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The Effect of Inorganic and Organic Macromolecular Structures on the Performance of Metallocene Polymerization Catalysts

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SUMMARY: After a short comparative analysis of different macromolecular ligands reported in the relevant literature, the presentation will be centered on the results obtained in the authors' laboratory using structurally defined inorganic supports in terms also of their macromolecular structure. Zeolites and mesomorphous silica can link, after proper chemical modification of their surface with MAO, unmodified metallocene complexes through cage entrapment and weak interactions, thus allowing the transfer from the solution to the solid phase. The metallocene complexes in their new phase are characterized by the catalytic behavior in olefin polymerization after activation with MAO. A decrease of productivity is generally observed depending on the type of support. The steric hindrance provided by the support is evidenced by the depression of chain transfer rate with formation of higher molecular weight polymers. Also shape selectivity is observed during copolymerization of ethylene with α-olefins having variable size. These steric effects are released when going from HY zeolite to MCM silica.

Introduction

It is generally accepted that Ziegler-Natta catalysts represent one of the earliest clear examples of molecularly defined heterogeneous catalysts. They have opened the era of the so called hybrid catalysts which combine physical separation from reagents and products with an at last partially known chemical structure of the active sites. However as they are prepared "*in situ*", the formed active chemical species are not uniform and multisites catalysis is obtained[1)]. One additional reason for complexity is the generally non specific structure of the support and of the linkage between support and catalytic species. Better defined hybrid catalysts have been successfully obtained by using the fundamental concept which contributes the theme of Macromolecular Metal Complexes Symposia, that is the heterogeneization of a transition metal complex by controlled binding to a macromolecular system insoluble in the reaction medium[2)]. This last approach was extended also to olefin polymerization catalyst and in particular to metallocene complexes by using as supports either organic polymers or inorganic

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materials for which a substantially macromolecular structure can be envisaged3). As far as organic polymer are concerned it is worth mentioning a few recent examples which also refer about previous work on the same topic. The use of starch4) and cyclodextrin5) was reported but the used support did not provide enough information for a defined structure of the complexed metal species.

Successively the attachment of various cyclopentadienyl ligands to polystyrene, allowed to support zirconocene type catalyst with interesting catalytic activity for 1-alkenes6) and styrene7) polymerization. Even in these cases the structure of the macromolecular metal complex is not fully defined even if reasonable hypotheses are proposed. Well defined polystyrene anchored Ni-complexes were obtained by covalently binding to the polymer P-O chelating ligands. Polymerization of ethylene with replica of support morphology was reported6). Poly(siloxane)s with different bis and mono benzodiclopentadienyl side chains were used to form complexes by reaction with $ZrCl_4$-2THF. These complexes show high activity for 1-alkene polymerization, and the polymer molecular weight is markedly dependent upon the substituents. However molecular weight distribution is often larger than 2.0, thus suggesting a non uniform structure of the supported zirconocenes9,10).

Among inorganic macromolecular ligands silica was used by several laboratories and previous reports had already mentioned the difficulty which are encountered in obtaining catalysts with the same structure as in the homogeneous phase.

Kaminsky and Renner11) reported that absorption of $Et(Ind)_2ZrCl_2$ on silica followed by treatment with MAO provided polypropylene with high melting point and molecular weight. As no evidences about catalyst structure was indicated, one cannot exclude that the new supported catalyst behaves in this way because the indenyl ligands were removed during the reaction with the silica surface12). This conclusion is substantially in agreement with the results reported by Sacchi *et al.*13) on the stereochemical analysis of polypropylene prepared with the same supported systems. Moroz *et al.*14) confirmed the need of pretreating the silica surface with Me_3SiCl or AlR_3 to remove silanol groups as reported by us for zeolites3). They also reported that using MAO of the cocatalyst the polymer morphology is similar to that obtained with the homogeneous system, thus suggesting that MAO detaches the metallocene from the support. Silica surface was also modified by aminopropyltrimethoxysilane15) and $Cp(CH_2)_3Si(OCH_2CH_3)_3$16). In this last case an accurate characterization of the supported complex structure was attempted in order to relate it to the catalytic activity.

