

Active site nature of magnesium dichloride-supported titanocene catalysts in olefin polymerization

Toshiaki Taniike, Keisuke Goto, Minoru Terano*

School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

Received: 17 November 2014, Accepted: 19 December 2014

ABSTRACT

Heterogeneous Ziegler-Natta and homogeneous metallocene catalysts exhibit greatly different active site nature in olefin polymerization. In our previous study [1], it was reported that MgCl_2 -supported titanocene catalysts can generate both Ziegler-Natta-type and metallocene-type active sites according to the type of activators. The dual active site nature of the supported titanocene catalysts was further explored in the present study: The influence of the ligand structure of titanocene precursors was studied on the nature of active sites when supported on MgCl_2 in ethylene and propylene homopolymerization, and ethylene/1-hexene copolymerization. It was found that the reducibility of titanocene precursors by alkylaluminum is closely related to the appearance of the dual active site nature, while the kind of olefin did not affect the type of active sites formed during polymerization. The Ziegler-Natta-type active sites produced poorly isotactic polypropylene and less branched polyethylene, while the metallocene-type active sites produced atactic polypropylene and exhibited much higher incorporation efficiency for 1-hexene. **Polyolefins J (2015) 2: 57-63**

Keywords: metallocene catalysts; Ziegler-Natta polymerization; poly(propylene) (PP)

INTRODUCTION

Heterogeneous Ziegler-Natta catalysts and group 4 metallocene catalysts are representative catalysts for industrial olefin polymerization processes. After 40 years since the discovery of methylaluminoxane (MAO) [2], the two types of the catalysts are nowadays employed in a way to complement the different product grades of polyolefin. For example, heterogeneous Ziegler-Natta catalysts are responsible for the industrial

production of > 99% of isotactic polypropylene, high-density polyethylene suited for housewares and food containers, and linear low-density polyethylene. On the other hand, metallocene catalysts are used to produce linear-low density polyethylene suited for heat-sealing films, ethylene-propylene and ethylene-propylene-diene rubber, and so on. Such compartmentalization mainly arises from different product properties of polyolefin made by the two types of the catalysts, i.e. different active site nature for the two types of the

* Corresponding Author - E-mail: terano@jaist.ac.jp

catalysts.

Ziegler-Natta catalysts are multi-site catalysts, whose active sites are non-uniform in terms of structures and catalytic performances. Nonetheless, the majority of active sites in Ziegler-Natta catalysts are regarded as neutral Ti(III) species in a pseudo octahedral symmetry [3], which is featured with excellent stereo- and region-specificity in α -olefin polymerization albeit with poor copolymerization properties. On the other hand, group 4 metallocene catalysts are single-site catalysts with cationic M(IV) active species in a pseudo tetrahedral symmetry [4,5]. The metallocene-type active species are characterized with superior copolymerization properties in terms of comonomer insertion efficiency and randomness, while they are at the same time susceptible to frequent stereo- and region-misinsertion [6]. These differences in the active site nature are closely related to the properties of produced polyolefin. For instance, the dominance of Ziegler-Natta catalysts in the production of isotactic polypropylene is mainly ascribed by a higher melting point of polypropylene based on a longer isotactic sequence [6]. The single-site nature of metallocene catalysts affords linear low-density polyethylene with high mechanical strength and high transparency originated from narrow molecular weight distribution and uniform chemical composition distribution. Thus, the direct connection with polymer structures and properties rationalizes the necessity for understanding and designing the nature of active sites.

In our previous paper, the active site nature of MgCl_2 -supported titanocene catalysts ($\text{Cp}_x\text{TiCl}_{4-x}/\text{MgCl}_2$, $x = 1$ or 2) was investigated in propylene polymerization [1]. MgCl_2 is the best known support for Ziegler-Natta catalysts, but has been much less employed for the heterogenization of metallocene catalysts [7]. It was found that the catalysts can exhibit dual-active site nature, where either Ziegler-Natta-type or metallocene-type active sites can be formed according to the type of activators employed in polymerization. In the present study, the dual-active site nature for MgCl_2 -supported titanocene catalysts was further explored, especially focusing on the ligand structure of titanocene precursors and on the type of polymerization. The active site nature of supported titanocene derivatives was investigated in propylene and ethylene homopolymerization as well as in ethylene/1-hexene copolymerization.

