Effect of the zeolite HY-support on the monoalkene polymerization by group IV metallocenes

M. Michelotti [a,1], G. Arribas [b], S. Bronco [c], A. Altomare [a,*]

[a] *Department of Chemistry and Industrial Chemistry, University of Pisa, via Risorgimento 35, I-56126 Pisa, Italy*
[b] *Universidad Central de Venezuela, Apartado 47102, Caracas, Venezuela*
[c] *INFM, Operative Unit of Pisa, Department of Chemistry and Industrial Chemistry, University of Pisa, via Risorgimento 35, I-56126 Pisa, Italy*

Abstract

Various metallocene complexes of the IV group transition metals supported on HY zeolites were investigated in the polymerization of ethylene and propylene. A comparative study with the same catalysts operating in solution was also performed. Generally, a decrease in the catalytic activity after support was observed, whose extent depends on the preliminary treatment of the support with aluminum alkyl. In general, better stability with the time and higher molecular weight of the polymers were obtained. The high isotactic stereospecificity of chiral metallocene catalysts for propylene polymerization was maintained after support. In the case of the aspecific bis(indenyl) complex, a modest but significant effect on the stereospecific control was observed due to the steric influence of the support. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Zeolite; Metallocenes; Supported catalysts; Homopolymerization; Ethylene; Propylene

1. Introduction

In the last few years, a number of studies have been performed to identify different kinds of supports such as silica, alumina, $MgCl_2$ and some other metal oxides, which can immobilize various metallocene catalysts. The common characteristic of these inorganic carriers is to have a broad pore size distribution and an amorphous structure [1–8]. The support has the advantage of allowing the use of homogeneous metallocenes [9–11] for the gas-phase and slurry polymerization and to reduce the large excess of expensive methylalumoxane (MAO) as cocatalyst. Furthermore, only in the presence of heterogeneous catalysts, the formation of uniform polymer particles and high bulk density can be obtained. The supported catalysts, only in a few cases, were able to polymerize olefins with activities comparable to those of the homogeneous catalysts, and, sometimes the peculiar stereoregulating capability of the catalytic system was modified [12].

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* Corresponding author. Tel.: +39-050-918271; fax: +39-050-918320; E-mail: altomare@dcci.unipi.it
[1] Present address: Replast S.r.l. via Pio La Torre I-55032 Castelnuovo Garfagnana (Lucca), Italy.

On the other side, HY zeolites exhibit crystalline structures, defined narrow pore size distribution and large surface area [13]. Previous studies in this context showed that these materials are suitable supports because of the possibility of entrapping organometallic complexes inside the pores [14–17]. The catalytic activity of these supported systems is only, in some cases, similar to that obtained in homogeneous conditions, but the molecular weight of the produced material is increased [18,19].

More recently, the metallocene system *rac*-Et(Ind)$_2$ZrCl$_2$ (Et: ethylene, Ind: indenyl) was supported on MCM-41 silica- and VPI-5 alumino–phosphate-based molecular sieves. The supported catalysts showed high catalytic activity in propylene polymerization [20].

In this paper, some results are presented concerning both aspecific biscyclopentadienyl and bisindenyl complexes and isospecific bridged ethylene–bisindenyl complexes supported on HY zeolites following different routes. The catalytic performance in monoalkene homopolymerization is also investigated with the aim of evaluating the support effect on the process.

2. Experimental

All operations were carried out under a dry argon atmosphere.

2.1. Materials

Degussa (Germany) HY zeolites were dehydrated at 600°C for 24 h and at 100°C for 24 h immediately prior to their use. Polymerization grade ethylene and propylene were obtained from Rivoira and used as received. Toluene and *n*-heptane were purified by refluxing and subsequent distillation over Na/K alloy. Dichloromethane was refluxed over CaH$_2$ and then distilled. 4-Methyl-1-pentene, 1-hexene, 1-octene and 1-dodecene were refluxed over Na/K alloy and successively distilled. Methylalumox-

ane (MAO) (Witco, 30% w/w toluene solution), trimethylaluminium (AlMe$_3$) (Aldrich, 2.0 M toluene solution), tri*iso*butylaluminium [Al-(*i*Bu)$_3$] and Cp$_2$ZrCl$_2$ (Janssen) were commercially obtained and used without further purification. Cp$_2$ZrMe$_2$ [21], Ind$_2$ZrCl$_2$ [22], Et(Ind)$_2$ZrCl$_2$ [23] and Et(Ind)$_2$HfCl$_2$ [24] were prepared according to the literature.

2.2. Preparation of the supported catalysts

All the supported catalysts were prepared according to the following typical procedures.