The (butylcyclopentadienyl)$_2$ZrCl$_2$ was also supported on silica from a solution of the metallocene and MAO in liquid 1-hexene or styrene or 1,7-octadiene by the “incipient wetness” method. The preformed polymers provides a protective layer to the supported complex thus improving its stability and exerting an interesting effect on catalytic activity17).

Highly hydroxylated alumina and silica reacted with MAO provided useful supports for the heterogeneization of ansametallocenes such as en(η^5-indenyl)$_2$ZrCl$_2$, Me$_2$Si(η^5-indenyl)$_2$ZrCl$_2$ and Me$_2$C(Cp)(η^3-Flu)ZrCl$_2$. The unmodified complex supportation was proposed on the basis of catalytic performances, particularly in producing uniform ethylene-1-hexene copolymers[18].

In the present paper the effect of more defined inorganic supports is discussed with the aim to show the possible advantages of their crystalline structure with properly sized cavities which can entrap metallocenes and exert shape selectivity effects. In doing that we were attracted by the idea of considering zeolites as solid solvents[19] that is as a tool transfer the metallocene from the liquid to the solid phase without modification.

2. Stability of HY-zeolite/Cp_2ZrCl_2 macromolecule-metal complexes under catalytic conditions

In a previous paper[20] HY-zeolite was pretreated with various reagents [$AlMe_3$, $ClSi(OMe)_3$] to remove -OH groups before its use as support. In the present paper the supported catalysts were prepared only after pretreating the surface with a MAO toluene solution and successive washing with toluene and addition of the metallocene in the same solvent. The solid was further washed with toluene and the amount of fixed metallocene determined spectrophotometrically by difference. A supported catalyst obtained in this way from HY/MAO and Cp_2ZrCl_2 was treated at 20 °C with MAO in toluene and the solution separated from the solid. As it can be observed from the data of Table 1, the solid phase after addition of MAO was 14 times more active than the related solution, thus indicating that more than 93 % of the polymer was produced by the complex attached to the support[21]. This conclusion is substantiated by the polymer morphology which is clearly very different from that obtained with the homogeneous catalyst[22].

Table 1. Polymerization activity of solid and solution from HY/MAO/Cp_2ZrCl_2 macromolecule metal complex at different temperatures[a].

Temperature °C	Catalytic system[b]	Polyethylene yield g
20	1) HY/MAO/Cp_2ZrCl_2	3.13
	2) Solution	0.22
	3) Solid	2.84
70	1) HY/MAO/Cp_2ZrCl_2	8.36
	2) Solution	3.49
	3) Solid	5.88

[a] Reaction carried out in toluene for 60 min.

[b] 1) Whole supported complex system, 2) decanted solution, 3) insoluble residue

This conclusion is no longer valid when the polymerization is carried out at 70 °C as the productivity of the soluble catalyst increases up to 35 %, thus showing substantial leaching of the metal at higher temperature, which can be related to the better penetration of the solvent and to the weakening to the complex/support interactions.

The successive experiments were then carried out at 20 °C with the supports indicated in Table 2 as discussed in section 3.

Table 2. Characteristics of inorganic supports.

Type	SiO_2/Al_2O_3	Surface area	Pore volume	Pore diameter
		m^2/g	cm^3/g	Å
HY-Zeolite	5.7	850	~ 0.3	8.0
Mesomorphic MCM-41	∞	1,100	1.3	29.7
Silica	∞	280	1.9	–

3. Metallocene complexes with mesoporous silica

Mesoporous siliceous solids with large diameter channel apertures are known; a typical example is MCM-41 which consists of tubes with inner diameter larger than 25 Å (Table 2).

Titanocene derivatives were attached to the inner walls of this mesoporous silica by using the reaction between Cp_2TiCl_2 and the free silanol groups of the walls. The fixation of Ti species [of the type $(\text{-SiO})_xTiCp_{2-x}$] inside the pores was confirmed by EXAFS and FTIR investigation, which were consistent with $x = 1$[23)]. $Et(Ind)_2ZrCl_2$ was attached to the surface of MCM-41 which had been pretreated with MAO. After activation with additional MAO the heterogeneous complex showed 30 % lower activity than the homogeneous analog in propylene polymerization, formation of higher molecular weight chain and higher slightly improved isotacticity[24)].

