Catalysis Today 41 (1998) 149–157

From homogeneous to supported metallocene catalysts

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Abstract

The mechanism of the monoalkene homogeneous polymerization with metallocene/methylalumoxane (MAO) system is reviewed with reference to structural and stereochemical control of the polymers as derived by the type of ligands around the transition metal (Zr and Ti).

Major disadvantages of these homogeneous catalysts are the lack of morphology control and reactor fouling. Supported catalysts can allow to overcome these drawbacks and be utilized in cheaper bulk or gas-phase processes. Also they may permit the use of less MAO, while still offering facile control of polymer properties by ligand variation.

Binding of well-defined transition metal complexes onto carefully prepared inorganic surfaces is certainly a very attractive approach to create new heterogeneous catalysts and to characterize highly reactive species. In this paper attention is on the use of alumina, silica and zeolites for supporting metallocenes of Ti and Zr.

The amount of metallocene which can be attached to the surface of these supports is much lower than expected on the basis of simple physical absorption. This seems to indicate that attachment takes place at specific sites of the surface. In any case the amount of hydroxyl groups seems to play a determining role as shown by structural analysis and catalytic activity of olefin polymerization of the resulting heterogenized complexes. The formation of cationic species on the inorganic surface was proposed in a very analogous way as proposed in solution.

Results concerning homo- and copolymerization of monoalkenes with different supported metallocene complexes are presented to discuss the effect of support nature and surface features.

Keywords: Define polymerization; Metallocenes; Supported catalysts

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1. Introduction

Supported transition metal catalysts based on titanium chloride with alkylaluminium chlorides are presently utilized in the production of more than half of the large volume plastic family, polyethylene (PE), and for all the polypropylene (PP) [1,2].

More recently Kaminsky and Sinn made the important discovery (from 1976) that methylaluminoxane [$(\text{–MeAlO–})_n$=MAO, the product of controlled hydrolysis of $AlMe_3$] as cocatalyst with Cp_2TiMe_2 yields active ethylene polymerization catalysts [3–5]. Moreover, chiral C_2-symmetry metallocenes lead to isotactic PP and C_s-symmetry forms syndiotactic PP. These results and the discovery of aluminoxane-free cationic metallocene catalysts [6] have led to a phenomenal growth of interest in uniform site polymerization [1,7–10]. In the present paper we shall first

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0920-5861/98/$32.00
PII S0920-5861(98)00045-5

summarize the main features of homogeneous metallocene catalyst as far as polymerization mechanism and stereochemistry are concerned.

Then attempts to support these systems on insoluble inorganic supports in a controlled way will be presented. The results of these last attempts will be finally discussed with reference to the structure of the active sites, polymerization activity and polymer structure.

2. Homogeneous metallocene catalyst

2.1. Chemical mechanism

Active homogeneous olefin polymerization catalysts are obtained on mixing bent metallocenes, Cp'_2MX_2 (Cp'=general cyclopentadienyl ligand; M=Zr, Hf, Ti; X=Cl, Me), with excess MAO (Table 1) in inert solvents such as toluene. A number of generalizations may be made about these catalysts [5,11–13]:

- Catalyst activity increases with increase in the MAO/transition metal ratio. Large excess of MAO (A1/M>500) is generally required for good activity up to tons of polymer per gram of transition metal.
- An increase in temperature results in lower average polymer molecular weight (Mw) and (for stereospecific catalysts) decreased stereoregularity.
- Activity decreases generally in the order Zr>Hf>Ti. Titanium is rapidly deactivated above ~50°C, presumably via reduction of Ti(IV) to Ti(III) [3].
- Aluminoxanes such as $(\text{–EtAlO–})_n$ or $(\text{–}i\text{-BuAlO–})_n$ and other alkylaluminium cocatalysts (e.g. the mixture of $AlMe_3$ and $AlMe_2F$) show inferior activity.

