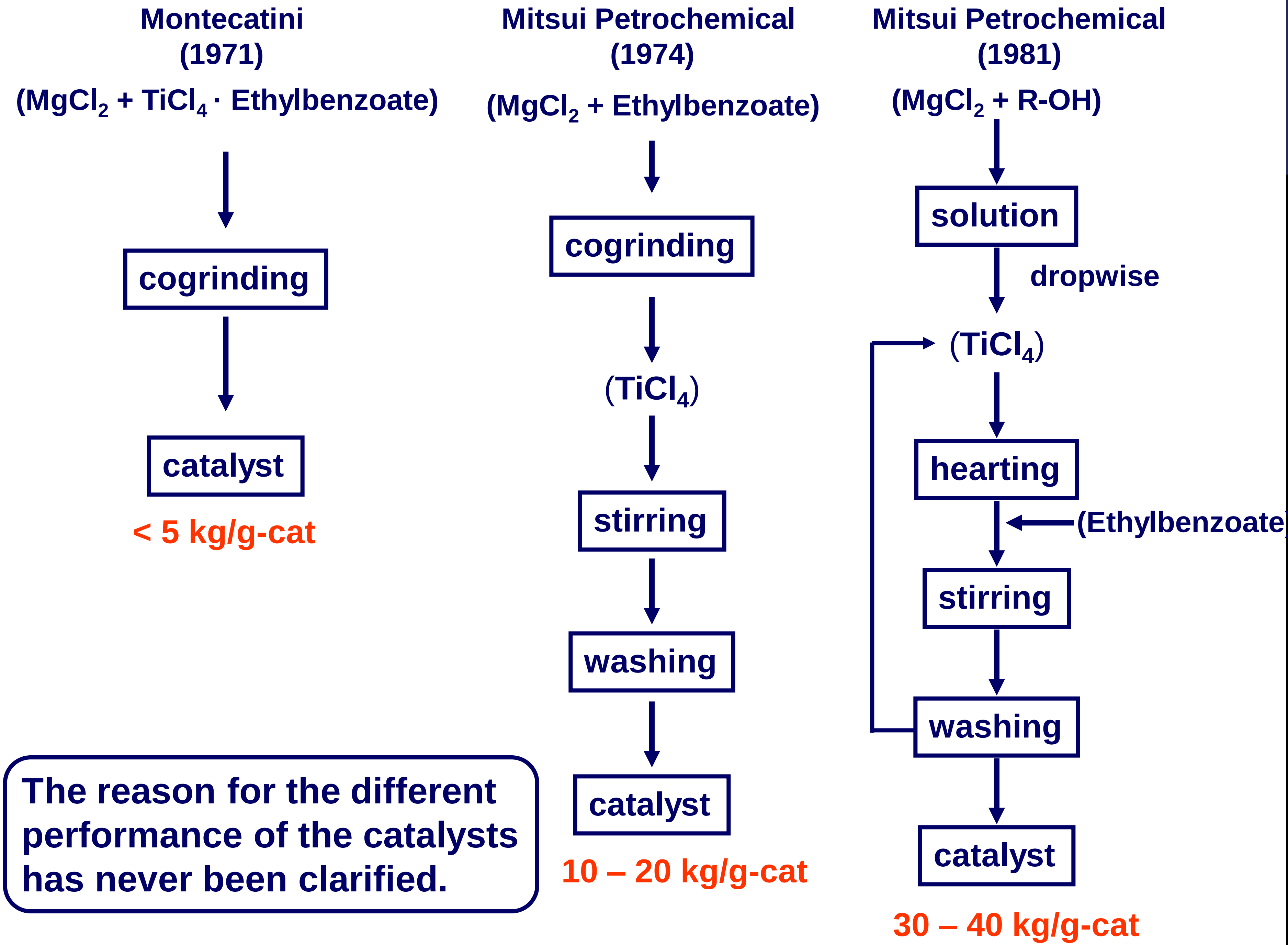
Bulk polymerizations at 70°C for 2h

G.Cecchin et.al., *Macromol.Symp.* ***173***, *195-209 (2001)*

Various internal donors



The reason for the different performance of these donors is not clear.



The reason for the different performance of the catalysts has never been clarified.

DEVELOPMENTS OF ZIEGLER-NATTA CATALYSTS FOR PP

① $TiCl_3 + AlEt_2Cl$

② $(TiCl_3 + InD) + AlEt_2Cl$

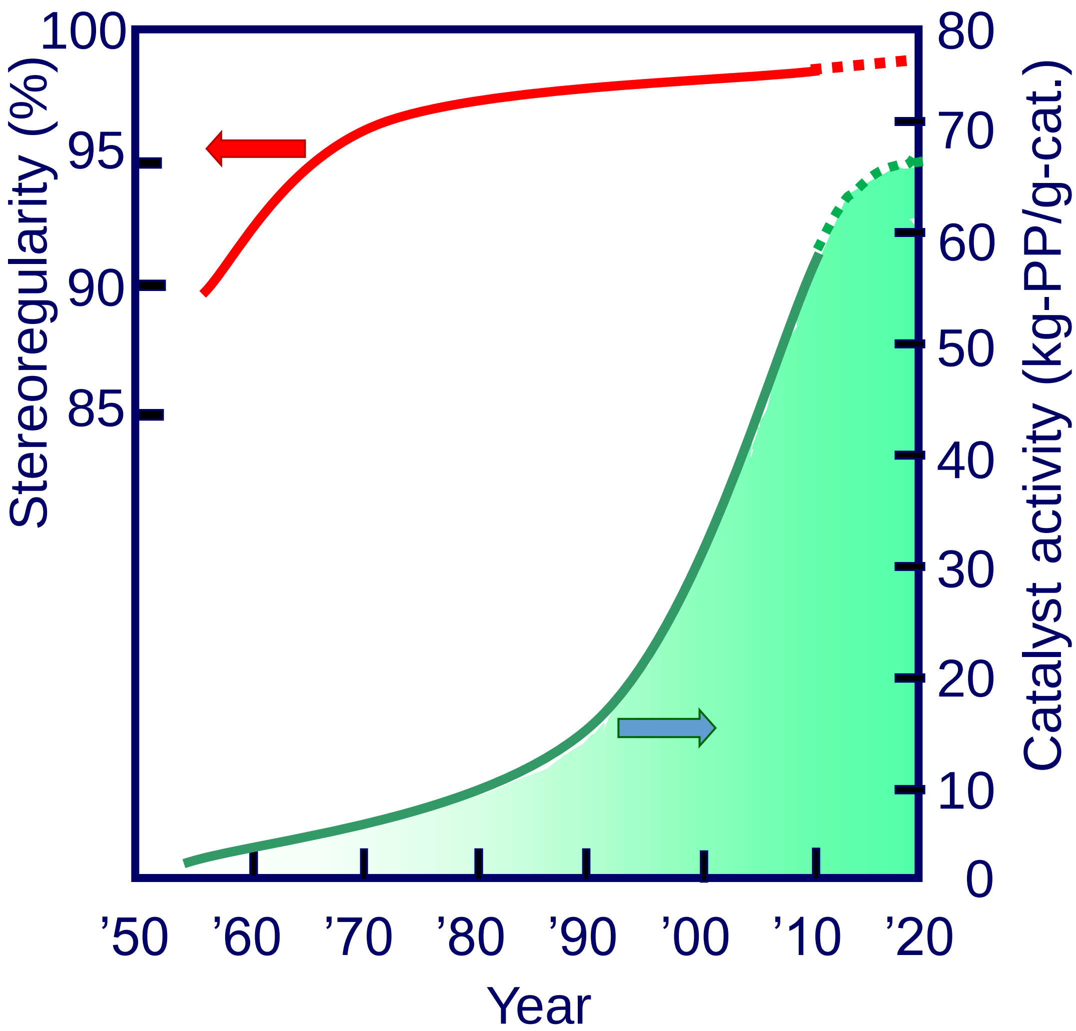
③ Modified $TiCl_3 + AlEt_2Cl$

④ $(TiCl_4$ + Benzoate) / $MgCl_2$ + $(AlEt_3$+ExD)

⑤ $(TiCl_4$ + Phthalate) / $MgCl_2$ + $(AlEt_3$+ExD)

⑥ $(TiCl_4$+Diether) / $MgCl_2$ $+AlEt_3$

⑦ $(TiCl_4$ + Succinate) / $MgCl_2$ + $(AlEt_3$+ExD)



Existing industrial targets for Ziegler-Natta catalysts

· Ultra high activity

· Ultimate isospecificity

· High hydrogen response

· Control of molecular weight distribution

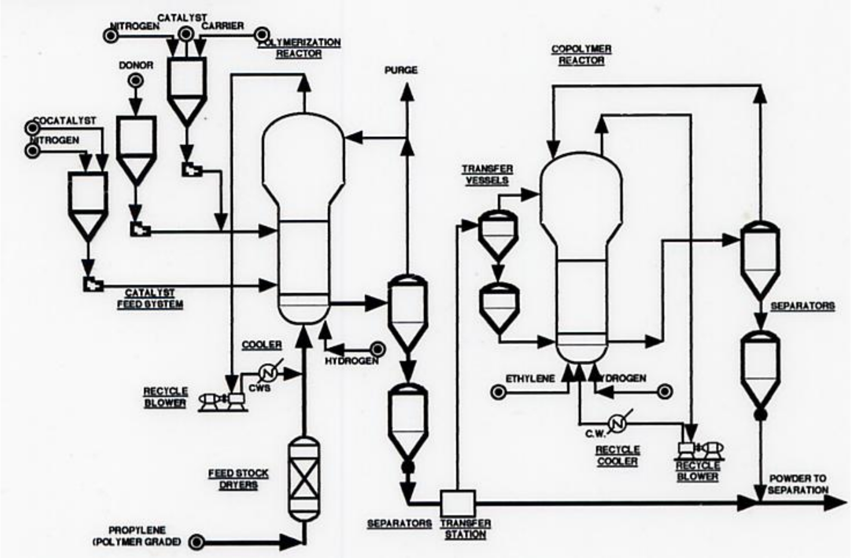
· High comonomer incorporation/distribution

· Control of particle morphology
(shape, size, distribution, B.D. ･･･)

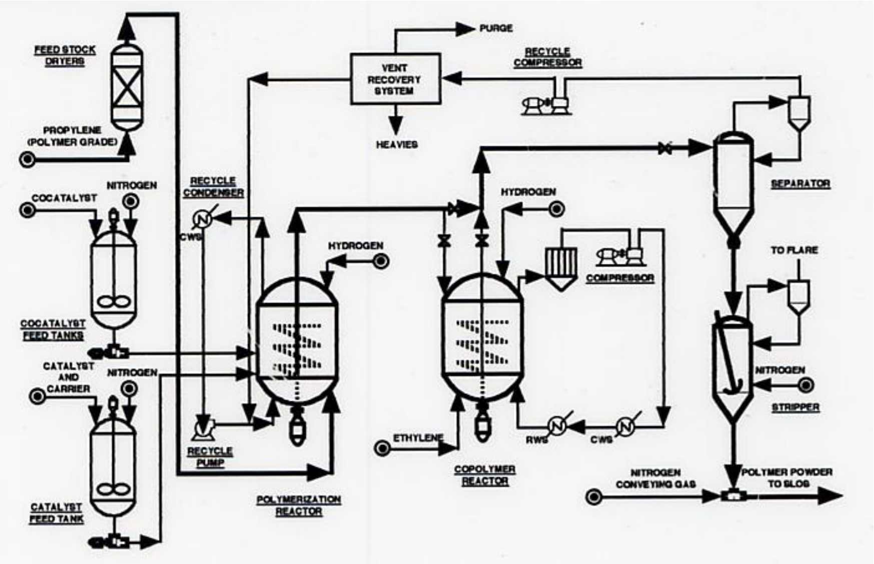
etc.