In our case substantially consistent results in ethylene (Table 3) and propylene polymerization (Table 4) were obtained by using complexes with different steric hindrance and stereospecific control confined in the pores of MCM-41 silica[25)].

A part of a partial (~30 to 50 % on average) reduction of productivity, the MCM-41 supported zirconocene complexes behave as in solution. The reduction of productivity is lower than for HY-complexes which however give rise to a marked increase of molecular weight. Even the copolymerization of ethylene with 1-hexene does not change this scenario. Indeed (Table 5) both homogeneous and MCM-41 heterogeneized catalysts give copolymers with comparable composition, for all metallocene complexes examined.

The rigidly shaped support appears to exert a physical deactivation by partially hindering or slowing down the access to the metallocenes by cocatalyst and monomer, while allowing a substantial unmodified supportation of the original metallocene.

Table 3. Polymerization of ethylene by various MCM-41 supported metallocene complexes[a)].

Catalytic complex	Duration	Productivity	M_v[b)]	T_m
	min	kg/mol Mt·h		°C
Cp_2ZrCl_2	20	1,210	132,000	134
MCM-41–MAO–Cp_2ZrCl_2[c)]	20	920	188,000	133
Ind_2ZrCl_2	30	870	169,000	136
MCM-41–MAO–Ind_2ZrCl_2	30	740	164,000	136
$Et(Ind)_2ZrCl_2$	20	2,090	105,000	136
MCM-41–MAO–$Et(Ind)_2ZrCl_2$	20	1,780	127,000	133
$Me_2Si(Ind)_2ZrCl_2$	20	1,680	169,000	132
MCM-41–MAO–$Me_2Si(Ind)_2ZrCl_2$	20	1,140	197,000	133
$Et(Ind)_2HfCl_2$	60	110	310,000	133
MCM-41–MAO–$Et(Ind)_2HfCl_2$	60	60	361,000	135
$Me_2Si(Ind)_2HfCl_2$	60	145	450,000	135
MCM-41–MAO–$Me_2Si(Ind)_2HfCl_2$	60	50	468,000	137

a) In 80 ml toluene at 20 °C; Mt (Mt = Zr, Hf): 5 μmol, cocatalyst: MAO, ethylene pressure: 2 bar, Al/Mt: 1,000.

b) Evaluated by viscometry in decalin at 135 °C.

c) Al/Z r = 300

Table 4. Polymerization of propylene by various MCM-41 supported metallocene complexes[a)].

Catalytic complex	Productivity	M_v[b)]	T_m
	kg/mol Mt·h	°C	
Ind_2ZrCl_2	1,360	2,000	–
MCM-41–MAO–Ind_2ZrCl_2	820	4,000	–
$Et(Ind)_2ZrCl_2$	2,270	31,000	137
MCM-41–MAO–$Et(Ind)_2ZrCl_2$	2,010	35,000	137
$Me_2Si(Ind)_2ZrCl_2$	2,520	61,000	147
MCM-41–MAO–$Me_2Si(Ind)_2ZrCl_2$	1,730	64,000	147
$Et(Ind)_2HfCl_2$	620	390,000	136
MCM-41–MAO–$Et(Ind)_2HfCl_2$	390	495,000	136
$Me_2Si(Ind)_2HfCl_2$	690	488,000	143
MCM-41–MAO–$Me_2Si(Ind)_2HfCl_2$	430	614,000	139

a) In 80 ml toluene at 20 °C; Mt (Mt = Zr, Hf): 5 μmol, cocatalyst: MAO, propylene pressure: 2 bar, Al/Mt: 1,500, duration 60 min.

b) Evaluated by viscometry in decalin at 135 °C.

Table 5. Copolymerization of ethylene with 1-hexene in the presence of MCM-41/MAO/zirconocenes and their not supported analogues[a].