According to several reports MAO plays at least three roles in polymerization: as an alkylating agent for the generation of transition metal-alkyl adducts; as a Lewis acid for anion abstraction from the complex generating an electrophilic species; and as a scavenger for removal of impurities, particularly water in the olefin and solvent. The structures of the active catalysts have been extensively investigated [14] but firm conclusions are scarce, largely due to the large excess of MAO present, which hinders spectroscopic study. However the catalytically active nature of discrete d^0 metallocenes, Cp'_2MR^{n+} (n=0,1), discussed below, and NMR and other studies of isolated catalysts formed with MAO [14] support a cationic 14-electron metallocene as the active site, loosely associated with the MAO-derived anion.

Table 1
The soluble metallocene/MAO system

$Cp_2MtCl_2+AlR_3$	Homogeneous system of moderate activity for C_2H_4 polymerization
Cp_2MtCl_2+MAO	Extremely active catalyst; activity is enhanced by a factor of about 100 000

Mt=Ti,Zr,Hf; $Cp=C_5H_5$

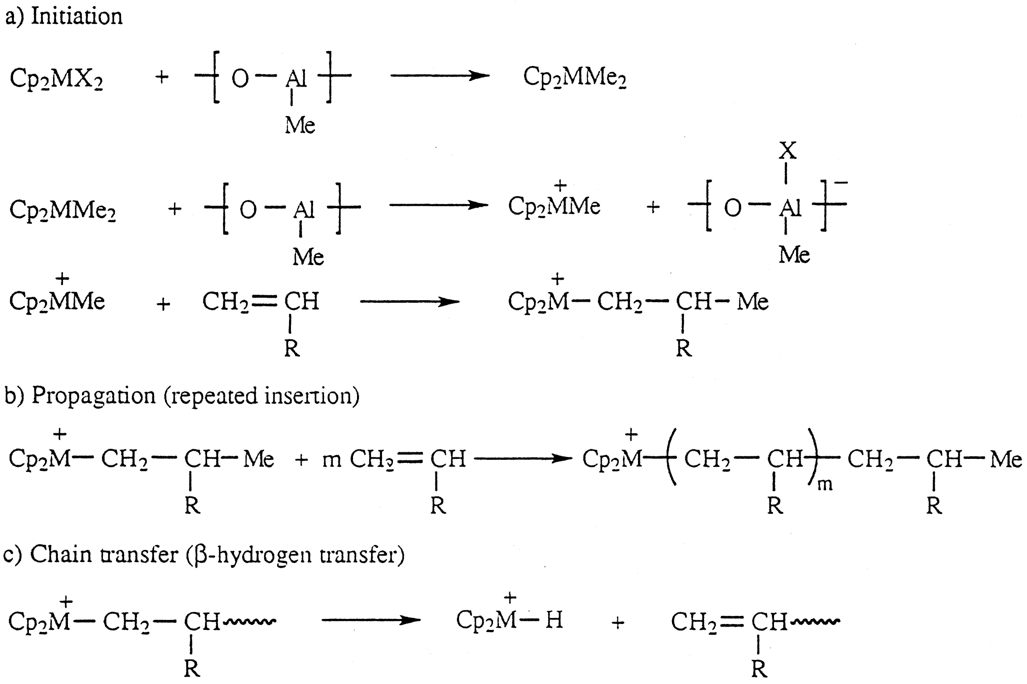
The key to the synthesis and activity of such active cationic metallocenes is the utilization of robust and poorly coordinating anions showing good solubility in inert aromatic solvents. In contrast, tetraphenylborates, alkyltriphenylborates and to a lesser extent, carborane anions have found wide use in cationic metallocene chemistry [15–21].

Thus the initiation step of this polymerization reaction consists of the formation of an alkylated cation of the transition metal, followed by the insertion of the olefin into the transition metal–carbon bond (Scheme 1).

Typical features of α-olefin insertion are the regiospecificity (1,2-insertion is normally found), the stereospecificity in case of α-olefins and the mode of stabilization of the insertion product (presumed to be via weak secondary bonding interactions).