2.2.1. Method 1

0.16 mmol of Cp$_2$ZrCl$_2$ (0.005 M toluene solution) were added to 1.8 g of HY zeolite, followed by vigorous stirring of the mixture at 60°C for 24 h. The solid part was then washed with toluene and the resulting solution analyzed by UV–visible spectrophotometry in order to determine the amount of unadsorbed metallocene.

2.2.2. Method 2

Nine millimoles of MAO (4.5 M toluene solution) were added to 4.5 g of HY zeolite in 40 ml of toluene. The mixture was vigorously stirred at room temperature for 24 h, then the solid part was washed more than 5 times with 40 ml of toluene. 0.40 mmol of Cp$_2$ZrCl$_2$ (0.005 M toluene solution) were successively added to the suspension of the HY-MAO precursor, followed by stirring at 60°C for 24 h. The solid part was then washed with toluene and the washing solutions were analyzed by UV–visible spectrophotometry.

2.2.3. Method 3

Five millimoles of AlMe$_3$ (2 M toluene solution) were added to 2.4 g of HY zeolite in 60 ml of toluene. The mixture was vigorously stirred at room temperature for 24 h, then the solid part was washed more than 5 times with 40 ml of toluene. 0.21 mmol of Cp$_2$ZrCl$_2$ (0.006 M

toluene solution) were successively added to the suspension of the HY-AlMe$_3$ precursor, followed by stirring at 60°C for 24 h. The solid part was then washed with toluene and the washing solutions were analyzed by UV–visible spectrophotometry.

2.2.4. Polymerizations

All polymerizations were carried out in a 200-ml glass reaction vessel (Büchi) equipped with a mechanical stirrer and a temperature controller. Eighty milliliters of toluene, MAO and the catalyst solution or slurry were transferred in this order under argon atmosphere. The reaction mixtures were degassed and then ethylene or propylene were introduced until the desired pressure was reached. The polymerization experiments were stopped by addition of a 5 vol.% HCl/methanol solution and the polymers were recovered by filtration, thoroughly washed with methanol and dried in vacuum at 50°C until constant weight. Specific reaction conditions may be found in the appropriate tables and in the text. The oligomerization experiments with liquid olefins were carried out in glass vials with 30 ml of toluene, 0.06 moles of α-olefin, MAO and the catalyst solution or slurry added in this order. The reactions were quenched by adding acidic water and the organic solutions were extracted with water, dried over anhydrous Na$_2$SO$_4$ and submitted to gas-chromatographic, IR and NMR analysis.

2.3. Polymer characterization

Molecular weights of the produced polymers were determined by intrinsic viscosity measurements in decahydronaphthalene (decalin) at 135°C using an Ubbelohde viscometer by a one-point method [25] and calculated accordingly [26,27]. The melting points of the polymers were measured by differential scansion calorimetric analysis (DSC) on samples which had been previously melted and recrystallized using a Mettler TA 3000 calorimeter with a heating rate of 15 K/min. The microstructure

of the poly(propylene) samples was determined by ^{13}C-NMR, recording spectra at 120°C with a Varian spectrometer operating at 50 MHz. The polymers were dissolved in 1,2,4-trichlorobenzene/benzene-d_6 (vol. ratio 9/1) up to 10 wt.%. ^{1}H-NMR analysis of the oligomeric mixtures of α-olefins was carried out after solvent and monomer evaporation in CDCl$_3$ solution with a Varian spectrometer operating at 200 MHz.

2.3.1. Metallocene release tests

Ten micromoles of zeolite supported Cp$_2$ZrCl$_2$ as toluene slurry and the prescribed amount of MAO solution ([Al]/[Zr] = 1.0) were precontacted at 20 or 70°C for 60 min in 80 ml of toluene and in the absence of the monomer. The mixture was filtered under argon and both the filtrate and the solid residue were successively used after further addition of the MAO solution to polymerize ethylene in the above described way.

3. Results and discussion

3.1. Polymerization of ethylene with HY zeolite supported Cp$_2$ZrCl$_2$

The catalyst support was carried out either by directly adding the metallocene complex to a HY zeolite suspension in toluene (Method 1) or after pretreatment of the support with alkyl aluminum compounds such as MAO or AlMe$_3$ (Methods 2 and 3, respectively). In this last way, no alteration of the catalyst structure takes place, because the hydroxyl groups on the support surface are transformed in non-acid groups (Scheme 1). The amount of entrapped metallocene was maintained below the saturation value.