Catalyst	Productivity	1-Hexene[b]	M_v[c]	T_m
	kg/mol Mt·h	%-mol		°C
Cp_2ZrCl_2	3,260	20	7,000	89/117
MCM-41–MAO–Cp_2ZrCl_2	3,140	17	10,000	96/114
Ind_2ZrCl_2	2,550	4	21,000	120
MCM-41–MAO–Ind_2ZrCl_2	2,120	<1	31,000	124
$Et(Ind)_2ZrCl_2$	2,340	36	15,000	125
MCM-41–MAO–$Et(Ind)_2ZrCl_2$	2,180	24	19,000	121
$Me_2Si(Ind)_2ZrCl_2$	3,050	21	21,000	121
MCM-41–MA⊖–$Me_2Si(Ind)_2ZrCl_2$	2,980	17	26,000	123
$Et(Ind)_2HfCl_2$	180	16	81,000	95/128
MCM-41–MAO–$Et(Ind)_2HfCl_2$	150	14	92,000	95/126

[a] In 80 ml ol 1 M solution of 1-hexene in toluene, at 20 °C for 30 min; cocatalyst: MAO, ethylene pressure: 6 bar, Mt (Mt = Zr or Hf): 5 μmol, [Al]/[Mt]: 2,000, duration 60 min.

[b] Evaluated by ^{1}H-NMR.

[c] Evaluated by viscometry in decalin at 135 °C.

4. Metallocene complexes with Y-zeolites

Previous data from our laboratory[3,20] with HY-zeolite and from other laboratory with NaY-zeolite[24,26] have shown that heterogenized metallocenes with interesting catalytic properties can be obtained by using these inorganic macromolecular structures as supports.

Now we wish to discuss some recent studies indicating that HY-zeolites with their well definite structure and smaller pores can affect more markedly the catalytic behavior of metallocenes. The homopolymerization of both ethylene and propylene with Cp_2ZrCl_2 and various ansametallocenes[21] supported on HY-zeolites has shown that a marked decrease of activity and a remarkable increase of molecular weight is observed in case of Cp_2ZrCl_2. These effects are less evident with ansametallocenes which because of their shape cannot enter the pores of the zeolite structure. On the other side the substantial confinement of Cp_2ZrCl_2 in the pores could be substantially supported by copolymerization of ethylene with α-olefins having variable shape[20]. While in the case of MCM-41 support, homogeneous and heterogenized catalysts give copolymers with similar structure, this is no longer the case when HY-zeolite is used, as indicated by the results obtained by using different α-olefins as copolymerization solvents (Table 6). In all cases the homogeneous Cp_2ZrCl_2/MAO catalyst gives oligomers with almost 1/1 α-olefin/ethylene composition, shoving that practically only initiation by ethylene followed by prompt transfer to the α-olefin occurs. With the supported catalyst the access to the active sites by the α-olefins is hindered by their confinement inside the zeolite pores, thus incorporation of the α-olefins is lower but the transfer rate is depressed and higher molecular weight is obtained. This result provides a clear indication of the shape selectivity exerted by the superstructure of the inorganic ligand. This concept has been used to produce ethylene/1-hexene copolymers with 5 % content of α-olefins but with a very uniform distribution, high molecular weight and a single melting point[20)].

Table 6. Copolymerization of ethylene with α-olefins in the presence of Cp_2ZrCl_2 and HY-zeolite-MAO/Cp_2ZrCl_2 complexes[a)].

Catalyst	Co-monomer	Productivity kg/mol Mt·h	Comonomer[b] %-mol	M_v[c)]
Cp_2ZrCl_2	1-hexene	9,380	~ 50	1,240
	4-methyl-1-pentene	8,680	~ 50	390
	1-octene	11,500	~ 50	560
HY–MAO–Cp_2ZrCl_2	1-hexene	1,740	22	19,000
	4-methyl-1-pentene	1,120	8	62,000
	1-octene	820	19	22,000

[a)] 5 μmol of homogeneous zirconocene or 10 μmol of supported zirconocene in 80 ml α-olefin; MAO/Zr = 2,000, ethylene pressure: 6 bar, duration 60 min.

[b)] Evaluated by ^{1}H-NMR.

[c)] Evaluated by viscometry in decalin at 135 °C.

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