Metallocene polymerization generally [9] affords macromolecules with one unsaturated end group. Almost complete suppression of chain transfer at low temperatures giving an unusual living polyethylene catalyst has recently been reported for an isoelectronic tantalum analogue of the group IV metallocene catalysts [22]. Three major chain transfer/termination mechanisms have been revealed by studying the end groups of low Mw oligomers:

- β-H elimination, proceeding via an agostic, βC–H…Zr interaction, affords, in the case of propylene polymerization, $H_2C{=}CH(Me)R$ products (Scheme 1) [15–17].
- β-Me elimination affords $H_2C{=}CHCH_2CH(Me)R$ as the product, and is favoured for crowded metallocenes [22].



Scheme 1.

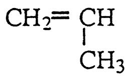
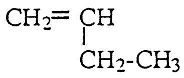
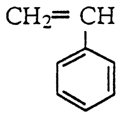
- σ-Bond metathesis between the Zr-alkyl bond and an ethylene C–H bond [23].

Most studies agree that the coordination of incoming olefin to a (theoretically convenient) "bare" metallocene alkyl cation is exothermic, and that the following olefin insertion step is rate-determining, with a small energy barrier (~25 kJ/mol in one calculation) [24].

2.2. Steric control

The symmetry of the metallocene is the main factor in determining polymer stereochemistry and minor effects may derive from the nature of the cocatalyst and the polymerization temperature. A certain stereochemical control can also arise simply from the chirality of the growing chain end (Table 2).

Table 2
Steric control of α-olefins polymerization with achiral titanocene/alumoxane catalyst

Monomer	Insertion	Polymer
 $CH_2{=}CH(CH_3)$	I°	Prevailingly isotactic (stereoblock)
 $CH_2{=}CH(CH_2\text{-}CH_3)$	I°	Less isotactic
	II°	Syndiotactic

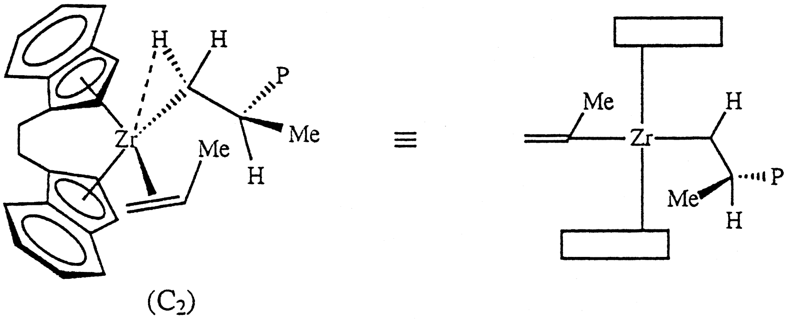
In addition to atactic PP (random orientation of methyl groups), isotactic PP (methyl groups all lie on one side of the outstretched polymer chain) and syndiotactic PP (alternating methyl groups), other stereoforms of PP have been obtained. In hemiisotactic PP, every second methyl group is oriented in the same direction, whereas the methyl groups in between adopt a random orientation. Stereoblock isotactic PP contains isotactic blocks of alternating orientation. Another form of stereoblock PP contains isotactic blocks alternating with atactic blocks [25] (Table 3).

Table 3
Relation of stereochemistry of the transition metal complex to polymer microstructure in the homogeneous polymerization of propylene

Transition metal complex		Polypropylene microstructure
Type	Stereochemistry (symmetry)	
bis-(cyclopentadienyl) Ti and Zr dichloride	Achiral (C_{2V})	Atactic or stereoblock (end group control)
Racemic ethylene *bis*-(indenyl) Zr and Hf dichloride	Stereorigid chiral (C_2)	Isotactic 95–99% (chiral site control)
Racemic ethylene *bis*-(4,5,6,7-tetrahydroindenyl) Zr (or Hf) dichloride	Stereorigid chiral (C_2)	Isotactic 86–91% (chiral site control)
Isopropyl-(cyclopentadienyl-1-fluorenyl) Hf and Zr dichloride	Stereospecific prochiral (C_s)	Syndiotactic 74–86%
(−)(R) or (+)(S)-ethylene *bis*(4,5,6,7-tetrahydroindenyl) Zr dichloride	Stereorigid chiral (pure enantiomer) (C_2)	High Mw isotactic low Mw optically active