Gas phase process

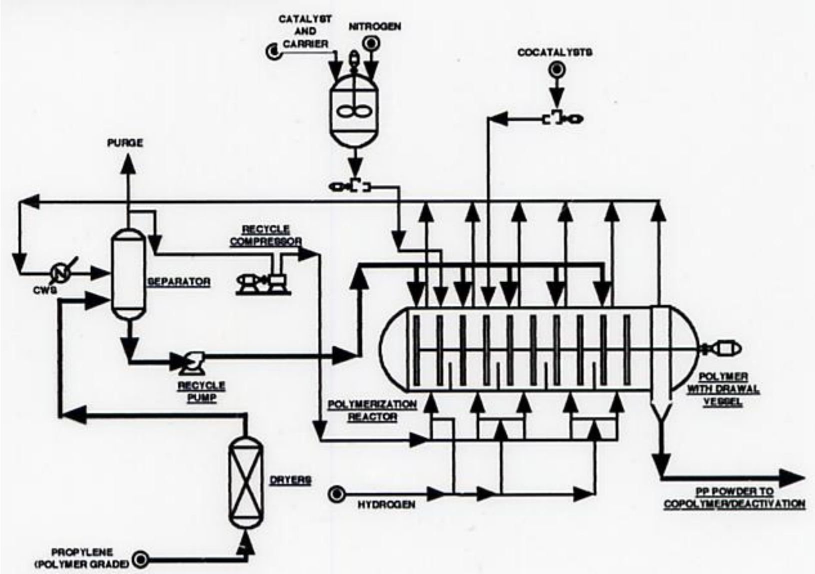
UCC



BASF



Amoco-Chisso



Existing industrial targets for Ziegler-Natta catalysts

· Ultra high activity

· Ultimate isospecificity

· High hydrogen response

· Control of molecular weight distribution

· High comonomer incorporation/distribution

· Control of particle morphology
(shape, size, distribution, B.D. ･･･)

etc.

It is very difficult to achieve these targets without real understanding about the catalysts.

Questions

Main catalyst

- states of Ti species (spatial, molecular)
- structure of active sites
- origin of stereospecificity
- copolymerization ability (difference of C_2' & C_3')
- origin of molecular weight distribution

Cocatalyst

- activation mechanism
- other roles (deactivation, stereospecificity, etc.)

Donor

- stereospecificity improvement mechanism
- other roles (H_2 response, MWD, etc.)

Polymerization

- propagation mechanism
- chain transfer mechanism
- decay mechanism

Existing industrial targets for Ziegler-Natta catalysts

- **Ultra high activity**
- **Ultimate isospecificity**
- **High hydrogen response**
- **Control of molecular weight distribution**
- **High comonomer incorporation/distribution**
- **Control of particle morphology (shape, size, distribution, B.D. ・・・)**

etc.

⇩

Need the innovation to the next generation catalysts !

Design of next generation catalysts

Micro

Active sites

- **Structure**
- **States**

etc.

Catalyst preparation method

Donor system

Macro

Particle

- **Shape / Structure**
- **Size / Distribution**

etc.

⇨ **For the innovation to the next generation Ziegler-Natta catalysts, the total design of active sites and catalyst particle should be achieved.**

Design of next generation catalysts

Micro

Active sites

- **Structure**
- **States**

isolated / clustered (coagulation)

Catalyst preparation method

Donor system

Macro

Particle

- **Shape / Structure**
- **Size / Distribution**

etc.

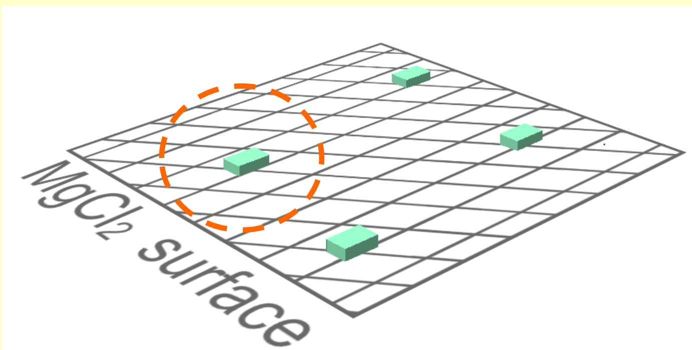
⇨ **For the innovation to the next generation Ziegler-Natta catalysts, the total design of active sites and catalyst particle should be achieved.**

Model catalyst-1 ($TiCl_3/MgCl_2$)

$$MgCl_2 + TiCl_3 \cdot 3Py \xrightarrow{AlEt_2Cl} TiCl_3/MgCl_2$$

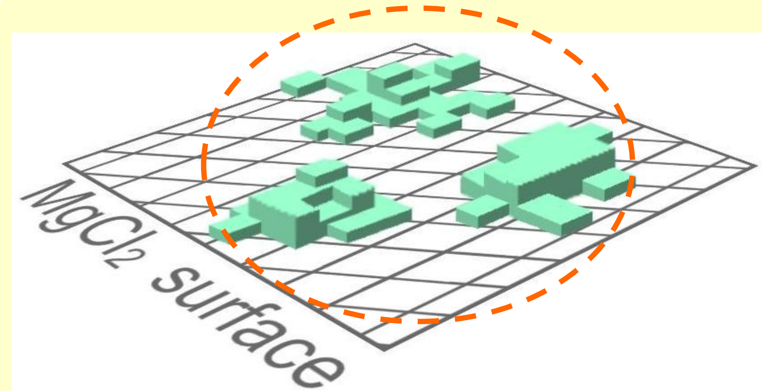
K. Soga, M. Terano, *et al. Makromol. Chem.* **1981**, *182*, 2439
T. Shiono, K. Soga, *et al. Polymer Bulletin* **1989**, *21*, 19

Isolated



Low Ti content

Clustered (Coagulated)



high Ti content

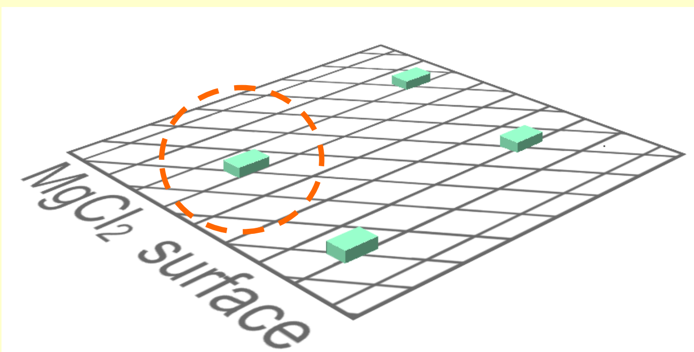
An uniform dispersion of $TiCl_3$ on $MgCl_2$ can be achieved using $TiCl_3 \cdot 3Py$ molecular precursor.

The dispersion states of $TiCl_3$ (isolated or clustered) are easily controlled by varying the Ti content.

Model catalyst-2 ($Cp_xTiCl_{4-x}/MgCl_2$)

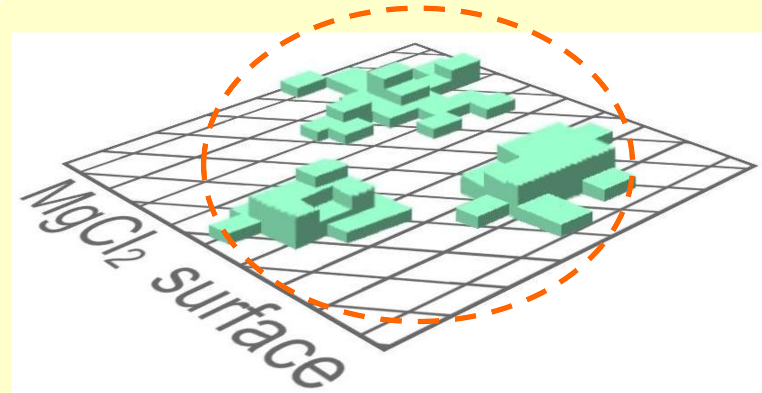
$MgCl_2$ + Cp_xTiCl_{4-x} $\xrightarrow{\text{co-milling}}$ $Cp_xTiCl_{4-x}/MgCl_2$

Isolated



Low Ti content

Clustered (Coagulated)



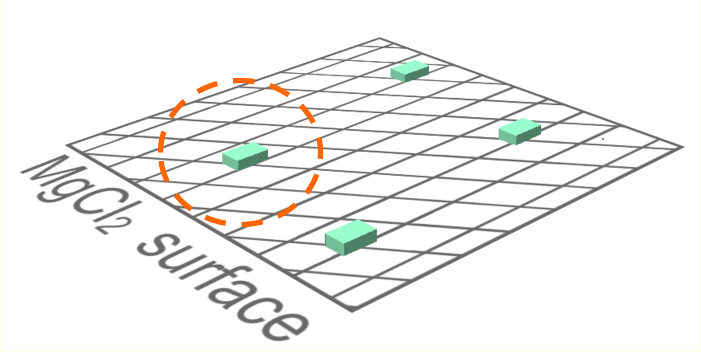
high Ti content

The effects of cluster formation (coagulation) on the isospecificity, activity, decay and copolymerization ability can be clarified by the catalyst.