EXPERIMENTAL

Materials

Propylene (donated by Japan Polychem Corporation) and ethylene (donated by Sumitomo Chemical Co., Ltd.) of research grade were used without further purification. Toluene as polymerization solvent and 1-hexene were dried over molecular sieves 4A followed by nitrogen bubbling. Toluene for catalyst preparation was refluxed over sodium and then distilled prior to use. Modified methylaluminoxane (MMAO-3A) and triethylaluminum (TEA) were donated by Tosoh Finechem Corporation. Anhydrous magnesium dichloride with a specific surface area of $65.1 \text{ m}^2 \text{ g}^{-1}$ (MgCl_2 , donated by Toho Titanium Co., Ltd.), bis(cyclopentadienyl) titanium dichloride (Cp_2TiCl_2 , Gelest, Inc.), cyclopentadienyl titanium trichloride (CpTiCl_3 , Gelest, Inc.), pentamethylcyclopentadienyl titanium trichloride (Cp^*TiCl_3 , Tokyo Chemical Industry Co., Ltd., 97.0%), indenyl titanium trichloride (IndTiCl_3 , Tokyo Chemical Industry Co., Ltd., 98.0%), bis(cyclopentadienyl) zirconium dichloride (Cp_2ZrCl_2 , Tokyo Chemical Industry Co., Ltd., 95.0%), and titanium tetrachloride (TiCl_4 , Wako Pure Chemical Industries, Ltd., 99%) were used as delivered.

Catalyst preparation

10.4 g of MgCl_2 and 1.18 mmol of Cp_2MCl_2 ($M = \text{Ti}, \text{Zr}$), LTiCl_3 ($L = \text{Cp}, \text{Cp}^*, \text{Ind}$) or TiCl_4 were stirred in the presence of 42 mmol of TEA in 371 mL of toluene at room temperature for 10 min [8]. The product was repeatedly washed with toluene until unsupported metal residues in supernatant liquid were not detected by UV-vis spectroscopy (JASCO V-670). The obtained catalysts were named as $\text{Cp}_2\text{TiCl}_2/\text{MgCl}_2$, $\text{Cp}_2\text{ZrCl}_2/\text{MgCl}_2$, $\text{CpTiCl}_3/\text{MgCl}_2$, $\text{Cp}^*\text{TiCl}_3/\text{MgCl}_2$, $\text{IndTiCl}_3/\text{MgCl}_2$, and $\text{TiCl}_4/\text{MgCl}_2$.

The Ti and Zr contents were measured by UV-vis spectroscopy. 500 mg of a catalyst was dissolved in 40 mL of distilled water, 20 mL of 19% H_2SO_4 and 20 mL of 7% HCl. After dissolving the catalyst at an elevated temperature, 0.2 mL of 30% H_2O_2 was injected to the mixture. The Zr content was measured in a similar procedure to that for the Ti content. 500 mg of a catalyst was heated and stirred with 40 mL of distilled water, 12.5 mL of 7% HCl and 15 mg of alizarin red S for several minutes.

Homopolymerization

Propylene and ethylene homopolymerizations were conducted in a 1 L stainless steel reactor equipped with an agitating blade. A specified volume of toluene was charged to the reactor under nitrogen atmosphere and then monomer gas was saturated at 5 atm and 40°C for 30 min. After monomer saturation, an activator was introduced into the reactor to prepare a desired concentration (20 mmol L⁻¹ for MMAO or 10 mmol L⁻¹ for TEA). Polymerization was initiated by the addition of a measured amount of a catalyst. Monomer was continuously supplied to keep 5 atm during polymerization at 40°C for 30 min. The polymerization was terminated by the addition of acidic ethanol. As references, polymerization was conducted using unsupported metallocene derivatives. The obtained polymer was then washed with distilled water three times and dried in vacuo at 60°C for 6 h. Thereafter, polymer was dissolved in xylene containing 0.03 wt% of 2,6-t-butyl-4-methylphenol and precipitated by an excess amount of cold acetone. The reprecipitated polymer was filtered and dried in vacuo at 60°C for 6 h.