The formation of iso- and syn-PP by C_2- and C_S-symmetry metallocenes, respectively, may result from enantiomeric-site control, in which the backbone ligand directly determines the orientation of the inserting olefin. However, some molecular mechanics studies support an indirect mechanism in which the asymmetry of the ligand skeleton determines the conformation of the polymer chain, which, in turn, determines the stereochemistry of the inserting olefin [24,26].

Scheme 2 shows the likely favoured structure of the propylene adduct of the alkylzirconocene cation with C_2-symmetry just prior to formation of the transition state. An α-agostic interaction of the growing polymer chain with zirconium may result in a relatively rigid structure with the polymer chain pointing out of the equatorial plane. For iso-PP formation using ethylene–*bis*(indenyl)zirconium dichloride, the polymer chain (P) is forced into one quadrant by a ligand benzene ring (Scheme 2); the chain forces the propylene methyl into the opposite quadrant, an effect reinforced by the other benzene ring. Successive migratory insertions afford identical enantiomeric centres yielding iso-PP; migration is not, however, essential for stereoregulation, in contrast to the case of syn-PP. In the transition state for syn-PP formation using [isopropyl-(η^5-cyclopentadienyl-1-η^5-fluorenyl)hafnium] or zirconium or titanium dichloride repulsion between the bulky fluorenyl group and the polymer chain forces the chain to the side of the cyclopentadienyl group (other studies have placed the chain on the fluorenyl side and the propylene methyl on the cyclopentadienyl side [27]). The propylene methyl is forced into the opposite quadrant into a "crevice" between the two benzene rings of the fluorenyl, farther away from the chain. The next olefin complex formed after migratory insertion has the propylene methyl in the adjacent quadrant to that in



Scheme 2.

the previous adduct, rather than the opposite quadrant as for iso-PP. Successive migratory insertions therefore afford new enantiomeric centres of opposite chirality, yielding syndiotactic polypropylene.

3. Supported metallocene catalyst

Major disadvantages of the homogeneous catalysts are the lack of morphology control and reactor fouling. Supported catalysts allow control of morphology, may be utilized in cheaper bulk propylene or gas-phase processes, and may permit the use of less MAO, whilst still offering facile control of polymer properties by ligand variation [1,7]. Active supported catalysts, showing similar stereospecificity to soluble catalysts, have been obtained by pretreatment of silica with MAO, followed by reaction of the SiO_2.MAO with a C_2-[ethylene(*bis*-η^5-indenyl)zirconium dichloride] or C_s-symmetry [isopropyl-(cyclopentadienyl-l-η^5-fluorenyl)zirconium dichloride] metallocene giving a solid, which may be activated with cheaper AlR_3 [28]. Reaction of metallocenes with the Lewis-acid supports, Al_2O_3 or $MgCl_2$, followed by activation with AlR_3 have also been reported to lead to MAO-free stereospecific catalysts [28].

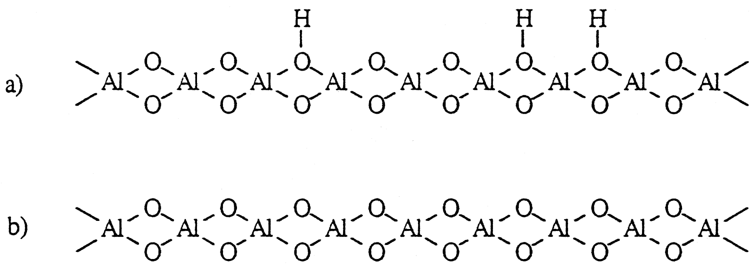
Economically feasible future plans to produce iso- or syn-PP commercially will probably rely on supported catalysts [1]. Addition of the supported catalyst as a free-flowing powder, and use of $AlEt_3$ as a scavenger, has been claimed by Hoechst to permit current iso-PP plants to be utilized for metallocene polymerization without expensive purification of the monomer feed [29]. Fina recently utilized their new catalysts to produce a batch of over 200 t syn-PP.