All the catalytic slurries were then tested in various ethylene polymerization experiments with different co-catalysts, by modifying the Al/Zr mole ratio, the reaction temperature and monomer pressure, according to what described in Tables 1 and 2. The zeolite samples used
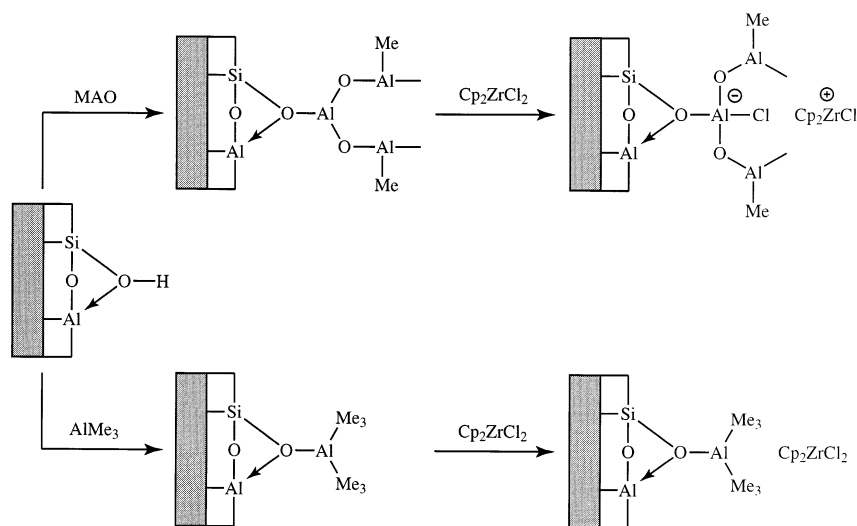
Scheme 1. Modification of HY-zeolite surface hydroxyl groups with MAO and AlMe$_3$ followed by reaction with Cp$_2$ZrCl$_2$.

were characterized by molar ratios SiO$_2$/Al$_2$O$_3$ = 27 and 5.7, respectively. It is to be underlined that the quoted Al/Zr mole ratio is only based on the co-catalyst added during polymerization, the alkyl aluminum adsorbed on the zeolite being not considered.

The support produced a remarkable decrease in the catalytic activity as compared to Cp$_2$ZrCl$_2$ in solution (run EZ01 vs. EZ03, Table 1). This effect was reduced by the use of pretreated zeolite. The preliminary treatment of the zeolite with MAO (Scheme 1a) is characterized by the formation of catalytic systems 2–3 times more active than those obtained by AlMe$_3$ pretreatment (Scheme 1b, run EZ05-EZ07 vs. EZ08-EZ11, Table 1), because of the likely creation of immobilized cationic complexes weakly coordinated to chemically bounded MAO. The replacement of Cp$_2$ZrCl$_2$ with the dialkylated metallocene Cp$_2$ZrMe$_2$ (run EZ09 vs. EZ11, Table 1) was not characterized by substantial modification either of the catalytic activity or of the polymer properties. Viscosity average molecular weights of polyethylene samples obtained with supported catalysts were fairly higher than those obtained with the homogeneous one (run EZ05 and EZ07 vs. EZ01). Higher values of the k_p/k_{tr} ratio (k_p = rate constant for propagation reaction and k_{tr} = rate constant for transfer reaction) could be originated by stabilized cationic species confined inside the pores of the support for which β-hydride elimination is sterically hindered.

An increase in the reaction temperature has the effect to increase the polymer productivity

Table 1
Ethylene polymerization with Cp$_2$ZrCl$_2$ supported on HY zeolite (SiO$_2$/Al$_2$O$_3$ = 27)[a]

Run	Support (type)	S.A.[b]	$\overline{M}_v \times 10^{-3c}$
EZ01[d]	none	1270	136
EZ03	HY	18	n.d.
EZ04[e]	HY	35	n.d.
EZ05	HY-MAO	190	232
EZ06[f]	HY-MAO	998	21
EZ07[e]	HY-MAO	316	252
EZ08	HY-AlMe$_3$	60	214
EZ09[f]	HY-AlMe$_3$	268	43
EZ11[g]	HY-AlMe$_3$	288	45

[a]Reaction carried out in 80 ml of toluene with 10 μmol of Zr, at 20°C; 2 bar ethylene pressure, 60 min polymerization time, MAO as cocatalyst and [Al]/[Zr] = 1000, catalyst preparation: EZ03/04 = method 1; EZO5-07 = method 2; EZ08-011 = method 3.
[b]Specific activity expressed as kg/mol Zr h.
[c]Determined by viscosity measurements in decalin at 135°C.
[d]Reaction carried out with 5 μmol of Zr in solution.
[e][Al]/[Zr] = 2000.
[f]60°C reaction temperature.
[g]Reaction carried out at 60°C with supported Cp$_2$ZrMe$_2$.

