

Modification of Ziegler–Natta Catalysts by Cyclopentadienyl-Type Ligands: Activation of Titanium-Based Catalysts

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ABSTRACT: Conventional Ziegler–Natta catalysts, based on TiCl_4 supported on MgCl_2 , were modified by substituting a part of the chlorides by cyclopentadienyl (and derivatives) ligands. Although these catalysts are very active (activities up to 10^5 g PE/g catalyst/h) they exhibit a conventional Ziegler–Natta behavior (methylaluminoxane is not necessary, polyethylene produced with a rather broad molar weight distribution, low sensitivity to hydrogen). It was attributed to cluster effects: an increase of the number of conventional TiCl_4 active sites by adding cyclopentadienyl ligands on titanium neighbors. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2281–2288, 1997

Key words: ethylene polymerization; catalyst; heterogeneous; metallocene

INTRODUCTION

Supporting Metallocene Catalysts

Despite the fact that the discovery of the activation of the group IV metallocene polymerization catalysts occurred almost 20 years ago and resulted in a huge number of interesting academic studies,¹ economic interest only appeared in recent years, as it became clear that these catalysts can compete with conventional Ziegler catalysts in industrial processes. But even though a large number of theoretical and practical problems have been solved, allowing the use of these new systems on industrial plants, their use remains essentially restricted to industrial processes producing polymers in solution.^{2,3} To use metallocene catalysts in modern solvent-free processes like slurry or gas-phase polymerization processes, it

is necessary to convert them to heterogeneous catalysts.^{4,5} To that end, many difficulties have been solved and new problems have appeared, chiefly concerning the activity of the supported catalysts. Most of the solid systems that have been reported cause a dramatic decrease of the activity when compared to the corresponding metallocenes in solution. Homogeneous metallocene systems are often more active than the conventional Ziegler–Natta catalysts, while supported ones are much less active.^{6,7}

Modern polymerization processes are solvent-free slurry (with liquid monomer) or gas-phase processes. They are based on heterogeneous catalysts not only because a controlled size, shape, and porosity of the catalyst particle is necessary for these processes but also because it allows production of polymers with controlled particle properties. A replication phenomenon is often observed, one catalyst particle being converted into one polymer particule with homothetic properties. Metallocene cannot be directly used in such processes.

Three main methods to support metallocene have been described in the literature: the non-

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modified metallocene can be adsorbed on a support, the metallocene can be modified by adding a chemically reactive group allowing a reaction with the support, and a metallocene can be entirely built on the surface of the support. The first method consists in contacting a prebuilt metallocene with a support (silica, magnesium chloride) modified or not by the presence of an activator [methylaluminoxane (MAO) or trimethylaluminum (TMA)]. Though this approach is academically interesting,^{8–12} the results are not as good: the catalytic activities are low compared to the activities obtained in homogeneous phase conditions. The second method uses a reactive group like an hydroxyl grafted on a ligand or on the bridge of a metallocene to link it chemically to a carrier using the silanol groups of the silica surface, for instance.^{13,14} The third method has been less studied: it consists on building the metallocene directly on the support, using, for instance, a silicon atom to start the bridge. Soga¹⁵ synthesized a metallocene supported on silica by grafting first silicium tetrachloride on the silanol groups and then exchanging the remaining chlorine by cyclopentadienyl groups. This catalyst shows stereospecificity in the case of propylene polymerization but presents almost no activity.

A simple direct approach is also possible: a conventional catalyst can be modified by grafting new ligands. Supported titanium chloride bear reactive chlorine, which are easily exchanged by other ligands. The exchange of a titanium–chlorine bond by a titanium–carbon bond is the starting point of the Cossee¹⁶ mechanism for olefin polymerization. Soga tried to exchange some chlorine ligands of a Ziegler–Natta catalyst¹⁷ (titanium chloride supported on magnesium chloride) with cyclopentadienyl ligands. He used the standard conditions for this reaction, which requires an ether as solvent. Thus, the catalyst supported on magnesium chloride was contacted with a solution of cyclopentadienyl sodium in tetrahydrofuran (which is a solvent or a swelling agent of magnesium chloride), and it resulted in a catalyst presenting a very poor activity in ethylene polymerization. If a catalyst is modified in that way, it will be important to know if the modification was successful and if we are able to identify to what family the new catalyst belongs. We are going to detail how the metallocene and conventional catalysts can be distinguished.