Binding of well-defined transition metal complexes onto carefully prepared inorganic surfaces is certainly a very attractive approach to create new heterogeneous catalysts and to characterize highly reactive species. For these reasons the use of inorganic supports has been very extended and many examples are available in the recent literature [30–32]. In this paper we focused our attention on the use of alumina, silica and zeolites for supporting metallocenes of Ti and Zr.

In a recent work concerning metalhydride alkyls bound to inorganic surfaces [33] both partially dehydroxylated alumina (PDA) and fully dehydroxylated alumina (Scheme 3) were used as supports. Interactions of these ligands with Cp_2ZrMe_2 are accompanied by CH_4 evolution, in comparatively lower amount with respect to the analogous Ti complex, probably because of the lower polar character of the Zr-alkyl bond.

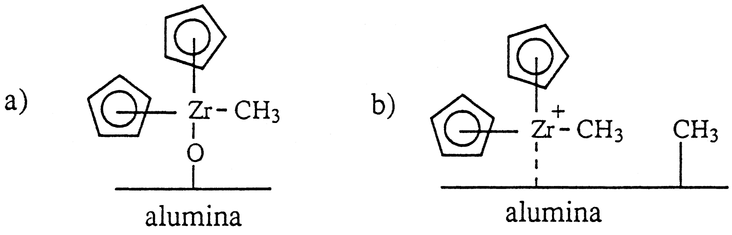
EPR measurements showed reduction to Zr(III) to be insignificant. The CPMAS ^{13}C-NMR spectra of $Cp_2Zr(^{13}CH_3)_2$/PDA indicated the presence of both μ-oxo and cationic species as reported in Scheme 4. The formation of the cationic species (zirconocene alkyl cations) explained the activity observed with these systems as heterogenized catalysts for ethylene polymerization [33].

In an analogous study [34] ethylenebis(η^5-indenyl)-zirconium dichloride ($Et[lnd]_2ZrCl_2$) and ethylenebis(η^5-tetrahydroindenyl)zirconium dichloride ($Et[IndH_4]_2ZrCl_2$) were supported on fully hydroxy-



Schematic representation of a) partially dehydroxylated alumina and b) fully dehydroxylated alumina.

Scheme 3.



μ-Oxo and cationic species on the surface of alumina.

Scheme 4.

lated, partially dehydroxylated and dehydroxylated SiO_2 and Al_2O_3. Also these supports were pre-treated with $AlMe_3$ prior to the addition of the metallocene complex.

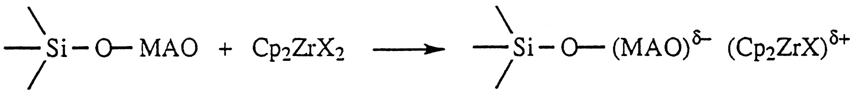
The amount of metallocene which can be attached to the surface of these supports is much lower than expected on the basis of simple physical absorption. This seems to indicate that attachment takes place at specific sites of the surface. In any case the amount of hydroxyl groups seems to play a determining role as shown by structural analysis and catalytic activity of olefin polymerization of the resulting heterogenized complexes.

The best catalytic activity was obtained in all cases by activation with methylalumoxane (MAO) of the zirconocene supported on partially dehydroxylated silica or alumina pretreated with $AlMe_3$.