Copolymerization

Ethylene/1-hexene copolymerization was conducted based on a similar procedure. A specified volume of toluene containing 3.0 mol L⁻¹ of 1-hexene was saturated with ethylene at 5 atm and 40°C for 30 min. Subsequently, MMAO or TEA was added at the same concentration with that in the homopolymerization, followed by the injection of a specified amount of a catalyst. The polymerization was continued at 40°C for 30 min and terminated by acidic ethanol. The obtained copolymer was similarly purified and recovered.

Polymer characterization

The stereostructure of polypropylene and the composition of ethylene/1-hexene copolymer were determined by ¹³C{¹H} NMR (Bruker 400 MHz) at 120°C using 1,2,4-trichlorobenzene as a diluent and 1,1,2,2-tetrachloroethane-d₂ as an internal lock and reference.

RESULTS AND DISCUSSION

The metal content widely varied according to the employed precursors (Table 1). It became smaller

Table 1. Metal content in the catalysts

Catalyst	Metal content (wt%)
Cp ₂ TiCl ₂ /MgCl ₂	0.044
CpTiCl ₃ /MgCl ₂	0.28
TiCl ₄ /MgCl ₂	0.61
IndTiCl ₃ /MgCl ₂	0.27
Cp*TiCl ₃ /MgCl ₂	0.13
Cp ₂ ZrCl ₂ /MgCl ₂	0.055

as the number of Cp-type ligands in the precursors increased (L₂MCl₂ < LTiCl₃ < TiCl₄), while similar contents were obtained for Cp and Ind in the case of LTiCl₃. It is clear that the molecular structure of the precursors greatly affected interaction with the MgCl₂ support. TiCl₄ accepts four Mg-Cl-Ti bridging bonds (two Cl come from TiCl₄ and the other two from MgCl₂) on its adsorption in an octahedral symmetry. On the other hand, Cp₂MCl₂ does not sterically allow an octahedral environment, resulting in a smaller number of Mg-Cl-M bridging bonds on its adsorption and consequently a weaker interaction with MgCl₂ surfaces. A Cp* ligand makes LTiCl₃ less flexible compared with Cp and Ind, and leads to the smallest Ti content among LTiCl₃-type precursors.

A series of propylene homopolymerizations were conducted using the prepared catalysts in the presence of either MMAO or TEA. Table 2 summarizes the polymerization results together with the results for the unsupported precursors activated by MMAO. The unsupported metallocene and its derivatives produced atactic polypropylene (*mmmm* = 1.5-5.1 mol%, *rrrr* = 6.4-15.3 mol%), while the TiCl₄/MgCl₂ catalyst (i.e. a typical Ziegler-Natta catalyst) led to poorly isotactic polypropylene (*mmmm* = 39.2-41.5 mol%, *rrrr* = 7.4-7.8 mol%). As had been described in Ref. [1], the atactic polypropylene was produced at a cationic M(IV) site (metallocene-type) based on chain-end-control, while the poorly isotactic one was produced at a neutral M(III) site (Ziegler-Natta-type) mainly based on the site-control.