The Typical Behavior of Metallocene Catalysts

Since the discovery of Kaminsky¹⁸ in the early eighties, it is well known that metallocene cata-

lysts are very active only in the presence of special activators,^{19,20} especially methylaluminoxane (MAO). In the presence of common alkylaluminum cocatalysts, they are not correctly activated and present a low activity.¹

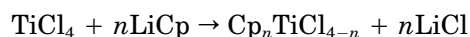
The metallocene catalysts are often well-defined compounds, resulting in a single-site behavior²¹: all the active sites are identical and possess the same reactivities, same propagation and termination constants, same copolymerization ratios. As a consequence, they produce polymers with the expected narrow molar weight distribution ($M_w/M_n \approx 2$) and copolymers with only one composition. In opposition, conventional Ziegler–Natta catalysts present a large variety of active sites with different kinetic constants, they produce polymers with broad molar weight distributions, and copolymers that can be fractionated by solvents.^{22,23}

Conventional Ziegler–Natta catalysts produce very high molar weight polymers. They require the use of a transfer agent, generally hydrogen: important concentrations of hydrogen are added to control these molar weights. On the contrary, for metallocene catalysts, β -H elimination is an important mechanism so that these catalysts often give rise to low molar weight polymers.²⁴ Addition of small amounts of hydrogen to the metallocene systems shows that hydrogen is a good transfer agent but deactivates the system in ethylene polymerization even at a very low concentration.²⁵

All these differences between metallocene and conventional Ziegler–Natta catalysts show that it is quite easy to know, even with an unknown catalyst, what kind of active sites one catalyst possesses.

The Problem of Grafting a Cyclopentadienyl Ligand on a Supported Titanium Chloride

There is a well-known method in organometallic chemistry,²⁶ consisting of exchanging a chlorine ligand by a cyclopentadienyl one (introduced as a cyclopentadienyl salt).



where Cp stands for Cp = cyclopentadienyl or derivative and $n = 1$ or 2.

The case $n = 1$ is only possible if the substituted species is immobilized on a support.

To avoid any interaction with magnesium chloride the catalyst will be suspended in toluene (which does not dissolve or swell the support) in-

stead of THF. The driving force is the precipitation of lithium chloride on the support. The poor solubility of lithium chloride in aprotic solvents compatible with Ziegler–Natta catalysts (alcanes, toluene) obliges to leave it on the support as it is expected not to act as a poison in Ziegler–Natta catalysis.

In the case of supported TiCl_4 , at least one chlorine is shared with the support: if two ligands are grafted on titanium, the coordination vacancy allowing the polymerization can be lost or the titanocene can be extracted by the solvent, so we think that it is necessary to graft not more than one ligand in order to synthesize a supported monofunctional CpTiCl_3 . A detailed characterization of supported species in small quantities (less than 4%) in an heterogeneous catalyst is very difficult. The new catalysts are identified by their behavior in ethylene polymerization and also by their sensitivity to hydrogen, the necessity (or not) to use MAO as cocatalyst and the rheological behavior of the synthesized polymers (melt index and melt flow ratio, related to M_w and M_w/M_n ²⁷). The important differences between a conventional Ziegler–Natta catalyst and a metallocene catalyst should allow us to know what kind of active specie is present on the studied catalyst.

EXPERIMENTAL

Catalyst Preparation

All the solvents were dried on molecular sieves under argon. The syntheses were conducted under an argon atmosphere in Schlenk tubes.

Conventional Catalyst Preparation²⁸

Magnesium Chloride-Supported Catalysts

Durene (1.8 g) was added to 22.2 g of anhydrous MgCl_2 and refluxed 4 h in THF. MgCl_2 was then precipitated by slow addition (about 1 h) of 150 mL of heptane. The powder is then washed twice with heptane and dried 1 h at room temperature and 3 h at 120°C under vacuum. The support obtained contains about 0.5 mol of THF by mol of MgCl_2 . This support is then contacted with an excess of pure TiCl_4 during 1 h at 80°C and washed three times with a mixture of 1,2 dichloroethane (DCE) and toluene (toluene/DCE = 1 v/v). This sequence is repeated three times (after the last TiCl_4 impregnation, the powder is washed three times with heptane instead of DCE/tolu-

ene). The catalyst (called MT for magnesium-titanium) is dried under vacuum for 30 min at 40°C and contains 5.1% Ti and 20% Mg (elementary analysis) and a negligible residue of THF.