Model catalyst-2 ($Cp_xTiCl_{4-x}/MgCl_2$)

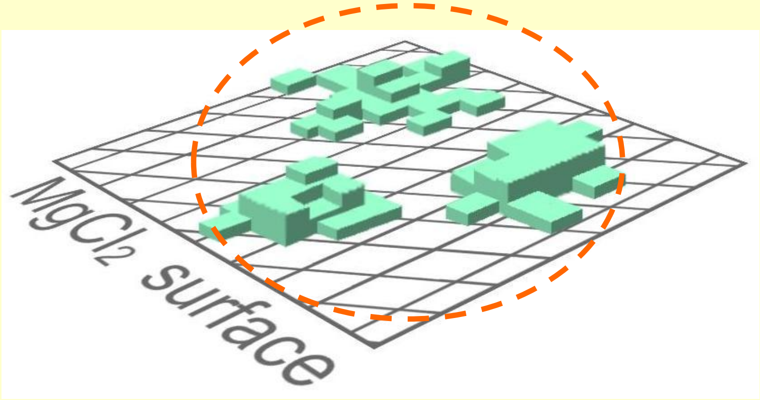
$$MgCl_2 + Cp_xTiCl_{4-x} \xrightarrow{\text{co-milling}} Cp_xTiCl_{4-x}/MgCl_2$$

Isolated



Low Ti content

Clustered (Coagulated)



high Ti content

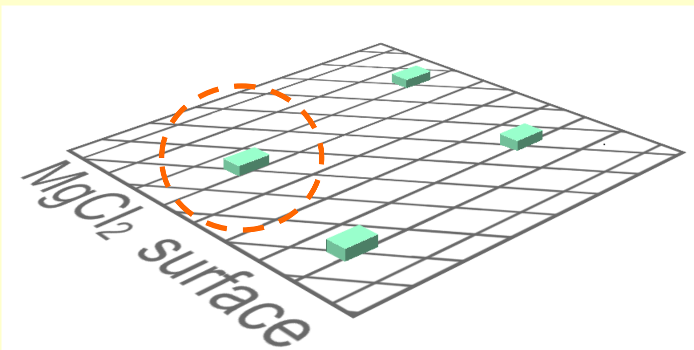
The effects of cluster formation (coagulation) on the isospecificity, activity, decay and copolymerization ability can be clarified by the catalyst.

Model catalyst-1 ($TiCl_3/MgCl_2$)

$$MgCl_2 + TiCl_3 \cdot 3Py \xrightarrow{AlEt_2Cl} TiCl_3/MgCl_2$$

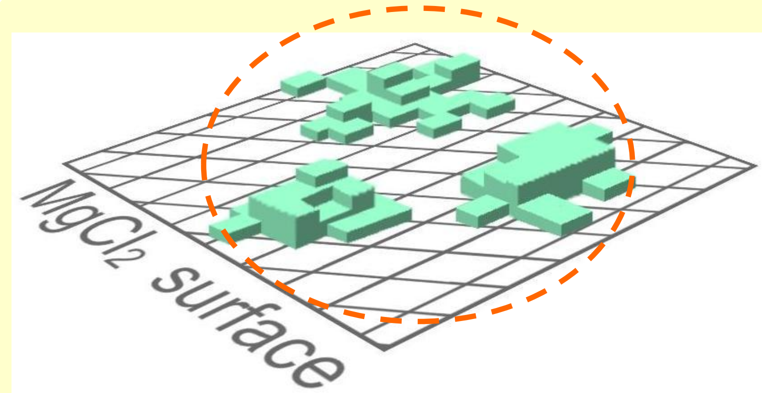
K. Soga, M. Terano, *et al. Makromol. Chem.* **1981**, *182*, 2439
T. Shiono, K. Soga, *et al. Polymer Bulletin* **1989**, *21*, 19

Isolated



Low Ti content

Clustered (Coagulated)



high Ti content

An uniform dispersion of $TiCl_3$ on $MgCl_2$ can be achieved using $TiCl_3 \cdot 3Py$ molecular precursor.

The dispersion states of $TiCl_3$ (isolated or clustered) are easily controlled by varying the Ti content.

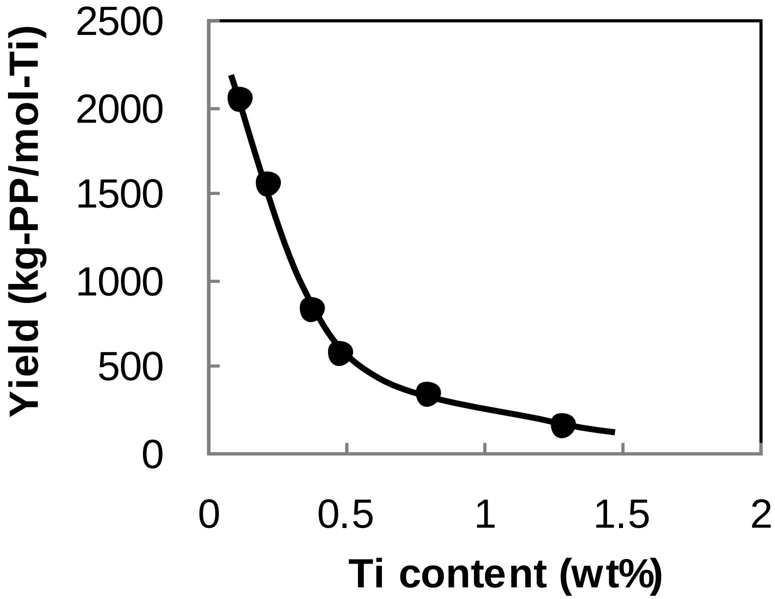
Typical catalyst preparation results

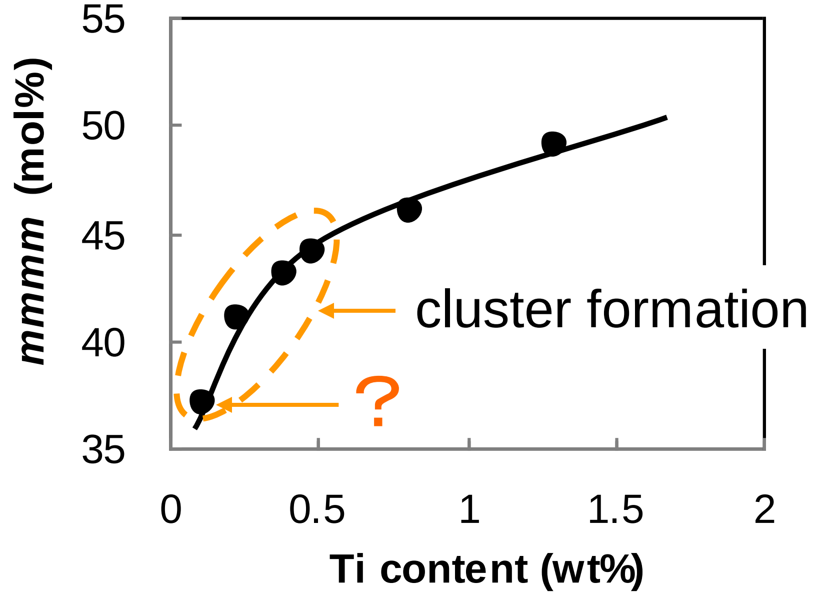
$MgCl_2$ (g)	$TiCl_3 \cdot 3Py$ (mg)	Et_2AlCl (mmol)	Al/Py (mol/mol)	Ti (wt%)
5	500	45	11.8	0.92
5	50	4.5	11.8	0.083
10	20	1.8	11.8	0.018

Ti contents can be controlled in a quite wide range.

Effects of Ti content

(Slurry polymerization, 30°C, 30min)

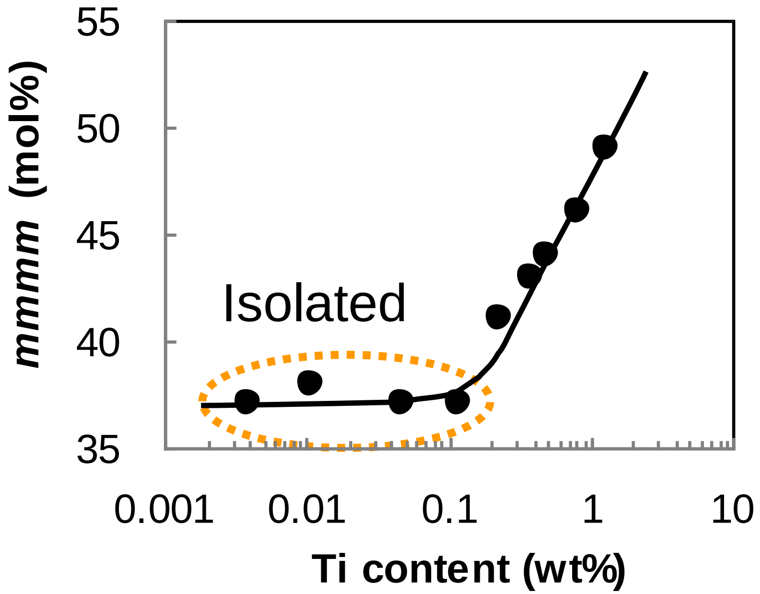


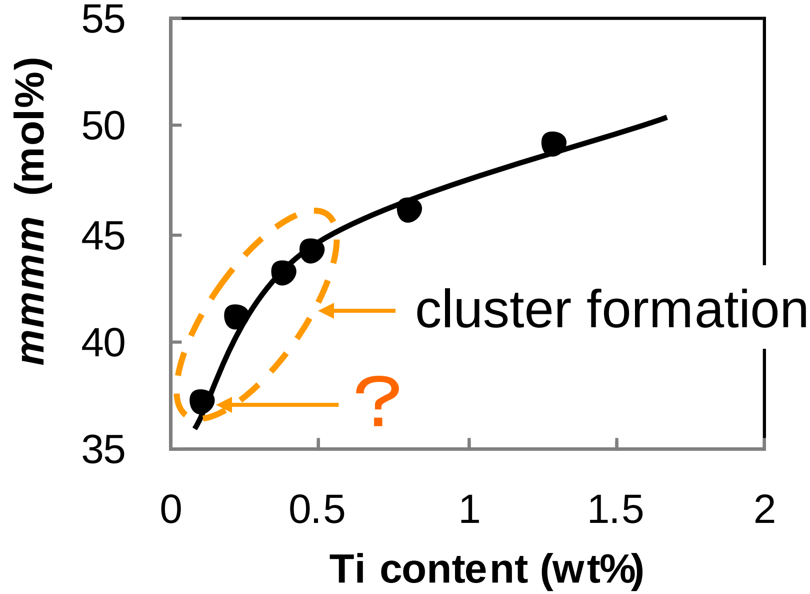


Low Ti content	→	high activity per Ti low stereospecific	→	isolated, monolayer
High Ti content	→	low activity per Ti high stereospecific	→	clustered, multilayer

Effects of Ti content

(Slurry polymerization, 30°C, 30min)