When the support has been pretreated with $AlMe_3$ the formation of $-O-AlMe_2$ groups on the surface allows the fixation of the unaltered metallocene. This conclusion is supported by the observation that isotactic polymer is produced and its microstructure is very similar to that obtained with the corresponding homogeneous catalyst. Also molecular weight distribution is much narrower than that normally obtained with heterogeneous catalyst. Highly active catalysts were also obtained by supporting zirconocenes on SiO_2 pretreated with a small amount of MAO [28]. The formation of cationic species on the inorganic surface was proposed in a very analogous way as proposed in solution (Scheme 5).

The structure indicated in Scheme 5 does not really grant for a fixed support of the catalytic complex on the inorganic matrix, but rather suggests that the catalyst interacts with the "solid MAO". In a similar way ethylene-*bis*(indenyl)zirconium dichloride was supported on silica. The structure proposed suggests for the complex a very similar situation as in solution [35].

The above data are representative of a large number of papers dealing with supportation of metallocenes of transition elements of the IV group with the aim to obtain heterogeneous catalysts with active sites of one type only. As shown here the difficulty in determining the molecular structure of these complexes is mainly due to their insolubility and the limited concentration of metal complex which involves only the inorganic surface. Also the macromolecular nature of the matrix is certainly responsible for the complexity with the possibility that the transition metal complex reacts



$$\equiv Si-O-MAO + Cp_2ZrX_2 \longrightarrow \equiv Si-O-(MAO)^{\delta-}\ (Cp_2ZrX)^{\delta+}$$

Formation of silica bound cationic species.

Scheme 5.

with different number of functional groups on the surface [36].

The possible and predictable formation of different organometallic species during the supportation on inorganic matrix has been clearly evidenced in the case of alumina/Cp*TiCl$_3$ (Cp*=pentamethylcyclopentadienyl) or alumina/CpTiCl$_3$ systems [37]. The resulting heterogeneous complex when activated with Al(i-C$_4$H$_9$)$_3$ gave both syndiotactic and isotactic polystyrene. This result was attributed to the presence in the alumina of a considerable amount of Lewis acid in addition to the surface hydroxyl groups, the reaction with CpTiCl$_3$ giving, respectively, cationic and noncationic species. The former would be responsible for the syndiotactic polymerization and the latter for the isotactic polymerization. This result emphasizes the need to use "purified" inorganic supports where only one binding site for the organometallic complex is present.

Moreover, these studies suggest the importance of providing a well-defined site for the metal complex to be attached to the matrix. Zeolite was also used as a support as it was considered more informative with the possibility of following the evolution of Al and Si resonances after the various chemical reactions in which the support was involved [38].

Indeed the dealuminated zeolite contains both Si-OH groups and extrareticular aluminium (Al^{NF}). The latter can be removed by exhaustive extraction at 50°C with a solution of acetylacetone in ethanol. After this treatment the ^{27}Al-NMR (MAS) spectrum shows a single resonance at 57.45 ppm of the tetrahedral Al [39], whereas resonances at 0 and 30–50 ppm of the extrareticular Al are completely lacking [40].

Treatment of this support with Cp$_2$ZrMe$_2$ is accompanied by CH$_4$ evolution associated with the Zr–carbon bond cleavage by Si–OH groups. In order to control the last reaction the zeolite was successively treated with AlMe$_3$; the resulting support shows in the ^{27}Al-NMR (MAS) spectrum three resonances at 60.4, 33.1 and 2.2 ppm, suggesting that two different species of aluminium, associated with absorbed AlMe$_3$ and the reaction product of AlMe$_3$ with

SIOH groups,

are now present. The addition of Cp$_2$ZrMe$_2$ to the modified zeolite does not produce any CH$_4$ evolution, and the ^{27}Al-NMR (MAS) spectrum shows the same resonance as before the zirconocene addition, the relative intensities resulting only in moderate changes. In the ^{29}Si-NMR (MAS) spectrum only the resonance of the Si(OAl) species at -107 ppm can be observed [41], indicating that no changes are detectable for Si after addition of the zirconocene to the zeolite pretreated with Al(CH$_3$)$_3$.