Silica-Supported Catalysts

The support is silica Grace 332 (surface area $\approx 300 \text{ m}^2/\text{g}$ and pore volume 1.65 mL/g) dried several hours at 450°C under vacuum and containing about 1 mmol of silanol by gram of silica.²⁹ It is contacted with a large excess of TiCl_4 diluted in heptane during 1 h at 50°C, then washed with heptane and dried under vacuum for 30 min at 40°C. It contains 5.3% Ti (elementary analysis), corresponding to 1.1 mmol of Ti per gram of silica. This shows that the majority of titanium are bonded to one silanol (very few titanium are bonded to two silanols) and possesses 3 chlorine atoms.

Ligand Salt Synthesis³⁰

This method is available whatever the ligand (cyclopentadiene, indene, fluorene). A commercial solution (Aldrich) of butyllithium 1.6M in hexane is added to the desired ligand (stoichiometric ratio) in a known volume of toluene (the concentration must be between 50 and 100 mM) and stirred several hours. The reaction is completed by heating 2 h at 80°C. A white powder of ligand salt is obtained, suspended in toluene (known concentration).

Modified Catalyst Preparation³⁰

The amount of ligand salt corresponding to the desired ratio of titanium is added in toluene suspension to 1.5 g of catalyst and heated for 4 h at 80°C, washed several times with toluene then dried under vacuum at 40°C for 30 min. All the catalysts contain between 18 and 19% of Mg, and between 3.4 and 3.8% of Ti.

Polymerization of Ethylene

The experimental conditions of slurry or gas phase polymerizations in a 2.5 L pressurized and thermoregulated reactor have been published previously.^{31,32} The slurry polymerizations were performed in 0.5 L of heptane, at 80°C, maintaining a constant pressure comprising 6 bars of ethylene. The gas phase polymerizations were performed at 85°C with 10 bars of ethylene.

Table I Characteristics of the Different Synthesized Catalysts

Name	Ligand Used	Stoichiometry
MT	unmodified Cl	
MT1Cp1	cyclopentadienyl	1 Cp per Ti
MT3Cp1	cyclopentadienyl	1 Cp per 3 Ti
MT1Ind1	indenyl	1 Ind per Ti
MT1Ind2	indenyl	1 Ind per 2 Ti
MTIndCp	indenyl + cyclopentadienyl	0.5 Cp + 0.5 Ind per Ti
MT1Fluo1	fluorenyl	1 Fluo per Ti

RESULTS AND DISCUSSION

The three main ligands of metallocenes (cyclopentadienyl, indenyl, and fluorenyl) were tested with different molar ratios between Ti and the ligand salt. The catalysts synthesized are summarized in Table I. We intended to check a one ligand per titanium stoichiometry to verify the behavior and activity of such catalysts, then to diminish the number of ligand per titanium in order to try to get a catalyst with two families of active sites (expecting an increase of the polydispersity of the polymer). The catalyst MT1Cp1 was first tested in a slurry polymerization, using 3 mM of triisobutylaluminium (TiBA) as cocatalyst. It is first to be noticed that the catalyst is very active in the presence of TiBA and even in the presence of an hydrogen concentration, which totally deactivates a metallocene catalyst used in similar conditions. The amount of hydrogen was varied during polymerization (0, 2, and 4 bars) by addition of batch quantities of hydrogen (keeping the pressure of ethylene constant at 6 bars). After two additions of hydrogen, the total pressure of the reactor was dropped to atmospheric pressure, and 6 bars of pure ethylene were reintroduced to resume the polymerization with a small residue of hydrogen left in solution. Hydrogen deactivates this catalyst (Fig. 1) but the deactivation is reversible as can be seen in the last part of the figure. Without hydrogen, the activity reaches 10⁵ g/g/h, a seldom reported value, and is still equal to 20,000 g/g/h with 4 bars (i.e., 40% v/v) of hydrogen. The replacement of the 3 mM of TiBA by 10 mM of MAO only increases the activity by less than 10% (the same effect is observed with the MT catalyst), in contradiction with what was expected with metallocenes. The same behavior was observed with all the catalysts described in Table I.