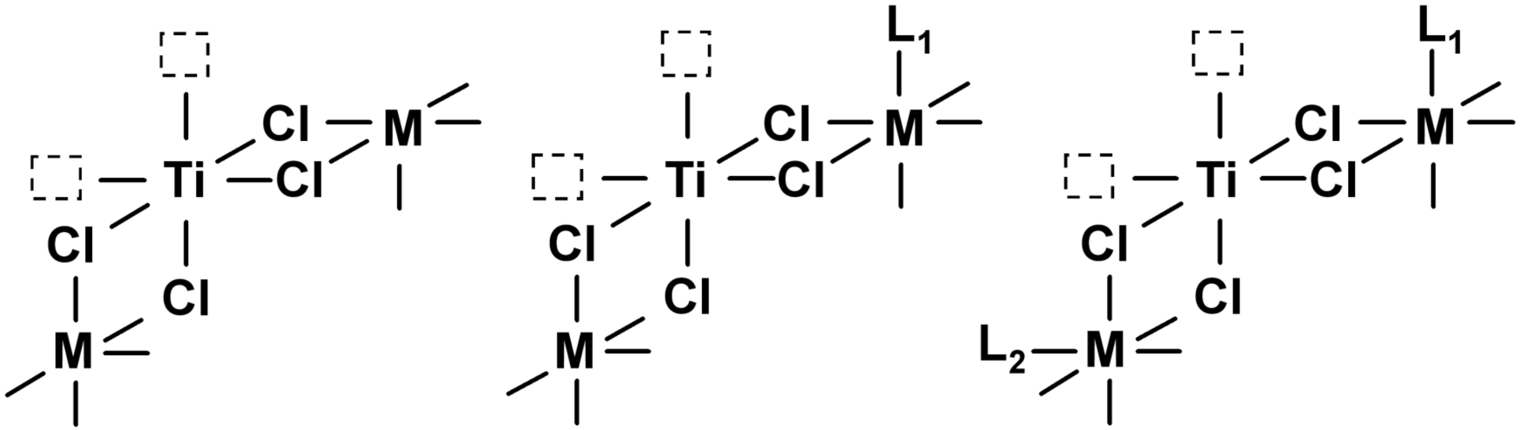




Low Ti content → high activity per Ti, low stereospecific → isolated, monolayer

The isospecificity of the isolated $TiCl_3$ single molecule supported on $MgCl_2$ was found to be 37%.

Three-sites and modified three-sites models



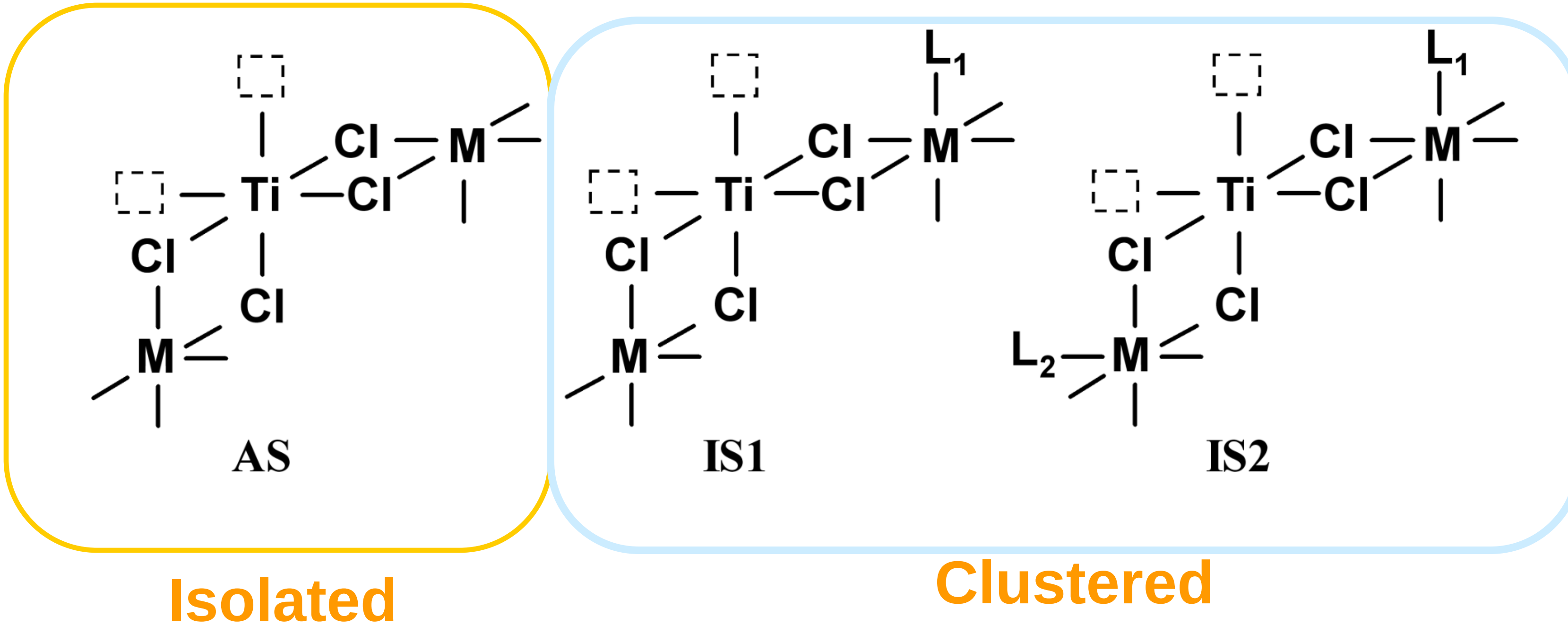
AS IS1 IS2

M: Ti, Mg or Al, and L: Cl, ethyl group, or donor

V. Busico, R. Cipullo, G. Monaco, G. Talarico, M. Vacatello, J. C. Chadwick, A. L. Segre, O. Sudmeijer, *Macromolecules* **1999**, *32*, 4173.
B. Liu, T. Nitta, H. Nakatani, M. Terano, *Macromol. Chem. Phys.* **2002**, *203*, 2412.

AS, IS1 and IS2 are considered to produce atactic (or syndiotactic), isotactoid and isotactic sequences, respectively.

Three-sites and modified three-sites models



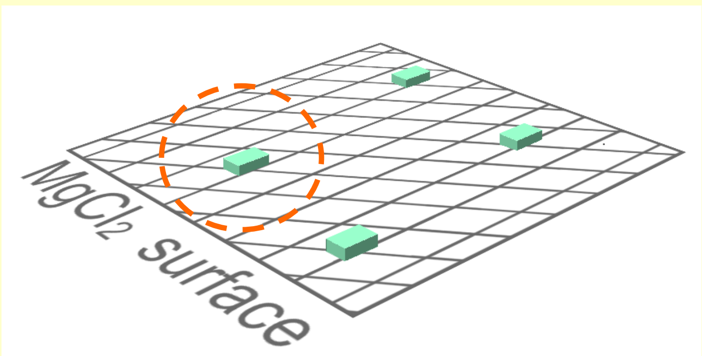
M: Ti, Mg or Al, and L: Cl, ethyl group, or donor

Either or both of L_1 or/and L_2 are mostly occupied by Cl for clustered $TiCl_3$ species, leading to the isospecific nature of active sites.

Model catalyst-2 ($Cp_xTiCl_{4-x}/MgCl_2$)

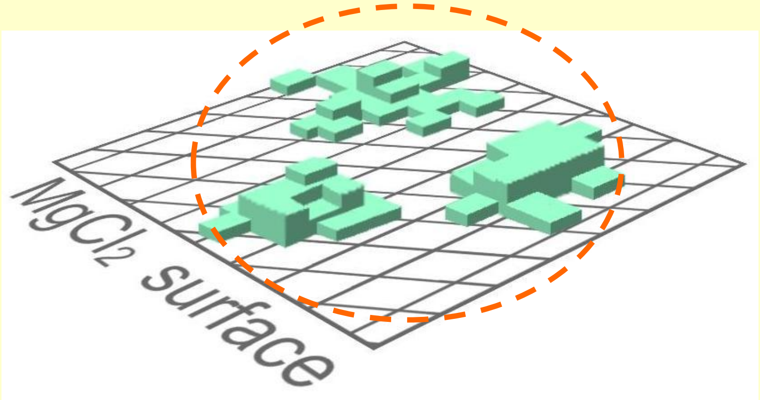
$$MgCl_2 + Cp_xTiCl_{4-x} \xrightarrow{\text{co-milling}} Cp_xTiCl_{4-x}/MgCl_2$$

Isolated



Low Ti content

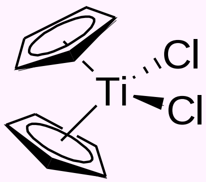
Clustered (Coagulated)



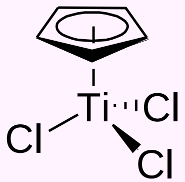
high Ti content

The effects of cluster formation (coagulation) on the isospecificity, activity, decay and copolymerization ability can be clarified by the catalyst.

Model catalyst-2 ($Cp_xTiCl_{4-x}/MgCl_2$)



titanocene



half-titanocene

Single-site nature of these complexes enables

- to suppress the formation of Ti clusters by bulky ligands
- to change steric and electronic environments of the Ti center
- to clarify effects of immobilization on $MgCl_2$

Direct information on the effects of coagulation of Ti species can be obtained.

Catalyst preparation

co-grinding method (G)

$MgCl_2$ (42 mmol)

← Cp_2TiCl_2, $CpTiCl_3$, $TiCl_4$ (0.3 mmol)

ball milling r.t., 40 h

washing toluene

↓

$Cp_2TiCl_2/MgCl_2$(G) (Ti:0.085 wt%)
$CpTiCl_3/MgCl_2$ (G) (Ti:0.075 wt%)
$TiCl_4/MgCl_2$ (G) (Ti:0.64 wt%)

alkylaluminum method (A)*

$MgCl_2$ (54.6 mmol)

← toluene

← $AlEt_3$ (21 mmol)

← Cp_2TiCl_2, $CpTiCl_3$, $TiCl_4$ (0.6 mmol)

stirring r.t., 10 min

washing toluene

↓

$Cp_2TiCl_2/MgCl_2$(A) (Ti:0.067 wt%)
$CpTiCl_3/MgCl_2$ (A) (Ti:0.28 wt%)
$TiCl_4/MgCl_2$ (A) (Ti:0.54 wt%)

*M. Kaminaka, K. Soga, *Makromol. Chem., Rapid Commun.* **1991**, *12*, 367

Polymerization

Toluene
(total slurry volume = 200 mL)

$AlEt_3$ (TEA) or MMAO
([Al] = 10, 20 mmol·L^{-1})

Propylene at 5 atm

Catalyst slurry
([Ti] = 2.0 x 10^{-2}, 4.0 x 10^{-2} mmol·L^{-1})

Polymerization
(40ºC, 5 atm, 30 min)

Polymerization results

co-grinding method (G)

Catalyst	Activator	Activity[a]	*mmmm*[b]	*rrrr*[b]
$Cp_2TiCl_2/MgCl_2$	MMAO	77.7	1.8	10.5
	TEA	9.1	48.8	3.7
$CpTiCl_3/MgCl_2$	MMAO	76.3	2.1	10.5
	TEA	6	43.9	5.3
$TiCl_4/MgCl_2$	MMAO	670	42.0	5.7
	TEA	824	45.6	6.9
Cp_2TiCl_2	MMAO	56.9	1.5	11.2
$CpTiCl_3$	MMAO	11.7	1.4	9.6

[a] $kg\text{-}PP \cdot mol\text{-}Ti^{-1} \cdot atm^{-1} \cdot h^{-1}$ [b] mol%

$Cp_xTiCl_{4-x}/MgCl_2$(G) combined with MMAO show almost the same stereospecificity as unsupported Ti species with activity enhancement.