Table 2
Ethylene polymerization with Cp_2ZrCl_2 supported on HY zeolite $(SiO_2/Al_2O_3 = 5.7)$[a]

Run	Support (type)	S.A.[b]	$\overline{M}_v \times 10^{-3c}$
EZ01	none	1270	136
EZ13	HY-MAO	58	170
EZ14	HY-MAO	844	33
EZ18[e]	HY*-MAO	313	352
EZ19[d,e]	HY*-MAO	836	44
EZ15	HY-AlMe$_3$	36	193
EZ16[f]	HY-AlMe$_3$	135	305
EZ17[d]	HY-AlMe$_3$	890	26

[a]Reaction carried out in 80 ml of toluene at 20°C, with 10 μmol of Zr, [Al]/[Zr] = 1000, 60 min polymerization time, 1 bar ethylene pressure, MAO as cocatalyst; catalyst preparation: EZ13/14/18/19 = method 2; EZ15-17 = method 3.

[b]Specific activity expressed as kgPE/mol h.

[c]Determined by viscosity measurements in decalin at 135°C.

[d]70°C reaction temperature.

[e]HY* = HY zeolite calcinated at 625°C.

[f]5 bar ethylene pressure.

(EZ05 vs. EZ06 and EZ08 vs. EZ09 in Table 1), but decreases the molecular weight of the produced polymer.

Moreover, the available data point out a dependence of the catalytic activity on the zeolite SiO_2/Al_2O_3 mole ratio: a reduction of this parameter from 27 to 5.7 was accompanied by a marked decrease in the polymer productivity (EZ13 and EZ15 in Table 2 vs. EZ05 and EZ08, respectively in Table 1) which is possibly related to the dealumination effect. This process could partially create mesopores in the zeolite framework, which are supposed to be able to accommodate more easily the polymer chain growing on the active site.

The use of either MAO or AlMe$_3$ pretreated supports gave rise to catalytic systems of widely different activity. Indeed, the MAO-pretreated slurry gave a catalytic system at 20°C sixfold more active (run EZ18, Table 2) than that obtained by employing the same zeolite pretreated with AlMe$_3$ (run EZ13, Table 2) and a polymeric product having higher molecular weight and melting point.

A detailed investigation on the different behavior of homogeneous and HY* supported catalysts was carried out by ethylene poly-merization tests at 20°C and variable time. The catalytic activity as a function of time in the two cases is illustrated in Fig. 1.

In the case of solution polymerization the maximum catalytic activity was reached in few minutes followed by an exponential decay. In the case of the supported-phase, the specific activity increased during the first 30 min reaching a constant value which was maintained for the following 60 min. This could prove at the same time the major difficulty in activation of zeolite anchored sites by the cocatalyst and their prevented deactivation.

The comparison between the behavior of Cp_2ZrCl_2 in solution and supported on HY* zeolite in ethylene polymerization experiments carried out at 20°C by varying the mole ratio Al/Zr in the range 200–1000 is shown in Fig. 2.

Although the homogeneous catalytic system was able to produce a higher yield, this advantage was fairly reduced as long as the Al/Zr ratio was decreased. On the other side, even if the supported catalyst was characterized by a lower yield at higher Al/Zr ratios, the observed catalytic activity was only slightly reduced by lowering this parameter. The two systems were characterized by almost the same productivity at about Al/Zr = 400.
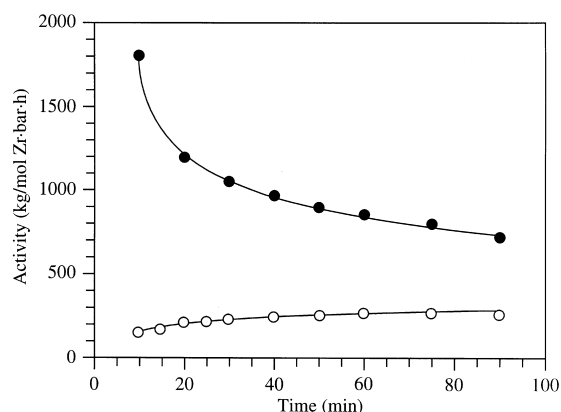

Fig. 1. Time dependence of ethylene polymerization rate with MAO activated Cp_2ZrCl_2 (●) and HY-MAO-Cp_2ZrCl_2 (○) systems.
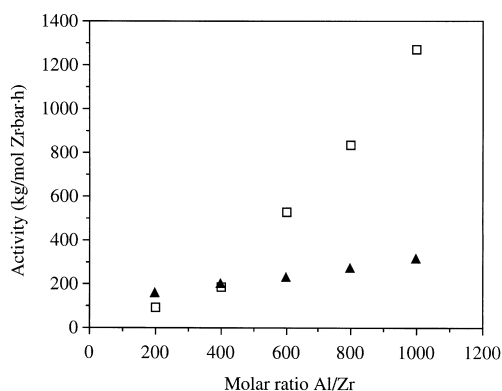
Fig. 2. Dependence of ethylene polymerization rate with MAO activated Cp_2ZrCl_2 ($\square$) and HY-MAO-Cp_2ZrCl_2 ($\blacktriangle$) systems on Al/Zr molar ratio.