These catalysts were then tested in slurry polymerization with various amounts of hydrogen and

their performances compared with the MT catalyst (Table II). The results can be summarized as follows: (a) hydrogen drastically reduces the catalytic activity whatever the ligand (and the stoichiometry) used, but is a good transfer agent as can be seen in the melt index (I_5) column; (b) without hydrogen, the melt index is zero, that is to say that M_w is larger than 5.10⁵ g/mol (limited transfer reactions as β -H elimination); (c) the cyclopentadienyl and indenyl ligands increase the catalytic activity (the most important activity is obtained with MTIndCp as if there was a synergetic effect); (d) the fluorenyl ligand deactivates the catalyst; (e) for the indenyl- and cyclopentadienyl-modified catalysts, the melt flow ratio (I_{21}/I_5) is roughly independent of the nature of the ligand and of its stoichiometry, and is lower than that obtained with MT catalyst.

SEC (Size Exclusion Chromatography) measurements have been made for two polymers synthesized with 2 bars of hydrogen with the following catalysts:

$$\begin{aligned} -\text{MT} \quad I_{21}/I_5 &= 13.3 \quad M_w/M_n = 7.9 \\ -\text{MT1Cp1} \quad I_{21}/I_5 &= 10.2 \quad M_w/M_n = 4.8 \end{aligned}$$

The polydispersity measured by SEC corresponds fairly to the melt flow ratio indexes. The values confirm that modified catalysts produce a polymer with less dispersity than the standard one. However, this polydispersity is larger than that usually obtained with homogeneous metallocenes (close to 2).

To complete the data about these modified catalysts, gas-phase polymerizations were performed (Table III). It can be seen that, as in slurry polymerization, modified catalysts exhibit a very high activity compared to the standard one.

In all these polymerizations (slurry or gas-phase processes), these modified catalysts did not

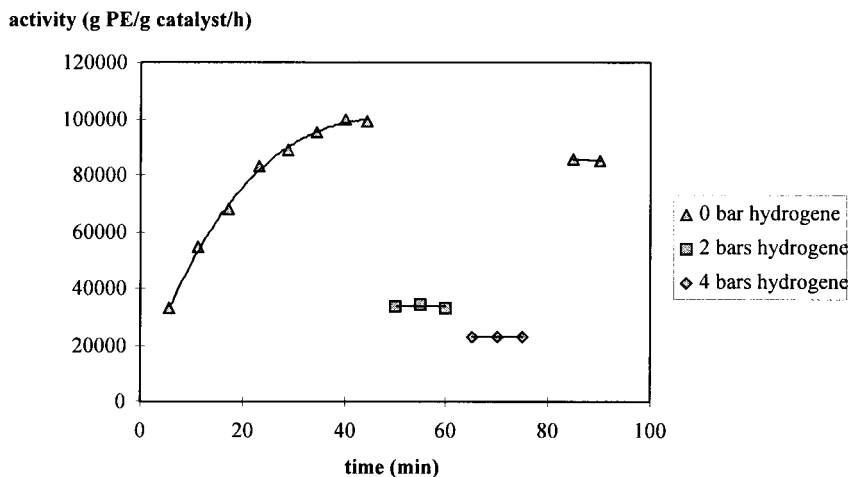


Figure 1 Activity of MT1Cp1 in slurry polymerization (6 bars of ethylene, 80°C, 3 mM of TiBA) with various hydrogen pressures.

show a metallocene behavior: (a) MAO is not necessary to make them polymerize ethylene (it gives results only less than 10% better than TiBA) and the hydrogen deactivation effect is moderated; (b) in the absence of hydrogen, the molar weight of the polymer is too high to be measured; (c) the polydispersity is larger than that generally obtained with homogeneous metallocenes, and roughly independent of the ligand stoichiometry.

An interpretation of this behavior should be that the reaction between a supported titanium and the ligand is not quantitative: but in this case, the stoichiometry of ligand should have an effect on the number of modified titanium (and on the catalytic activity), and the polydispersity of the produced polymers should have increased (presence of both conventional and modified active

sites). So we tried to increase the number of modified titanium in two ways. The first one uses a higher ligand exchange reaction temperature: two new modified catalysts were synthesized with a stoichiometry of one cyclopentadienyl per titanium using xylene instead of toluene (higher boiling point): MT1Cp1(80) synthesized as already described at 80°C in xylene (to compare to catalysts made with the same solvent), MT1Cp1(140) synthesized in the same way but at 140°C. Tested in slurry polymerization with 2 bars of hydrogen (Table IV, two first lines), MT1Cp1(140) happened to be less active than MT1Cp1(80), producing a polymer with a similar melt flow ratio.