When activated with MAO (Al/Zr=3000) the HY zeolite-supported Cp$_2$ZrMe$_2$ gives polyethylene with the same productivity (590 kg PE/mol Zr h) as the complex in the solution as expected in case of fixation on the zeolite surface and inside the channels [38] of unmodified zirconocene species. When the surface of the zeolite was pretreated with Me$_3$SiCl (Scheme 6) a similar activity as in solution was again observed thus indicating that the surface species derived in the former case from the reaction of free –OH groups with AlMe$_3$ had no significant role in the catalytic process.

Moreover, the kinetic analysis indicated that some interesting differences existed between soluble and zeolite-supported species in the case of Cp$_2$ZrMe$_2$ on HY**-AlMe$_3$. Variation of polymerization rate with time indicated that the soluble system is initially more active than the supported one, but shows a typical decay profile of polymerization rate (Rp) vs. time [42]. By contrast Rp of the zeolite-supported system remains almost constant for the first 60 min and already after 20 min is higher than that for the soluble catalyst. Then the comparable productivity of the zeolite-supported catalysts with respect to the corresponding systems in solution, despite the lower initial activity, is a consequence of the better stability of the active sites in the former systems.

$$\text{Zeolite—OH} \quad + \text{Cl—Si—(CH}_3)_3 \xrightarrow{\text{- HCl}} \text{Zeolite—O—Si—(CH}_3)_3$$

Scheme 6.

Table 4
Polymerization of propylene by MAO activated 1,2-ethylene bis (η^5-1-indenyl)-(I) and 1,2-ethylene bis (η^5-1-tetrahydroindenyl)-zirconium dichloride(II) supported on silica or alumina (from [34])

Catalyst support[a]	Isotacticity (%)[b]	$M_n \times 10^{-3}$	$Mw \times M_n$
I/PDA-$AlMe_3$	89.7	19.5	1.61
I/PDS-$AlMe_3$	89.0	19.0	1.68
I/none	89.9	18.0	1.68
II/PDS-$AlMe_3$	91.8	6.8	2.80
II/none	90.4	6.0	2.70

[a] PDA(S)-$AlMe_3$=Partially dehydroxylated alumina (or silica) pretreated with $AlMe_3$.
[b] Evaluated as % content of MMMM pentad in the methyl region of ^{13}C NMR spectrum.

As far as stereospecific control is concerned it has been shown [34] that chiral (racemic) zirconocenes are able to produce isotactic propylene when supported on partially dehydroxylated alumina or silica when these are pretreated with aluminium trimethyl (Table 4). Again this result suggests that the complex has been supported without remarkable structural modification.

Many other studies are reported in the literature showing that isotactic polypropylene with high stereoregularity can be produced in the presence of chiral metallocene complexes supported on alumina and silica [34,43,44]. However, only few cases report some attempts to confirm the active site structure and correlate the behaviour of the supported system to that of the corresponding homogeneous complex. In several studies a lower activity of the supported catalyst is accompanied by improved polypropylene properties. In particular silica supported on $(Ind)_2ZrCl_2$ gave the same high molecular weight and melting point as the commercial heterogeneous catalyst [44], but it is not clear how much of this behaviour arises from the support and/or from the modification of the complex during the interaction with the support surface.

4. Final remarks

The investigation of the supportation of metallocene catalyst on inorganic supports is still at an early stage, but has already provided significant results suggesting the actual possibility of preparing physically heterogeneous mono-site catalyst for monoalkene polymerization. These catalyst can be anticipated as the catalyst of the future for producing with high efficiency polyolefins with controlled properties.

The understanding of the detailed structure of these "mono-site" catalysts is still far from complete. Indeed many points remain open about the type of interaction between transition metal complex and support for the fixation of the latter. Also additional work is needed in order to clarify the role of the cocatalyst in connection to the possible activating effect of acidic species on the surface of the support. Finally, the possibility of controlling stereochemistry and morphology by the heterogeneous phase is a matter of active study.

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