In Table 2, some of MgCl₂-supported titanocene catalysts formed different types of polymer, i.e. different types of active sites, depending on the employed activator. The Cp₂TiCl₂/MgCl₂ and Cp*TiCl₃/MgCl₂ catalysts produced atactic polypropylene when MMAO was used as an activator (see Figure 1a). On the other hand, poorly isotactic polypropylene was given in the case of TEA (see Figure 1b). Namely, these catalysts can exhibit metallocene-type active sites for MMAO

Table 2. Propylene homopolymerization results^(a)

Catalyst	Activator	Activity [kg PP mol M ⁻¹ atm ⁻¹ h ⁻¹]	mmmm (mol%)	rrrr (mol%)
Cp ₂ TiCl 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
IndTiCl ₃ /MgCl ₂	MMAO	69.6	42.6	6.6
	TEA	43.5	48.3	6.5
Cp*TiCl ₃ /MgCl ₂	MMAO	53.5	2.8	14.3
	TEA	14.0	44.7	5.5
Cp ₂ ZrCl ₂ /MgCl ₂	MMAO	254.0	5.5	4.2
	TEA	trace	n.d.	n.d.
Cp ₂ TiCl ₂	MMAO	56.9	1.5	11.2
CpTiCl ₃	MMAO	11.7	1.4	9.6
IndTiCl ₃	MMAO	231.2	2.8	10.0
Cp*TiCl ₃	MMAO	663.4	2.0	15.3
Cp ₂ ZrCl ₂	MMAO	1463.7	5.1	6.4

^(a)Solvent: 200 mL of toluene, activator: MMAO (20 mmol L⁻¹) or TEA (10 mmol L⁻¹), Al/metal molar ratio: 500, propylene pressure: 5 atm, temperature: 40°C, and polymerization time: 30 min.

and Ziegler-Natta-type active sites for TEA. On the contrary, the CpTiCl₃/MgCl₂ and IndTiCl₃/MgCl₂ catalysts led to the poorly isotactic polypropylene

produced at Ziegler-Natta-type active sites, regardless of the activators. The different response of the catalysts to the type of activators was related to the