But, $Cp_xTiCl_{4-x}/ MgCl_2$(G) combined with TEA changed the stereospecificity into isospecific with activity decrease because of coagulation.

Polymerization results

co-grinding method (G)

Catalyst	Activator	Activity[a]	*mmmm*[b]	*rrrr*[b]
$Cp_2TiCl_2/MgCl_2$	MMAO	77.7	1.8	10.5
	TEA	9.1	48.8	3.7
$CpTiCl_3/MgCl_2$	MMAO	76.3	2.1	10.5
	TEA	6	43.9	5.3
$TiCl_4/MgCl_2$	MMAO	670	42.0	5.7
	TEA	824	45.6	6.9
Cp_2TiCl_2	MMAO	56.9	1.5	11.2
$CpTiCl_3$	MMAO	11.7	1.4	9.6

[a] $kg\text{-}PP \cdot mol\text{-}Ti^{-1} \cdot atm^{-1} \cdot h^{-1}$ [b] mol%

$Cp_xTiCl_{4-x}/MgCl_2$(G) combined with MMAO show almost the same stereospecificity as unsupported Ti species.

But, $Cp_xTiCl_{4-x}/ MgCl_2$(G) combined with TEA has the isospecific nature because of the coagulation of Ti species.

Polymerization results

alkylaluminum method (A)

Catalyst	Activator	Activity[a]	*mmmm*[b]	*rrrr*[b]
$Cp_2TiCl_2/MgCl_2$	MMAO	42.6	3.1	10.2
	TEA	33.8	48.2	4.2
$CpTiCl_3/MgCl_2$	MMAO	74.4	41.6	6.4
	TEA	61.2	49.5	6.1
$TiCl_4/MgCl_2$	MMAO	142.2	41.5	7.4
	TEA	98.4	39.2	7.8
Cp_2TiCl_2	MMAO	56.9	1.5	11.2
$CpTiCl_3$	MMAO	11.7	1.4	9.6

[a] $kg\text{-}PP \cdot mol\text{-}Ti^{-1} \cdot atm^{-1} \cdot h^{-1}$ [b] mol%

$Cp_2TiCl_2/MgCl_2$ combined with MMAO has the same non-isospecific character as the catalyst prepared by the method (G).

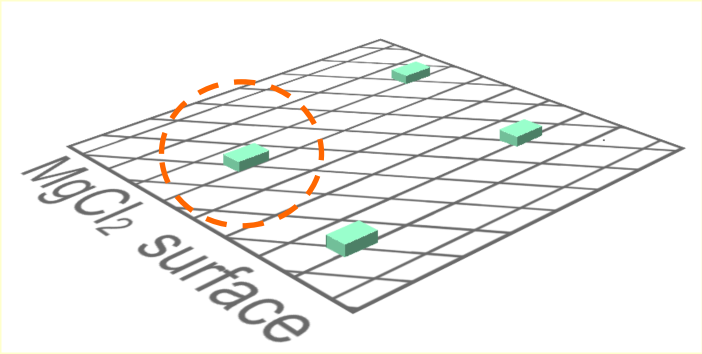
The other catalysts including $CpTiCl_3/MgCl_2$ have the isospecific character because of the coagulation.

Model catalysts ($TiCl_3/MgCl_2$, $Cp_xTiCl_{4-x}/MgCl_2$)

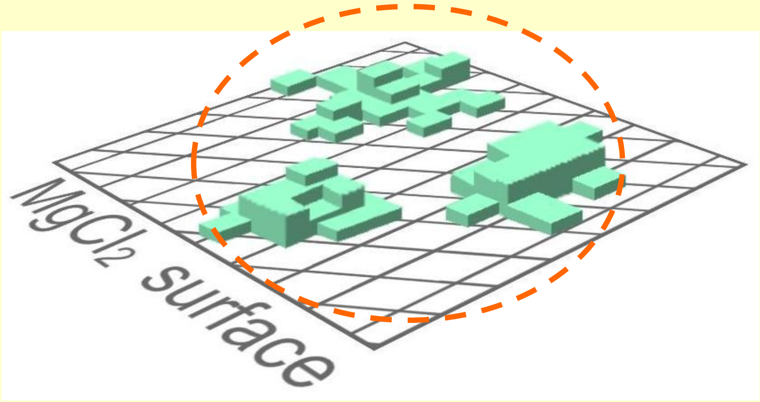
$$MgCl_2 + TiCl_3 \cdot 3Py \xrightarrow{AlEt_2Cl} TiCl_3/MgCl_2$$

$$MgCl_2 + Cp_xTiCl_{4-x} \xrightarrow{\text{co-milling}} Cp_xTiCl_{4-x}/MgCl_2$$

Isolated



Clustered (Coagulated)



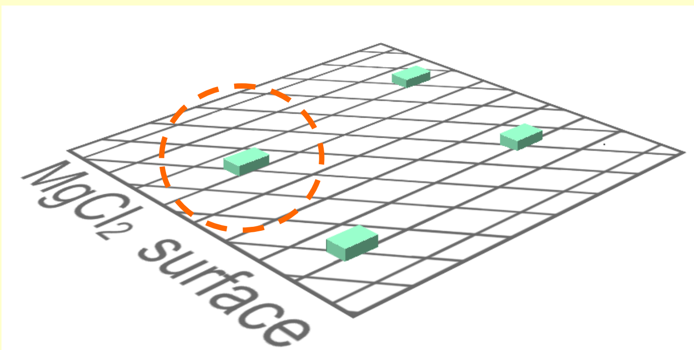
The isospecific nature of active sites was found to be created by the cluster formation (coagulation) of the Ti species on $MgCl_2$.

Model catalysts ($TiCl_3/MgCl_2$, $Cp_xTiCl_{4-x}/MgCl_2$)

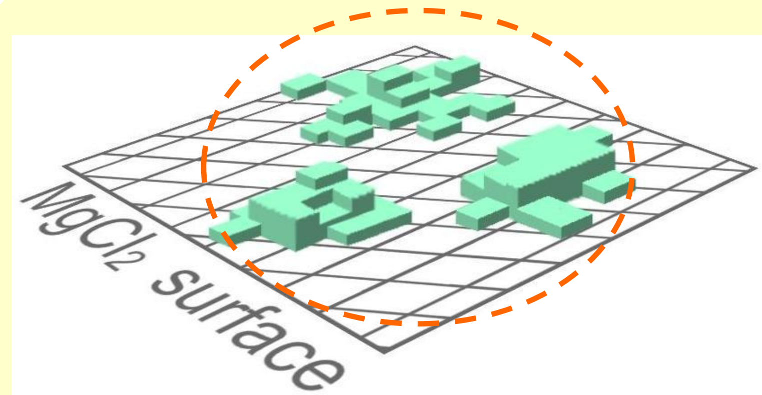
$MgCl_2$ + $TiCl_3 \cdot 3Py$ $\xrightarrow{AlEt_2Cl}$ $TiCl_3/MgCl_2$

$MgCl_2$ + Cp_xTiCl_{4-x} $\xrightarrow{\text{co-milling}}$ $Cp_xTiCl_{4-x}/MgCl_2$

Isolated



Clustered (Coagulated)



The isospecific nature of active sites was found to be created by the cluster formation (coagulation) of the Ti species on $MgCl_2$.

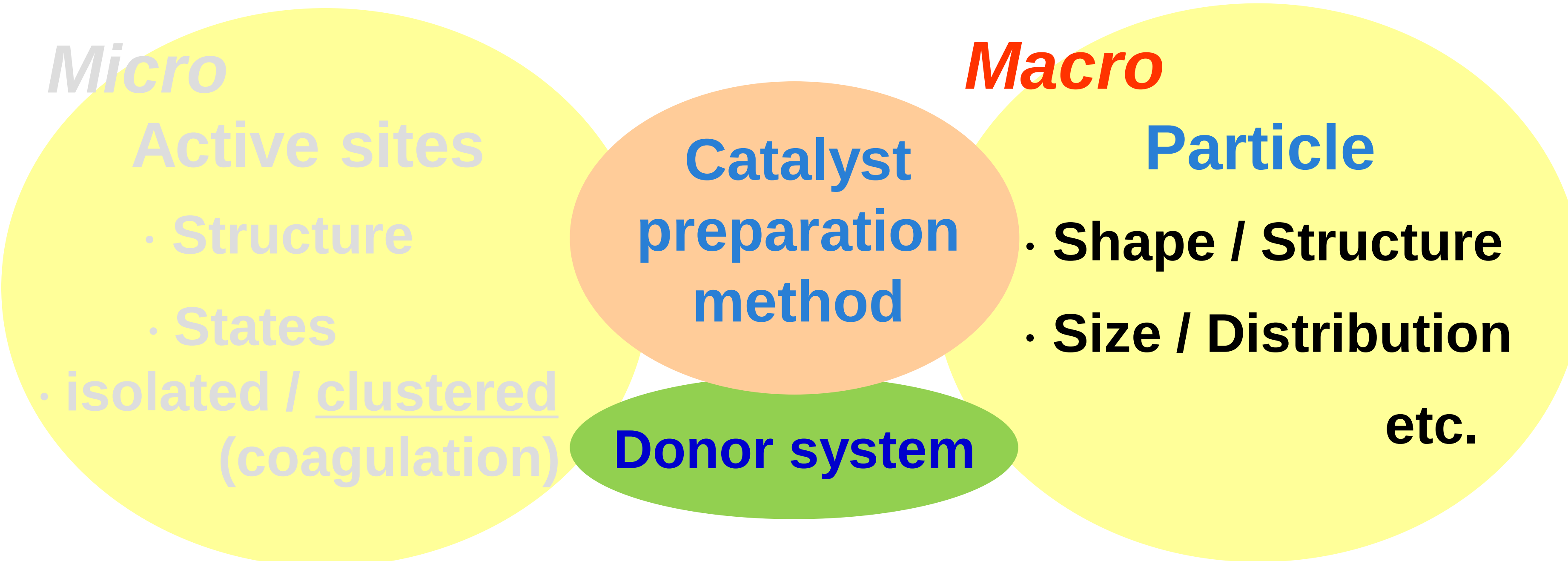
(Experimental confirmation of 3-site model)