The second way was to use an excess of ligand during the synthesis. As the aim is not to graft two ligands on a single titanium, we investigated

Table II Activity of the Different Catalysts of Table I in Slurry Polymerization (6 Bars of Ethylene, 80°C, 3 mM of TiBA in the Presence of Hydrogen at Different Concentrations)

Catalyst	P (H_2) (bar)	Maximum Activity (g PE/g Catalyst/h)	Productivity (g PE/g Catalyst in 1 h)	I_5 (g/10 min)	I_{21}/I_5
MT	2	16000	10000	1.5	13.3
MT1Cp1	0	100000	63000	0	
MT1Cp1	2	42000	35000	1.5	10.2
MT1Cp1	4	31000	20500	4.6	10.5
MT3Cp1	0	72000	54000	0	
MT3Cp1	2	40000	36000	2	11.3
MT1Ind1	2	47000	36000	0.4	9.8
MT1Ind1	4	28500	19000	2.7	10.7
MT2nd1	2	40000	34500	1.8	10.3
MTIndCp	2	71000	36000 in 45 min	0.9	9.9
MT1Fluo1	2	6500	4500	0.3	14

Table III Activity of Different Catalysts in Gas Phase Polymerization (10 Bars of Ethylene, 85°C, 1 mmol of TiBA)

Catalyst	<i>P</i> (H ₂) (bar)	Initial Activity (g PE/g Catalyst/h)	Productivity (g PE/g Catalyst in 1 h)	I ₅ (g/10 min)	I ₂₁ /I ₅
MT	2.7	6000	5000	5	10.2
MT1Cp1	2.7	29000	14500	4.9	8.6
MT2Ind1	3.0	28000	19000	7	10

the effect of an excess of indenyl, which is larger than cyclopentadienyl and less able to form bisindenyl species with a supported titanium (already sterically hindered by the support). MT1Ind5 was synthesized with a large excess of 5 indenyl per titanium in the way described in the Experimental section. As it was the case for the catalyst synthesized at 140°, a test in slurry polymerization with two bars of hydrogen showed a reduced activity (8000 g/g/h of maximum activity) when compared with MT1Ind1 or MT2Ind1. These two experiments tend to increase the number of modified titanium: their result is a decrease of the activity. So, it can be supposed that active sites are not modified titanium but still unreacted TiCl₄.

Another way to verify this hypothesis was to decrease the number of unreacted TiCl₄ without changing the number of modified ones. One possible way is to heat the modified catalyst under vacuum: unmodified TiCl₄ can either evaporate (if it is not well fixed to the support) or migrate into the MgCl₂ network (so that it will be inaccessible for polymerization). A first thermal treatment of 1 h at 90°C under vacuum did not show any effect on the catalytic activity (Table IV). But a second treatment of 1.5 h at 120° drastically decreased the catalytic activity. The effect of such treatments on the unmodified catalyst is the same. It seems to confirm the hypothesis that unmodified titanium are the active sites of the polymeriza-

tion. The ratio Ti/Mg value remains almost unchanged by these thermal treatments, showing that very few TiCl₄ are extracted from the support (the increase of the percentage of both titanium and magnesium is probably caused by residual solvent evaporation). However, it is generally assumed that only a small fraction, not more than 10% of the titanium atoms, of the supported catalysts are active towards polymerization, so that even if very few TiCl₄ are extracted, it can have an important effect on activity.

If we suppose that the active sites are unreacted TiCl₄, there are still two main problems: what about the modified titanium sites, and why does activity increase after the ligand exchange?

To answer the first question, we worked on a very simple (and poorly active) catalyst composed of TiCl₄ supported on silica (one titanium per silanol), noted ST. This catalyst was contacted as described in the Experimental part with one equivalent of cyclopentadienyl salt to obtain a modified catalyst noted ST1Cp1. In opposition with magnesium supported titanium catalysts were titanium atoms form clusters, this type of silica supported catalysts contains isolated titanium, allowing cyclopentadienyl to react with all the titanium atoms. Slurry polymerizations were performed with these two catalysts (polymerization conditions are described in Table IV) using TiBA (as for magnesium supported titanium catalysts, MAO