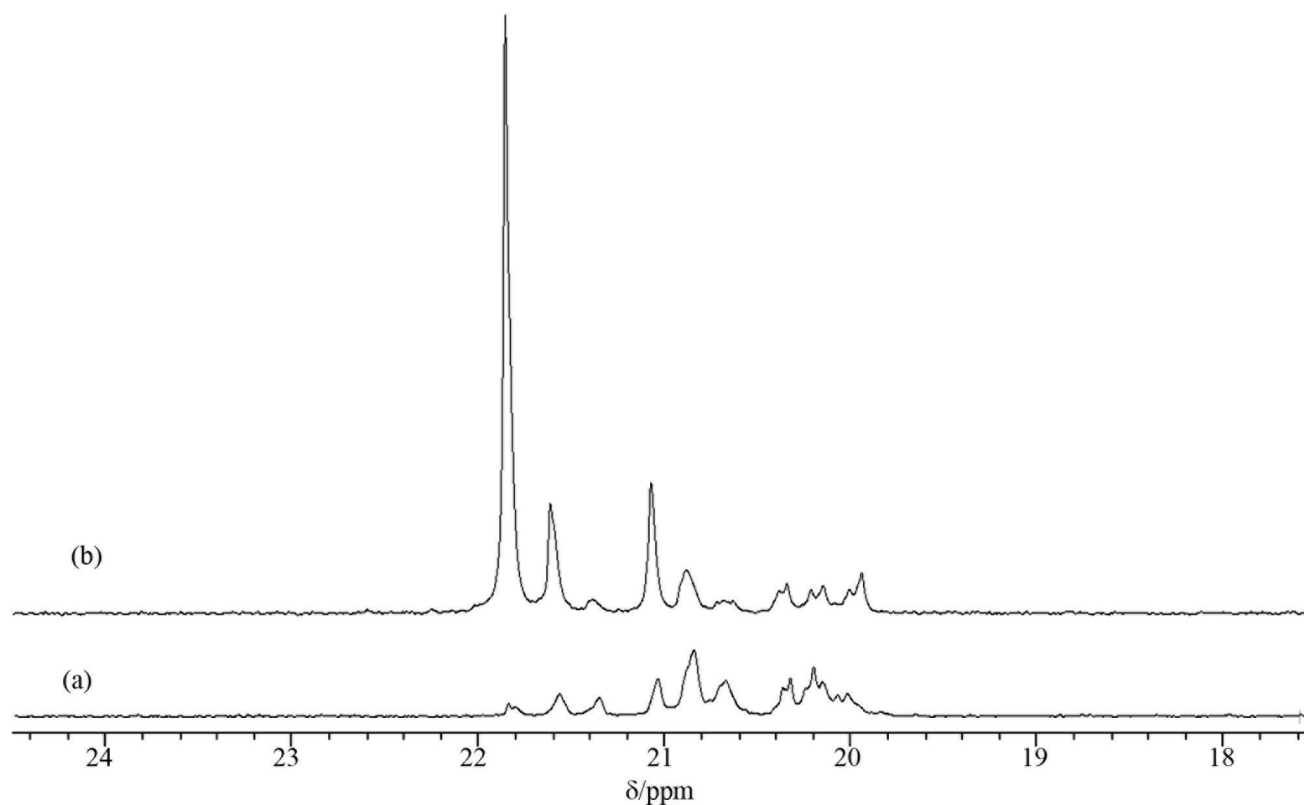


Figure 1. Typical NMR spectra for synthesized polypropylene: (a) Atactic one given by Cp₂TiCl₂/MgCl₂ and MMAO, and (b) poorly isotactic one given by Cp₂TiCl₂/MgCl₂ and TEA

reducibility of the M(IV) precursors during catalyst preparation using TEA. When a precursor was fully reduced during the preparation, only Ziegler-Natta-type active sites were formable even with MMAO. On the other hand, the dual active site nature was realized when a precursor was not reduced in the preparation. In this sense, Cp_2TiCl_2 and Cp^*TiCl_3 which exhibited the dual active site nature were considered to be more resistant to the reduction compared with IndTiCl_3 and CpTiCl_3 .

The activity of MgCl_2 -supported titanocene catalysts increased in the order of $\text{Cp}^*\text{TiCl}_3/\text{MgCl}_2 < \text{Cp}_2\text{TiCl}_2/\text{MgCl}_2 < \text{IndTiCl}_3/\text{MgCl}_2 < \text{CpTiCl}_3/\text{MgCl}_2$ when TEA was used as an activator. It was considered that the activity was related to the amount of Ti(III) species, which could be converted into Ziegler-Natta-type active sites (although the Ti oxidation state could not be analyzed due to the scarce Ti contents). The lower activities for $\text{Cp}_2\text{TiCl}_2/\text{MgCl}_2$ and $\text{Cp}^*\text{TiCl}_3/\text{MgCl}_2$ were reasonable based on the fact that these precursors were not reduced by TEA in the preparation.

The active site nature of $\text{Cp}_2\text{ZrCl}_2/\text{MgCl}_2$ was also investigated in propylene homopolymerization. The catalyst formed metallocene-type active sites when MMAO was used as an activator, where the activity was greatly decreased compared with the unsupported one. On the other hand, the catalyst was hardly activated when TEA was used as an activator.

It was believed that the neutral Zr(III) species was not formed in the $\text{Cp}_2\text{ZrCl}_2/\text{MgCl}_2$ -TEA system. Huang et al. have studied the oxidation states of the metals when Cp_2MCl_2 (M: Ti or Zr) were contacted with MAO using electron paramagnetic resonance [9]. Over 40% of Ti(IV) was reduced into Ti(III) by MAO at 25°C, while the reduction of Zr(IV) was less than 1%.