Poster 6

Propylene Polymerization with Ziegler-Natta Model Catalysts Having $MgCl_2$-Supported Titanocene

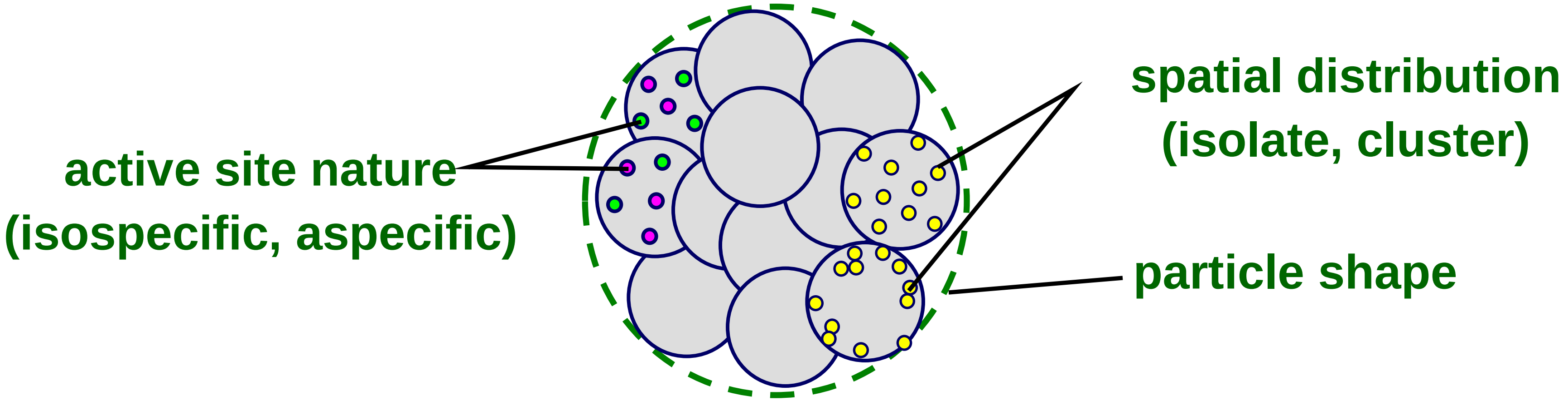
K. Goto, T. Taniike, M. Terano

Design of next generation catalysts



⇨ **For the innovation to the next generation Ziegler-Natta catalysts, the total design of active sites and catalyst particle should be achieved.**

Catalyst particle



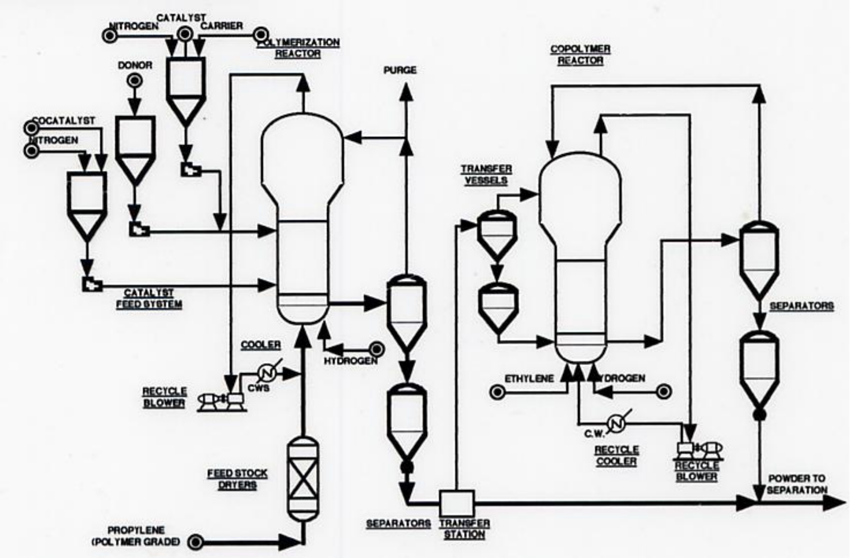
It is not clear how the catalyst preparation method affects the specific catalyst properties.

⇩

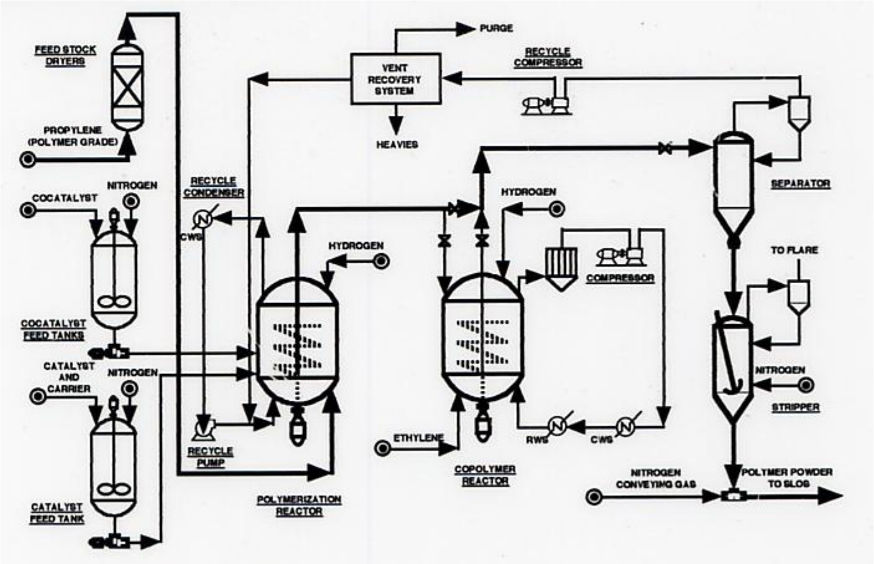
Investigation of the effects of catalyst preparation method on the particle is necessary.

Gas phase process

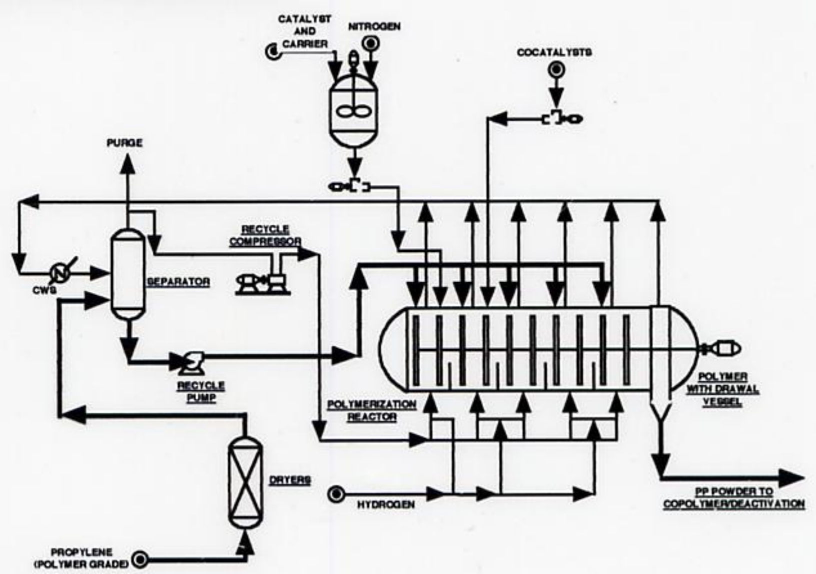
UCC



BASF

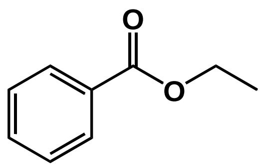


Amoco-Chisso

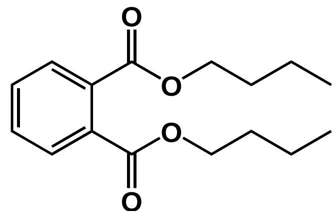


Catalyst preparation

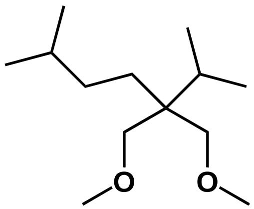
InD



Ethylbenzoate (**EB**)



di-*n*-butylphtalate (**DBP**)



2-isopentyl-2-isopropyl-1,3-dimethoxypropane (**DE**)

- **Grinding method**

$$(MgCl_2 + InD)_{grinding} + TiCl_4 \longrightarrow$$

Mitsui PetroChemicals (1974)

Cat-G (EB)
Cat-G (DBP)
Cat-G (DE)

- **Chemical reaction method**

$$Mg(OEt)_2 + InD + TiCl_4 \longrightarrow$$

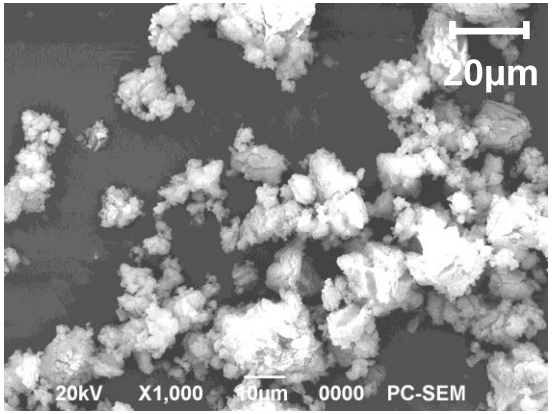
Toho Titanium (1987)

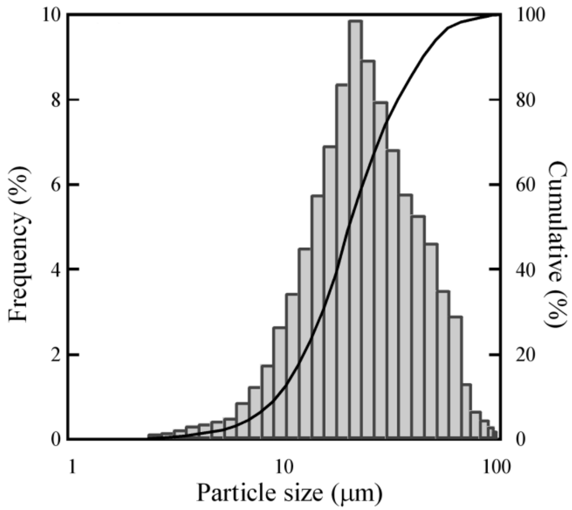
Cat-C (EB)
Cat-C (DBP)
Cat-C (DE)

Catalyst morphology (SEM image and PSD*)