Because of the obvious concern about the possibility that the added MAO may cause desorption of some of the metallocene compound from the support, leading to the production of a soluble catalyst, a few experiments were carried out to investigate this effect (Table 3).

The supported catalyst (HY*-MAO-Cp_2-$ZrCl_2$) was precontacted with a MAO solution in toluene at 20 and 70°C, respectively. The suspensions were filtered and the filtrates (Cat-A) used to polymerize ethylene according to the usual procedure (runs EX1 and EX3 in Table 3). The solid residues (Cat-B) were employed as polymerization catalysts after addition of a MAO solution (runs EX2 and EX4 in Table 3). The soluble portion (Cat-A) obtained at 20°C is characterized by a very low content of catalyst desorbed by MAO during the ageing of the catalyst, whereas the Cat-B original catalytic activity was almost restored on addition of MAO. A rather different behavior was observed after the ageing at 70°C: in this case, a partial release of the metallocene was evidenced by comparing the yields obtained in the presence of Cat-A (EX3 vs. EX1) and Cat-B (EX4 vs. EX2). The reaction temperature can, therefore, affect the transfer of the complex coordinated to MAO on support surface to MAO in solution. From these results, it is apparent that the bulk of the polymer is mainly derived from a supported

catalyst in the case of polymerization experiments performed at room temperature, whereas a partial extraction of the active sites by the added cocatalyst cannot be avoided at higher temperatures.

A number of polymerization tests were also carried out by changing the reaction solvent, thus varying the polarity of the medium (Table 4) [28].

The homogeneous catalyst showed only a slight increase in the specific activity, ingoing from toluene (EZ01) to dichloromethane (EZ20) and a 30% decrease if *n*-heptane was used (EZ22). No relevant effects on the molecular weight and melting point of the produced poly(ethylene)s were observed. For the supported system, on the contrary, solvent change substantially affected the polymer productivity and the formation of less active catalysts by the support process was once more confirmed. Higher polymer productivity (EZ21 vs. EZ18 and EZ23 in Table 4) associated with a decrease in the molecular weight and the melting point of the polymer was reached in a polar solvent, whereas an opposite effect was observed in *n*-heptane. As a possible explanation of these results, an increase or reduction in the swelling of the support can be proposed. For this reason a partial desorption of the metallocene compound could not be excluded in the case of dichloromethane as solvent.

A few ethylene polymerization experiments were carried out in the presence of HY*-MAO-

Table 3

Ethylene polymerization with HY*-MAO supported Cp_2ZrCl_2 and the catalysts Cat-A and Cat-B[a]

Run	Catalyst	Temperature (°C)	Yield (g)
EZ18[b]	HY*-MAO-Cp_2ZrCl_2	20	3.13
EX1	Cat-A	20	0.22
EX2	Cat-B	20	2.84
EZ19[b]	HY*-MAO-Cp_2ZrCl_2	70	8.36
EX3	Cat-A	70	3.49
EX4	Cat-B	70	5.88

[a] Reaction carried out in 80 ml of toluene, polymerization time 60 min.

[b] HY* = HY zeolite calcined at 625°C.

Table 4
Ethylene polymerization with Cp_2ZrCl_2 in solution or supported on HY zeolite ($SiO_2/Al_2O_3 = 5.7$) in different solvents[a]

Run	Catalyst	Solvent	S.A.[b]	$\overline{M}_v \times 10^{-3c}$	T_m (°C)[d]
EZ01	Cp_2ZrCl_2	Toluene	1270	136	134.7
EZ18[e]	HY*-MAO-Cp_2ZrCl_2	Toluene	313	352	140.2
EZ20	Cp_2ZrCl_2	Dichloromethane	1320	112	133.6
EZ21[e]	HY*-MAO-Cp_2ZrCl_2	Dichloromethane	645	179	135.2
EZ22	Cp_2ZrCl_2	*n*-Heptane	880	126	134.0
EZ23[e]	HY*-MAO-Cp_2ZrCl_2	*n*-Heptane	35	330	138.5

[a]Reaction carried out at 20°C, in 80 ml of solvent, with 5 μmol of Zr in solution or 10 μmol of supported Zr, 1 bar ethylene pressure, polymerization time 60 min, [Al]/[Zr] = 1000.

[b]Specific activity expressed as kg/mol Zr bar h.

[c]Determined by viscosity measurements in decalin at 135°C.

[d]Determined by DSC.

[e]HY* = HY zeolite calcinated at 625°C.

Cp_2ZrCl_2 with a cocatalyst system made of a mixture obtained by partially replacing MAO with Al(*i*-Bu)$_3$ while maintaining a total Al/Zr mole ratio of 1000. The results shown in Table 5 gave evidence of a decrease in the polymer productivity brought by the gradual replacement of MAO with Al(*i*-Bu)$_3$ with a discontinuity region at about MAO/Al(*i*-Bu)$_3$ = 1 (EZ28) and the complete disappearance of the catalytic

activity when MAO was totally replaced by the trialkylaluminum compound (EZ33).