Ethylene homopolymerization and ethylene/1-hexene copolymerization were conducted using the $\text{Cp}_x\text{TiCl}_{4-x}/\text{MgCl}_2$ ($x = 0-2$) catalysts. The results are summarized in Table 3. In both of the polymerization, the activities were decreased by the immobilization of the precursors on MgCl_2 , which is a general tendency for supported metallocene catalysts [10]. The activities became higher in the order of $\text{Cp}_2\text{TiCl}_2/\text{MgCl}_2 < \text{CpTiCl}_3/\text{MgCl}_2 < \text{TiCl}_4/\text{MgCl}_2$ when TEA was used as an activator. This order was totally the same as that for propylene polymerization. It is known that ethylene polymerization with Ziegler-Natta catalysts occurs at either of Ti^{3+} or Ti^{2+} , while propylene polymerization only at Ti^{3+} [11]. Thus, catalytically relevant Ti oxidation states are not identical between ethylene and propylene polymerization. Nonetheless, both types of the polymerization require the reduction of Ti species. It was reasonable that the activity order for propylene polymerization, which was determined by the reducibility of the precursors, more or less coincided with the activity order for

Table 3. Ethylene homopolymerization and ethylene/1-hexene copolymerization results^(a)

Catalyst	Activator	1-Hexene concentration (mol L ⁻¹)	Activity [kg Poly mol Ti ⁻¹ atm ⁻¹ h ⁻¹]	1-Hexene content (mol%)
$\text{Cp}_2\text{TiCl}_2/\text{MgCl}_2$	MMAO	0	596.2	0
	MMAO	3.0	251.1	25.8
	TEA	0	107.5	0
	TEA	3.0	34.7	5.9
$\text{CpTiCl}_3/\text{MgCl}_2$	MMAO	0	296.4	0
	MMAO	3.0	278.3	5.4
	TEA	0	264.2	0
	TEA	3.0	252.7	5.1
$\text{TiCl}_4/\text{MgCl}_2$	MMAO	0	772.5	0
	MMAO	3.0	1017.0	3.1
	TEA	0	1120.5	0
	TEA	3.0	1890.3	2.9
$\text{Cp}_2\text{TiCl}_2^{(b)}$	MMAO	0	3774.1	0
	MMAO	3.0	723.2	29.4
$\text{CpTiCl}_3^{(b)}$	MMAO	0	1121.6	0
	MMAO	3.0	1042.4	43.6

^(a)Solvent: 200 mL of toluene, activator: MMAO (20 mmol L⁻¹) or TEA (10 mmol L⁻¹), Al/Ti molar ratio: 500, ethylene pressure: 5 atm, temperature: 40°C, and polymerization time: 30 min; ^(b) Solvent: 400 mL of toluene, activator: MMAO (20 mmol L⁻¹), and Al/Ti molar ratio: 5000

ethylene polymerization. It is notable that TiCl_4 as the most easily reducible precursor exhibited the largest difference between the two activities for ethylene and propylene polymerization.

Compared with the unsupported precursors, the supported titanocene catalysts exhibited much lower 1-hexene incorporation, where the comonomer content became higher as the number of the Cp ligand increased. Senso et al. examined the effect of the Ti oxidation state on the incorporation of 1-hexene in ethylene/1-hexene copolymerization, and reported that a higher Ti oxidation state led to greater comonomer incorporation [12]. Accordingly, our results might be interpreted in the following manner: the reduction of Ti was inevitable in the presence of TEA to form Ziegler-Natta-type active sites, but the over-reduction into Ti^{2+} was decelerated by increasing the number of the Cp ligand, thereby suppressing the loss in the 1-hexene incorporation efficiency.

When MMAO was used as an activator, the ethylene homopolymerization activity increased in the order of $\text{CpTiCl}_3/\text{MgCl}_2 < \text{Cp}_2\text{TiCl}_2/\text{MgCl}_2 < \text{TiCl}_4/\text{MgCl}_2$, slightly different from $\text{Cp}_2\text{TiCl}_2/\text{MgCl}_2 < \text{CpTiCl}_3/\text{MgCl}_2 < \text{TiCl}_4/\text{MgCl}_2$ for the propylene polymerization. The 1-hexene incorporation for $\text{Cp}_2\text{TiCl}_2/\text{MgCl}_2$ was found to be as high as that for the unsupported one, while the 1-hexene incorporation for $\text{CpTiCl}_3/\text{MgCl}_2$ was comparable with that for $\text{TiCl}_4/\text{MgCl}_2$. Likewise, active sites for $\text{Cp}_2\text{TiCl}_2/\text{MgCl}_2$ in the presence of MMAO were obviously assigned to metallocene-type, which was in line with the results for propylene polymerization.