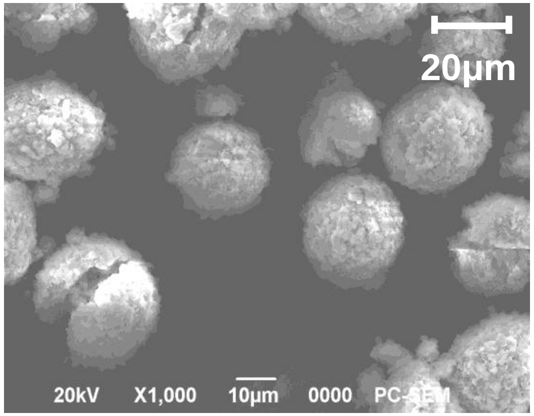
*PSD : particle size distribution

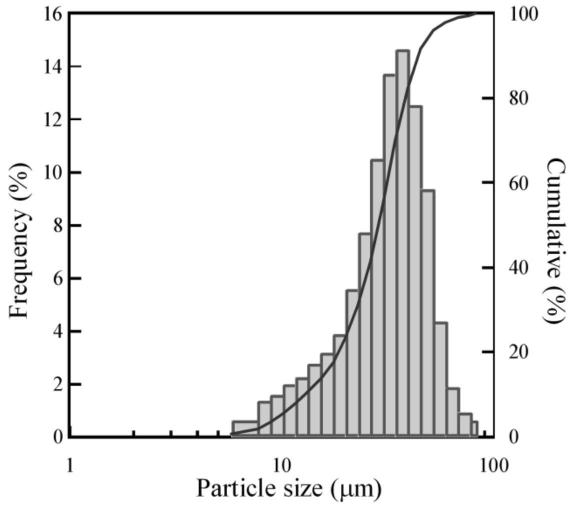
Cat-G





Cat-C



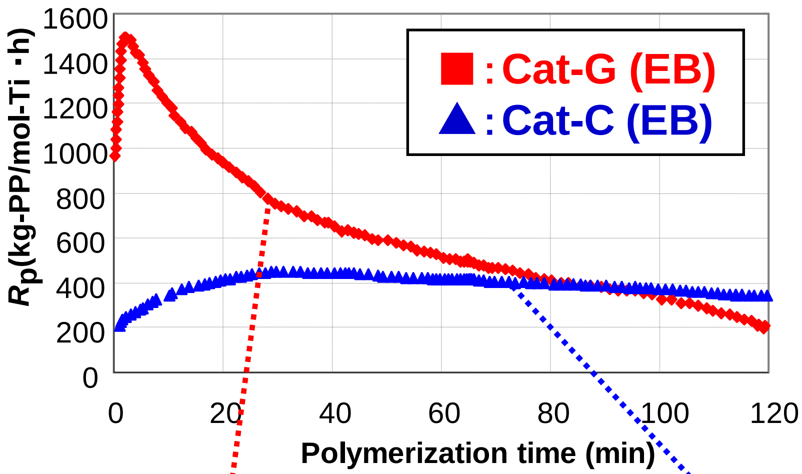


Cat-G : irregular shape with a broad PSD

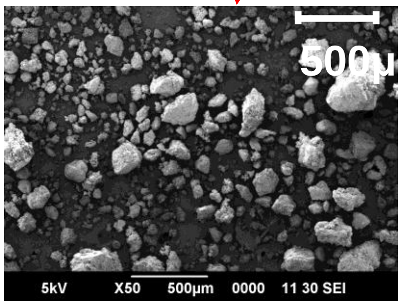
Cat-C : mostly spherical with a narrower PSD

A. Dashti, T. Taniike, M. Terano, et al., *Macromol. Symp,* **2009**, *285*, 52

Polymerization kinetics and resulting morphology

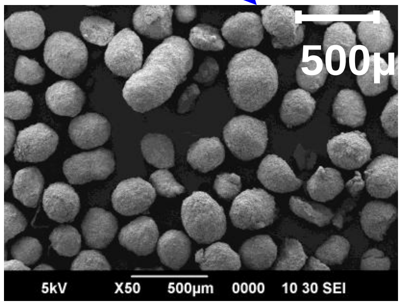


PP(Cat-G)

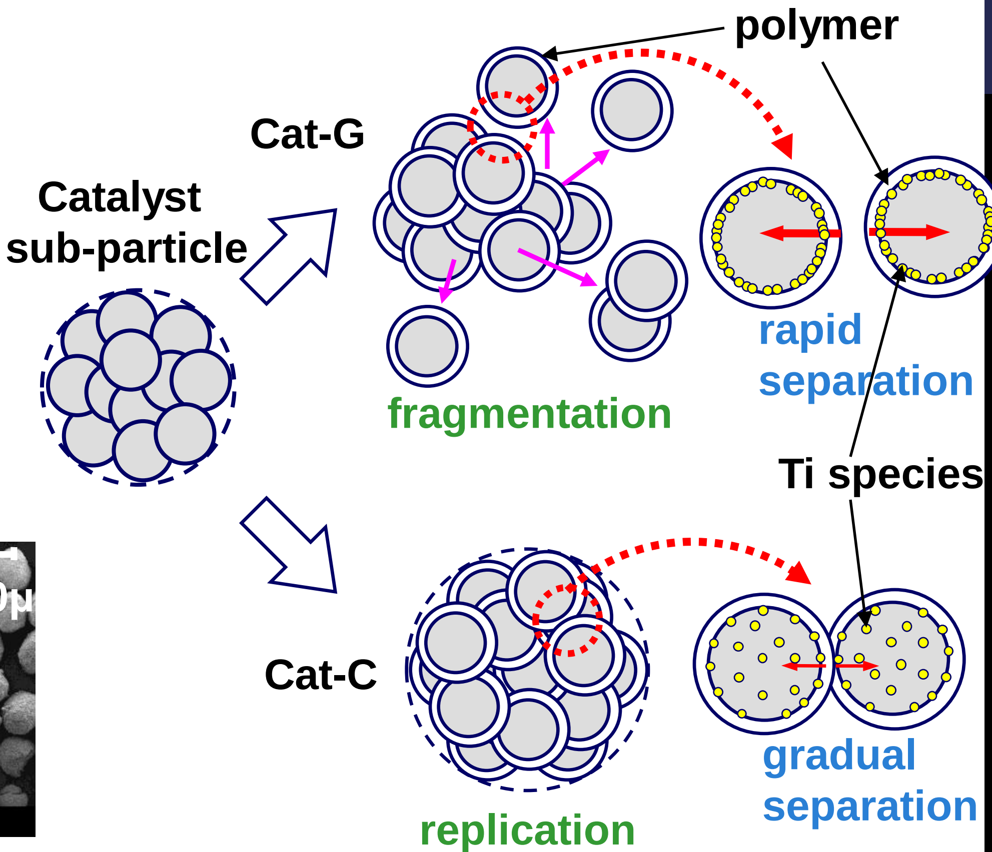


0.42 kg-PP/g-cat·h·bar

PP(Cat-C)



0.26 kg-PP/g-cat·h·bar



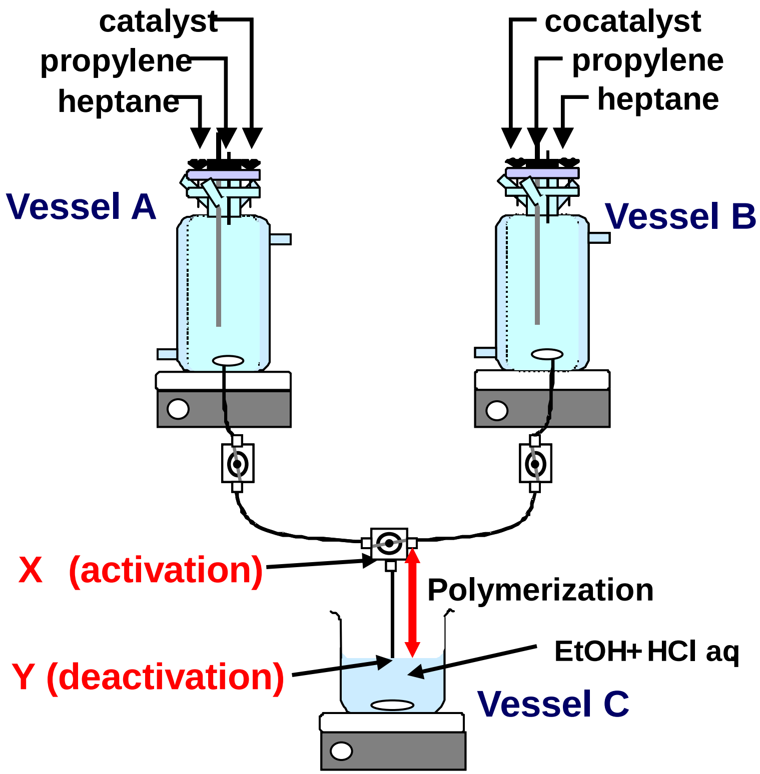
Cat-G : High initial activity and rapid decay with hard fragmentation

⇒ Ti species are relatively localized on the sub-particle surface.

Cat-C : Gradual separation and homogeneous particle growth

⇒ Ti species are relatively dispersed in the whole particle.

Stopped-flow polymerization

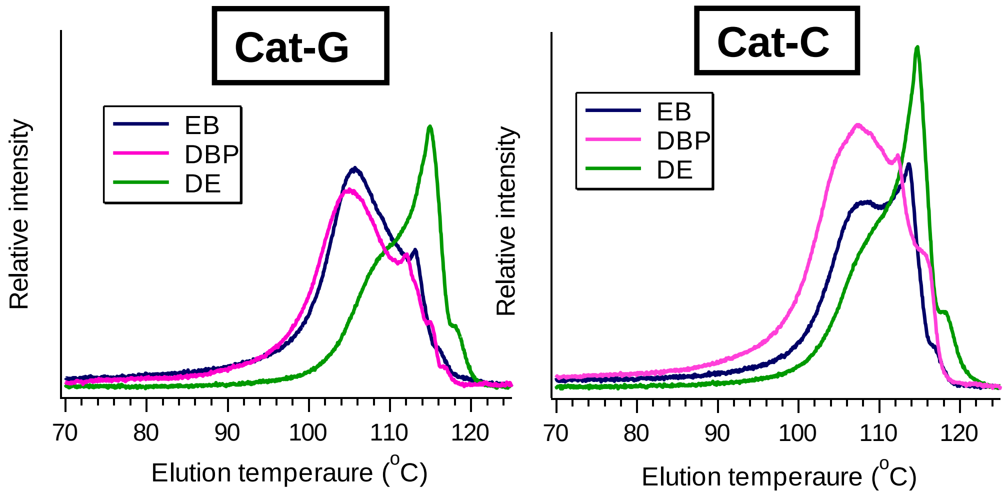


Polymerization proceeds within an extremely short period (ca. 0.1s) in the teflon tube from the point X to the point Y.