Furthermore, the progressive substitution of MAO with Al(*i*-Bu)$_3$ was accompanied by an exponential decrease in the molecular weight of the produced poly(ethylene)s, following a more pronounced incidence of the transfer reaction to the alkylaluminum compound. The observed behavior with mixed cocatalyst systems could be

Table 5
Ethylene polymerization with Cp_2ZrCl_2 supported on HY*[a] zeolite ($SiO_2/Al_2O_3 = 5.7$) and the mixed cocatalyst system MAO/Al(*i*-Bu)$_3^b$

Run	[MAO]/[Zr]	[Al(*i*-Bu)$_3$]/[Zr]	S.A.[c]	$\overline{M}_v \times 10^{-3d}$	T_m (°C)[e]	X_c (%)[f]
EZ18	1000	0	313	352	140.2	56
EZ24	900	100	294	172	137.8	55
EZ25	800	200	280	111	135.2	55
EZ26	700	300	271	97	133.9	54
EZ27	600	400	255	84	132.7	51
EZ28	500	500	148	75	131.8	49
EZ29	400	600	125	69	130.4	45
EZ30	300	700	94	64	128.9	43
EZ31	200	800	72	59	127.8	39
EZ32	100	900	40	56	127.4	39
EZ33	0	1000	0	–	–	–

[a]HY* = HY zeolite calcinated at 625°C.

[b]Reaction carried out at 20°C in 80 ml of toluene with 10 μmol of Zr, 2 bar ethylene pressure, polymerization time 60 min.

[c]Specific activity expressed as kg/mol Zr h.

[d]Determined by viscosity measurements in decalin at 135°C.

[e]Determined by DSC.

[f]$X_c = \Delta H_f \times 100/\Delta H_f^\circ$, where ΔH_f is the heat of fusion of the sample as determined from the DSC curve and ΔH_f° is the heat of fusion of folded-chain polyolefine crystals for polyethylene (269.9 J/g) [31].

explained by variations in the nature or in the number of the active sites or by the presence of various species at the equilibrium [29].

3.2. Ethylene and propylene homopolymerization with zeolite supported bis(indenyl) and ethylenebis(indenyl)Zr(Hf)Cl₂

Further supported catalysts were prepared by immobilizing aspecific bis(indenyl) and isospecific ethylenbis(indenyl) complexes on MAO pretreated HY* zeolite ($SiO_2/Al_2O_3 = 5.7$). From the data of ethylene polymerization with different metallocenes, some considerations can be made (Table 6).

The substitution of the cyclopentadienyl rings by indenyl groups decreased the specific activity but increased the melting point and the molecular weight of the produced polymeric material (run IZ1 vs. EZ01). The presence of an ethylene bridge between the indenyl ligands positively affected the catalyst activity, whereas the replacement of zirconium with hafnium depressed it (run AH1 vs. AZ1) [30]. The support of the various complexes on the HY-zeolite was

accompanied by a marked reduction of productivity, which was again particularly relevant when the support surface was not pretreated with alkyl aluminum compounds. Supported Ind_2ZrCl_2 shows a similar behavior to Cp_2ZrCl_2 with comparable productivity and molecular weight much higher than in solution. In the presence of $Et(Ind_2)ZrCl_2$, the molecular weight was little increased with respect to the former cases. Soluble and supported bridged metallocene complexes showed a similar response to the exchange of $Al(iBu_3)$ for MAO and HF for Zr (Table 6).

The microstructure of a polymer is essentially dependent on the structural features of the complexes used, in particular the class of symmetry. For this reason, the influence of the inorganic support on the stereospecificity of the propylene polymerization process was investigated by testing a complex with free ligands, such as Ind_2ZrCl_2, and the stereorigid $Et(Ind)_2ZrCl_2$ and $Et(Ind)_2HfCl_2$. The results related to the specific activity, molecular weight and melting point obtained in propylene homopolymerization, reported in Table 7, reflected

Table 6
Ethylene polymerization with bis(indenyl) and ethylenebis(indenyl)zirconium and hafnium complexes in solution or supported on HY* zeolite ($SiO_2/Al_2O_3 = 5.7$)[a]