Table IV Effect of the Ligand Exchange Temperature and Drying Conditions on Productivity (Slurry Polymerization, 6 Bars of Ethylene, 2 Bars of Hydrogen, 80°C, 3 mM of TiBA) of Cyclopentadienyl Modified Catalysts

Catalyst	Additional Thermal Treatment	Catalyst Composition	Productivity (g PE/g Catalyst in 1 h)
MT1Cp1 (80)	none	3.8% Ti 19% Mg	17000
MT1Cp1 (140)	none	3.4% Ti 17% Mg	10000
MT1Cp1 (140)	1 h at 90°C	3.9% Ti 18% Mg	10000
MT1Cp1 (140)	1.5 h at 120°C	4.1% Ti 19% Mg	4500

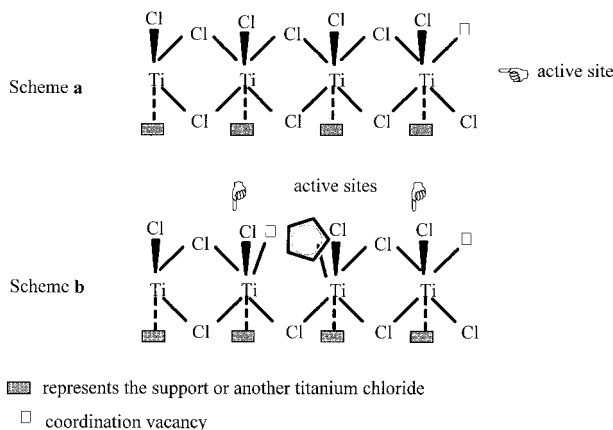


Figure 2 Possible model of active site creation by ligand exchange.

only slightly increases the activities). While ST exhibited a 100 g/g/h activity, the activity of ST1Cp1 only reached 30 g/g/h. In this case, the activity was decreased by the reaction of ligand exchange, supporting the fact that modified titanium atoms are not the active sites.

So, what can explain the increase in the catalytic activity observed with magnesium-supported modified titanium catalysts? It can be attributed to the creation of new (conventional) active sites by grafting a ligand on inactive titanium. Magnesium chloride-supported catalysts are made of titanium chloride clusters, where most of the titanium atoms are bridged together by chlorine atoms (Fig. 2, Scheme a): so they do not possess any coordination vacancy and are inactive towards polymerization. Only titanium atoms situated on the edge of a cluster possess coordination vacancies and are able to be converted into active sites. Exchanging a chlorine ligand by a cyclopentadienyl (or derivative) suppresses chlorine bridges and creates a defect inside the cluster creating new active sites (Fig. 2, Scheme b). The titanium modified by one cyclopentadienyl ligand are then supposed not to be active at all in ethylene polymerization, as it is the case for CpTiCl_3 .

This hypothesis of active site creation agrees with the results presented in this text. The active sites are active only on the edges of the titanium chloride clusters and the chemical modification of the catalyst creates new edges. (1) The catalyst activation is roughly independent of the stoichiometry of ligand (below one ligand per titanium): a titanium situated inside a cluster is not easily modified (high steric hindrance). So very few reactions of exchange may happen, less than the

number of introduced ligand. The creation of a little number of new active sites can explain the very high activation observed because, from the beginning, less than 10% of the titanium atoms are active. (2) If we try to increase the number of modified titanium (large excess of ligand, increase in the temperature reaction), possible active sites may be isolated between two modified titanium. In this case, these possible active sites should be poorly active because the cluster is necessary to activate titanium chloride. (3) The molar weight distribution of the synthesized polyethylene is narrowed with the modified catalysts: while all the active sites of classic Ziegler–Natta catalysts possess very different kinetic constants because of their differences of environment, the supposed new active sites are possibly built in rather similar environments, favoring the chlorine–ligand exchange.

CONCLUSION

Cyclopentadienyl ligand exchange on titanium based Ziegler–Natta catalysts resulted in unexpected effects. It happened to greatly activate these catalysts. However, their behavior remains very close to the conventional system and not, as expected, to a metallocene one (MAO cocatalyst not required, moderate hydrogen effect, rather large molecular weight distribution). We propose to attribute it to cluster effects. The formation of titanium chloride clusters on the surface of magnesium chloride limits the number of active sites on the conventional catalysts, the modification of a small fraction of the titanium inside the clusters results in the formation of new active sites in the neighboring of the modified titanium.

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