CONCLUSION

The active site nature of various MgCl_2 -supported metallocene catalysts was investigated in ethylene and propylene homopolymerization as well as in ethylene/1-hexene copolymerization. The molecular structure of metallocene precursors significantly affected the interaction with MgCl_2 and TEA, resulting in greatly different polymerization behaviors. Precursors that were susceptible to the TEA-mediated reduction could form only Ziegler-Natta-type active sites, leading to poorly isotactic polypropylene and poor 1-hexene incorporation. On the other hand, less reducible precursors could form both metallocene- and Ziegler-Natta-type active sites, depending on

the type of activators employed in polymerization. The former active sites were featured with atactic polypropylene and high 1-hexene incorporation efficiency. In conclusion, the present contribution clarified some important aspects to design MgCl_2 -supported metallocene catalysts with desired active site nature.

ACKNOWLEDGEMENTS

The Authors are deeply grateful to Japan Polychem Corporation, Sumitomo Chemical Co., Ltd., Tosoh Finechem Corporation, and Toho Titanium Co., Ltd. for reagents.

REFERENCES

- Goto K, Taniike T, Terano M (2013) Dual-active-site nature of magnesium dichloride-supported cyclopentadienyl titanium chloride catalysts switched by an activator in propylene polymerization. *Macromol Chem Phys* 214: 1011-1018
- Sinn H, Kaminsky W (1980) Ziegler-Natta catalysis. *Adv Organomet Chem* 18: 99-149
- Albizzati E, Giannini U, Collina G, Noristi L, Resconi, L (1996) Catalysts and polymerizations. In *polypropylene handbook*, Moore EP Ed. 11-98
- Jordan RF, Bajgur CS, Willett R, Scott, B (1986) Ethylene polymerization by a cationic dicyclopentadienyl zirconium(IV) alkyl complex. *J Am Chem Soc* 108: 7410-7411
- Yang X, Stern CL, Marks TJ (1991) Cation-like homogeneous olefin polymerization catalysts based upon zirconocene alkyls and tris(pentafluorophenyl)borane. *J Am Chem Soc* 113: 3623-3625
- Busico V, Cipullo R (2001) Microstructure of polypropylene. *Prog Polym Sci* 26: 443-533
- Severn JR, Chadwick JC, Duchateau R, Friederichs N (2005) "Bound but not gagged" - immobilizing single-site α -olefin polymerization catalysts. *Chem Rev* 105: 4073-4147
- Kaminaka M, Soga. K (1991) Polymerization of propene with the catalyst systems composed of Al_2O_3 - or MgCl_2 -supported $\text{Et}[\text{IndH}_4]_2\text{ZrCl}_2$

- and AlR_3 ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$). *Die Makromol Chem Rapid Commun* 12: 367-372
9. Huang YH, Yu Q, Zhu S, Rempel GL, Li L (1999) ESR studies on oxidation state of titanocene and zirconocene catalysts. *J Polym Sci Part A: Polym Chem* 37: 1465-1472
 10. Chien JCW (1999) Supported metallocene polymerization catalysis. *Top Catal* 7: 23-36
 11. Fregonese D, Mortara S, Bresadola S (2001) Ziegler-Natta MgCl_2 -supported catalysts: relationship between titanium oxidation states distribution and activity in olefin polymerization. *J Mol Catal A: Chem* 172: 89-95
 12. Senso N, Praserttham P, Jongsomjit B, Taniike T, Terano M (2011) Effects of Ti oxidation state on ethylene, 1-hexene comonomer polymerization by MgCl_2 -supported Ziegler-Natta catalysts. *Polym Bull* 67:1979-1989