Run	Catalyst	Cocatalyst	[Al]/[Mt]	S.A.[b]	$\overline{M}_v \times 10^{-3c}$	T_m^d
EZ01	Cp_2ZrCl_2	MAO	1000	1270	136	134.7
EZ18	HY^*-MAO-Cp_2ZrCl_2	MAO	1000	313	352	140.2
IZ1	Ind_2ZrCl_2	MAO	1000	865	169	135.6
IZ2	HY^*-MAO-Ind_2ZrCl_2	MAO	1000	300	330	136.5
AZ1	$Et(Ind)_2ZrCl_2$	MAO	1000	1020	110	136.8
AZ2	HY^*-MAO-$Et(Ind)_2ZrCl_2$	MAO	1000	390	155	136.0
AZ3	HY^*-$Et(Ind)_2ZrCl_2$	MAO	1000	20	143	131.3
AZ4	$Et(Ind)_2ZrCl_2$	$Al(i$-$Bu)_3$	50	165	136	137.6
AZ5	HY^*-MAO-$Et(Ind)_2ZrCl_2$	$Al(i$-$Bu)_3$	50	45	178	133.1
AZ6	HY^*-MAO-$Et(Ind)_2ZrCl_2$	$Al(i$-$Bu)_3$	100	30	164	132.7
AZ7	HY^*-$Et(Ind)_2ZrCl_2$	$Al(i$-$Bu)_3$	50	0	–	–
AH1	$Et(Ind)_2HfCl_2$	MAO	1000	110	310	132.6
AH2	HY^*-MAO-$Et(Ind)_2HfCl_2$	MAO	1000	40	423	131.9

[a] Reaction carried out at 20°C in 80 ml of toluene with 5 μmol of Mt (Mt = Zr or Hf) in solution or 10 μmol of supported Mt, polymerization time 60 min, 2 bar ethylene pressure.
[b] Specific activity expressed as kg/mol Mt h, HY^* = HY zeolite calcinated at 625°C.
[c] Determined by viscosity measurements in decalin at 135°C.
[d] Melting point in °C determined by DSC.

Table 7
Propylene polymerization with bis(indenyl)zirconium and hafnium complexes in solution or supported on HY* zeolite $(SiO_2/Al_2O_3 = 5.7)$[a]

Run	Catalyst	S.A.[b]	$\overline{M}_v \times 10^{-3c}$	T_m (°C)[d]	$[mm]$[e]	$[mr]$[e]	$[rr]$[e]	I
IZ5	Ind_2ZrCl_2	1360	2	–	0.30	0.50	0.20	0.55
IZ6	$HY-MAO-Ind_2ZrCl_2$	560	9	136.9[f]	0.43	0.40	0.17	0.63
AZ14	$Et(Ind)_2ZrCl_2$	5480	31	137.1	0.94	0.04	0.02	0.96
AZ15	$HY-MAO-Et(Ind)_2ZrCl_2$	885	38	134.9	0.93	0.05	0.02	0.97
AZ16	$HY-Et(Ind)_2ZrCl_2$	15	48	136.0	0.94	0.04	0.02	0.96
AZ17[g]	$HY-Et(Ind)_2ZrCl_2$	70	12	120.5				
AH5	$Et(Ind)_2HfCl_2$	620	390	136.1	0.89	0.06	0.05	0.92
AH6	$HY-MAO-Et(Ind)_2HfCl_2$	160	480	130.4	0.91	0.04	0.05	0.93

[a] Reaction carried out at 20°C in 80 ml of toluene with 5 μmol of Mt (Mt = Zr or Hf) in solution or 10 μmol of supported Mt, cocatalyst MAO, Al/Zr = 1500, 2 bar propylene pressure, polymerization time 60 min, HY* = HY zeolite calcinated at 625°C.
[b] Specific activity expressed as kg/mol Mt h.
[c] Determined by viscosity measurements in decalin at 135°C.
[d] Melting point in °C determined by DCS measurements.
[e] Triad assignments determined by ^{13}C-NMR analysis.
[f] Melting point of the chloroform insoluble part.
[g] Reaction carried out at 70°C.

the data already discussed for poly(ethylene)s. In particular, it is known that aspecific complexes are not able to produce high molecular weight polymers of α-olefins, whereas a bridge between the indenyl ligands allows their coordination. For this reason, the product obtained in the presence of Ind_2ZrCl_2 was an oligomeric mixture (run IZ5 vs. AZ14 and AH5).

The ^1H-NMR analysis confirmed the high isospecificity of the *ansa*metallocenes and the formation of an atactic polymer in the case of the Ind_2ZrCl_2 in solution (Fig. 3). The possibility of free rotation of the indenyl ligands around the metal center gave no chiral features to the active site and consequently the possibility to distinguish between the prochiral faces of the olefin. The ^{13}C-NMR analysis showed signals corresponding to atactic sequences in the spectrum of the polymer obtained with Ind_2ZrCl_2 and to long isotactic sequences when $Et(Ind)_2ZrCl_2$ was used.