H. Mori, and M. Terano, *Trends Polym.* **1997**, *5*, 314

TREF analysis

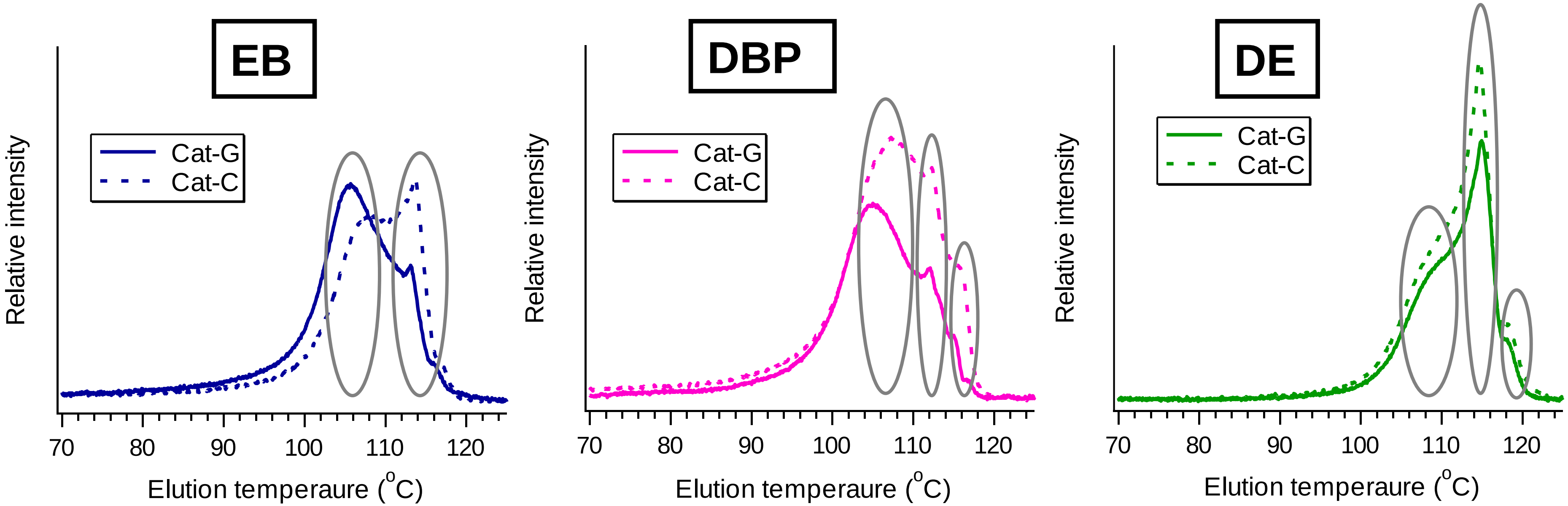
Elution peaks reflect each microstructure of PPs, that is, the stereospecificity of active sites.



The isospecificities of the catalysts with the same InD are clearly dominated by the preparation method.

TREF analysis

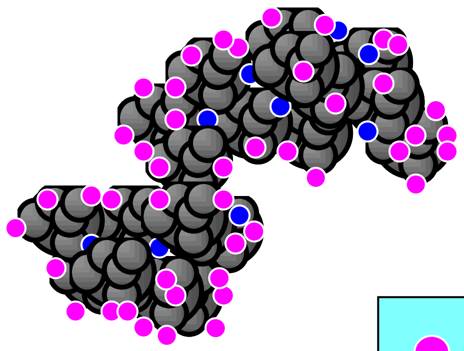
Elution peaks of TREF reflect each microstructure of PPs, that is, the stereospecificity of active sites.



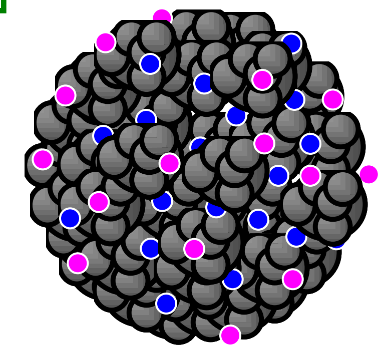
The variation of active sites existing on Cat-G and Cat-C are quite similar for each donor, but their existing ratio is greatly different for each preparation method.

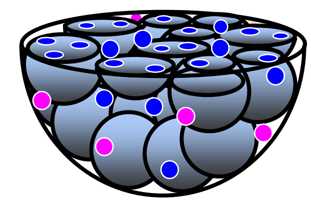
Plausible models of the particles

Cat-G



Cat-C

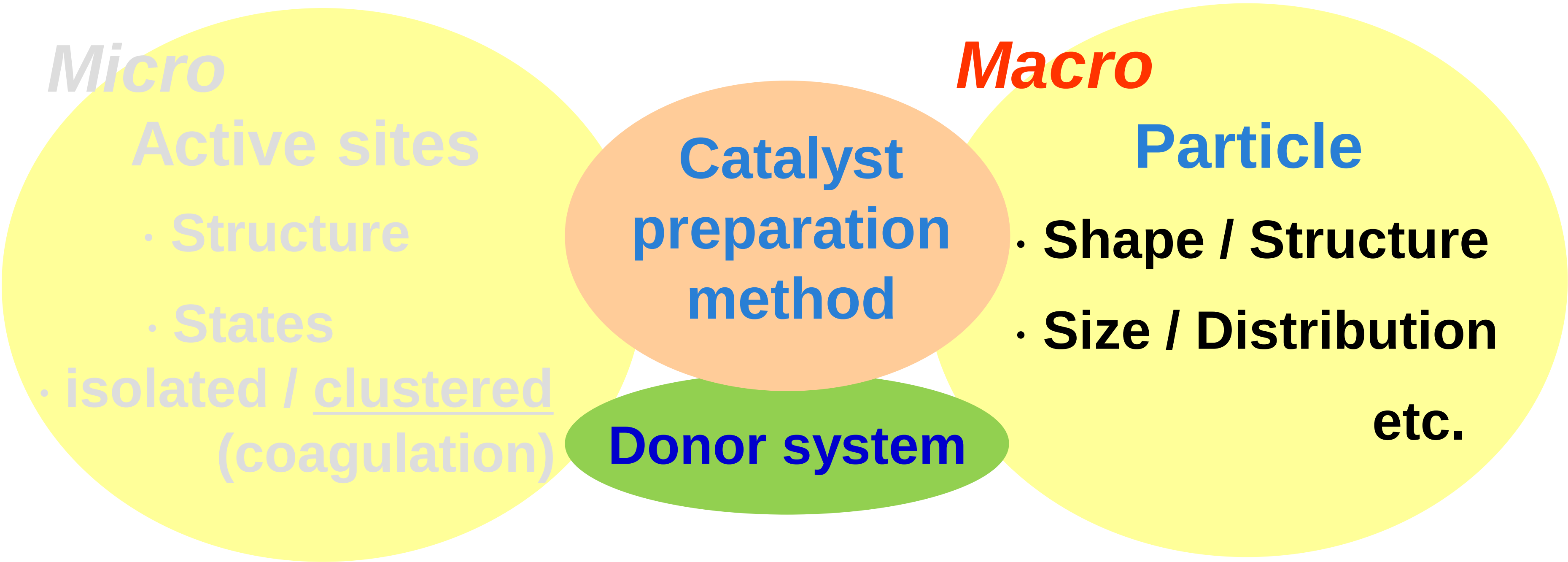




- Exposed Ti species
- Hidden Ti species
- $MgCl_2$ primary particle

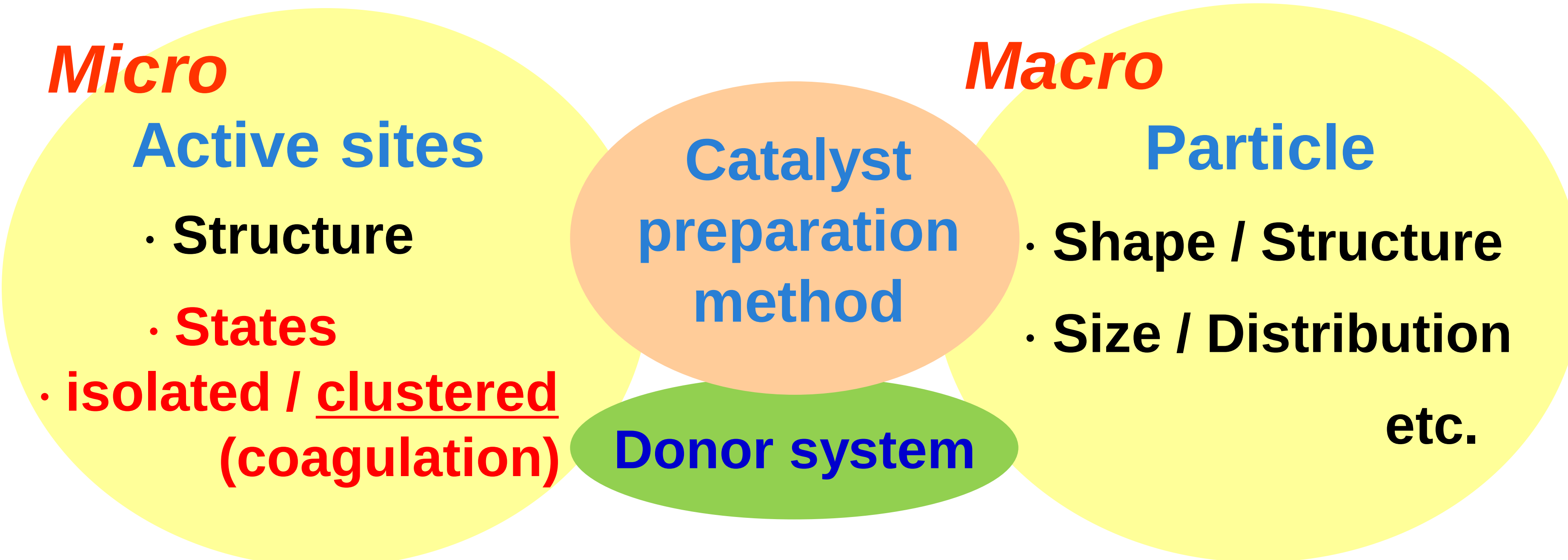
- The preparation method affected the spatial distribution and the existing ratio of Ti species as well as the types of active sites on the catalyst.
- The internal donor dominantly affected the active sites nature as well as the total isospecificity of the catalyst.

Design of next generation catalysts



The catalyst preparation method dominates not only the particle morphology but also the catalyst properties. The total catalyst performance was determined by the states of active sites and their existing ratio, originated by the catalyst preparation method and donor system.

Design of next generation catalysts



The important aspects for the design of next generation catalysts were obtained from the combination of micro-scopic and macro-scopic studies using model catalysts and typical industrial catalysts.

8th International Colloquium on Heterogeneous Ziegler-Natta Catalysts

Kanazawa, Japan
March 27～30, 2012

Kanazawa Station

Kanazawa

Kenroku Garden

Kanazawa Castle

Contact to
terano@jaist.ac.jp

Thank you very much !!

for the beautiful future