The distribution of the triads *mm*, *mr* and *rr*, related to the methyl carbon atom, and the index of isotacticity $(I = [mm] + 0.5[mr])$ are reported in Table 7. The experimental data indicated that the immobilization of the $Et(Ind)_2$-$ZrCl_2$ and $Et(Ind)_2HfCl_2$ complexes gave indistinguishable polymers from the microtacticity

point of view as compared with those obtained in solution (run AZ14 vs. AZ15 and AZ16; run AH5 vs. AH6). This result could be tentatively explained by assuming that the support preserves the spatial characteristics around the active site, possibly due to the immobilization on the external surface of the support due to the dimension of the bridged complexes.

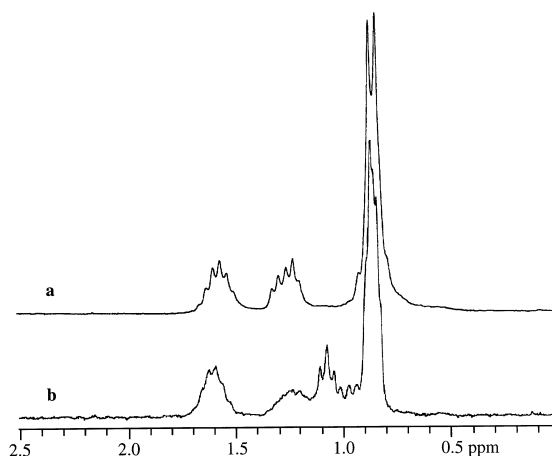Comparison of the behavior of the Ind_2ZrCl_2 complex (run IZ5) in solution and after support

Fig. 3. ^1H-NMR spectra of poly(propylene) samples obtained in the presence of $Et(Ind)_2ZrCl_2/MAO$ (a) and Ind_2ZrCl_2/MAO (b).
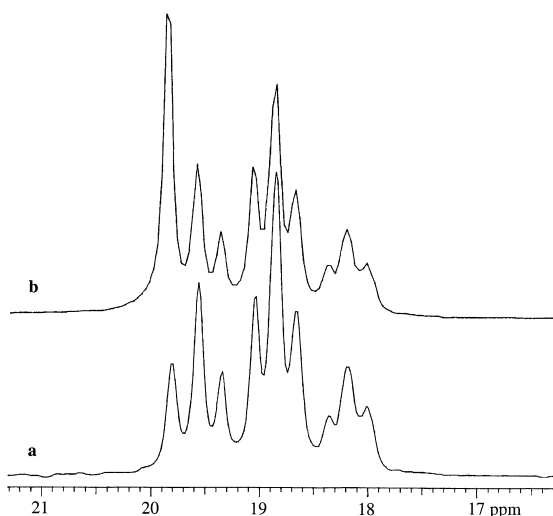
Fig. 4. ^{13}C-NMR spectra of poly(propylene) samples obtained in the presence of MAO activated Ind_2ZrCl_2 /MAO (a) and HY-MAO-Ind_2ZrCl_2 /MAO (b) in the methyl group region.

on the zeolite (run IZ6) is rather interesting. A small increase in the isotacticity was evident in the product obtained with HY*-MAO-Ind_2ZrCl_2. ^{13}C-NMR analysis of the crude samples in the region of the methyl group showed an increase in the *mmmm* pentad with respect to the other stereosequences with the support (Fig. 4). Fractionation of this product with boiling chloroform brought a 38% weight of insoluble crystalline portion having molecular weight and melting point of 24,000 and 136.9°C, respectively. This could indicate a partial immobilization on the catalyst inside the zeolite α-supercage. A portion of the complex could be blocked in enantiomorphic conformation, which could be responsible of the isospecific control of the propylene polymerization mechanism.

4. Conclusions

A number of homopolymerization experiments of ethylene and various α-olefins were performed in order to investigate the influence of immobilization of different metallocene complexes on HY-zeolites. The comparative analy-

sis with the results of the same catalysts operating in solution allows some concluding remarks.

A general decrease in the catalytic activity was observed after support, which can be reduced by treatment of the surface –OH groups with MAO and alluminoalkyls thus preventing ligand abstraction from the catalyst. In the case of ethylene polymerization with Cp_2ZrCl_2, the lower activity seemed to be associated with a lower number of active sites, but the catalytic activity remained practically constant within time, indicating a larger stability of the catalytic sites themselves. Also the polymerization products obtained with supported catalysts showed an increase in the molecular weight as a consequence of a higher k_p/k_{tr} ratio. This might indicate that due to the inclusion of the active sites inside the cages of the zeolite, the β-hydride elimination reaction could be prevented.

The *ansa*metallocene supported on the inorganic matrix showed the same isospecificity index in propylene homopolymerization. The results indicate that the complex can be supported without substantial modification of the spatial surroundings of the active site. The increase in the isotactic fraction in the presence of the aspecific complex Ind_2ZrCl_2 can be explained with the presence of a portion of the catalytic species, which assumes sterically modified conformations inside the zeolite cage.

Acknowledgements

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